PARTITIONING STUDIES OF POLYCHLORINATED BIPHENYLS BETWEEN AQUEOUS SOLUTION AND SOIL AND SEDIMENT SYSTEMS OF UMNGENI RIVER, KWAZULU-NATAL, SOUTH AFRICA

GBADEBO CLEMENT ADEYINKA

Submitted in fulfilment of the academic requirements for the degree of

DOCTOR OF PHILOSOPHY IN SCIENCE

School of Chemistry and Physics
College of Agriculture, Engineering and Sciences
University of KwaZulu-Natal

Westville, Durban, South Africa

Supervisor: Dr. B. Moodley

September 2018

PARTITIONING STUDIES OF POLYCHLORINATED BIPHENYLS BETWEEN AQUEOUS SOLUTION AND SOIL AND SEDIMENT SYSTEMS OF UMNGENI RIVER, KWAZULU-NATAL, SOUTH AFRICA

GBADEBO CLEMENT ADEYINKA

2018

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

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

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

Supervisor

Name: Dr. B. Moodley

Signed [redacted]

Date…20 February 2019…

PREFACE

The research work described in this thesis was carried out in the School of Chemistry and Physics, University of KwaZulu-Natal, Westville, Durban from July 2015 to June 2018, under the supervision of Doctor Brenda Moodley.

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

SIGNED: -[redacted]----------

G C ADEYINKA

M.Sc (UKZN) B.Sc (OOU)

I hereby certify that the above statement is correct

[redacted]

SIGNED: ----------

Dr. B. Moodley
P*h*.D (UKZN)

DECLARATION 1 – PLAGIARISM

I, GBADEBO CLEMENT ADEYINKA----------declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. This thesis has not been submitted for any degree or examination at any other university.
3. This thesis does not contain other person's data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
4. This thesis does not contain other person's 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, then their writing has been placed in italics and inside quotation marks, and referenced.

5. This thesis does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the thesis and references sections.

Signed…… 

DECLARATION 2 – PUBLICATIONS

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

Publication 1 (published)

Adeyinka, G. C., Moodley, B., (2018). **Kinetic and thermodynamic studies on partitioning of polychlorinated biphenyls (PCBs) between aqueous solution and modelled individual soil particle grain sizes.** *J. Environ. Sci*. http://doi.org/10.1016/j.jes.2018.04.003
Contribution: The experimental was done by myself under the supervision of Dr. B. Moodley (my supervisor). I also analysed the data as well as wrote-up the publication, and it was edited by my supervisor.

Publication 2 (published)

Gbadebo Clement Adeyinka, Brenda Moodley (2018). **Effect of aqueous concentration of humic acid on the sorption of polychlorinated biphenyls onto soil particle grain sizes: Influence of pH, thermodynamic and sorption isotherm.** *J. Soils Sediments* https://doi.org/10.1007/s11368-018-2147-4

Contribution: The experimental work was done by myself under the supervision of Dr. B. Moodley (my supervisor). I also analysed the data as well as wrote-up the publication, and it was edited by my supervisor.

Publication 3

- **Gbadebo Clement Adeyinka,** Brenda Moodley (2018). **Effect of stereochemistry on the sorption of polychlorinated biphenyls between soil and aqueous solution**
- (Manuscript ready for submission).

Contribution: The experimental work was done by myself under the supervision of Dr. B. Moodley (my supervisor). I also analysed the data as well as wrote-up the publication, and it was edited by my supervisor.

Publication 4

Gbadebo Clement Adeyinka, Brenda Moodley, (2018). **Porewater/sediment partitioning of polychlorinated biphenyls onto five surface sediments collected along uMngeni River, KwaZulu-Natal, South Africa**

- (Manuscript ready for submission).

Contribution: The experimental work was done by myself under the supervision of Dr. B. Moodley (my supervisor). I also analysed the data as well as wrote-up the publication, and it was edited by my supervisor.

Conference contribution

- **Gbadebo Clement Adeyinka** and Brenda Moodley (2016). The effect of pH on the partitioning of polychlorinated biphenyls (PCBs) between sediment grain sizes and water. ChromSAAMS2016 Conference, (Analitika 2016) Vanderbijlpark. Riverside Sun, Vanderbijlpark, Gauteng, South Africa. 11 – 14th September 2016 (Poster).
- **Gbadebo Clement Adeyinka** and Brenda Moodley (2016). An investigation on the partitioning of polychlorinated biphenyls (PCBs) between aqueous solution and modelled soil particle grain sizes and the factors that affect their partitioning. Postgraduate Research Day, College of Agriculture, Engineering and Sciences. Howard College Campus, Durban, South Africa, 29th November 2016 (Poster)
- **Gbadebo Clement Adeyinka;** Brenda Moodley (2017). The effect of pH on the partitioning of polychlorinated biphenyls (PCBs) between sediment grain sizes and water. 6th Young Environmental Scientists Meeting, Stockholm University, Sweden, 16 – 20 February 2017 (Poster).
- **Gbadebo Clement Adeyinka** and Brenda Moodley (2017). Sorption studies of polychlorinated biphenyls (PCBs) between aqueous solution and soil particle grain sizes: Effects of temperature and ionic strength. KZN ChromSAAMS Seminar, Durban University of Technology, Durban, South Africa, 5th April 2017 (Oral presentation).

- **Gbadebo Clement Adeyinka** and Brenda Moodley (2017). Sorption studies of polychlorinated biphenyls (PCBs) between aqueous solution and soil particle grain sizes: Effects of temperature and ionic strength. SETAC Europe 27th Annual Meeting in Brussels, Belgium, 7 – 11 May 2017 (Poster).
- **Gbadebo Clement Adeyinka** and Brenda Moodley (2017). Effect of aqueous concentrations of humic acid on the sorption of polychlorinated biphenyls onto soil particle grain sizes: Influence of pH, thermodynamics and sorption isotherms. Postgraduate Research Day, College of Agriculture, Engineering and Sciences. Westville Campus, Durban, South Africa, 26th October 2017 (Poster).

Signed…  ……

ABSTRACT

The significance of soil and sediment physicochemical properties and the environmental parameters such as pH, temperature, ionic strength, humic acid (HA) and time on the partitioning action of eight selected polychlorinated biphenyl (PCB) congeners were critically evaluated in this study to better understand the mobility, transportation, fate and distribution of hydrophobic organic pollutants in environmental media. Natural soil samples used in this study were collected along uMngeni River of KwaZulu-Natal province of South Africa. The mineral properties of soil samples were determined using the Walkley Black method, barium chloride compulsive exchange method and Brunauer-Emmet-Teller (BET) adsorption-desorption isotherm. All these were employed to observe the surface characteristics of the modeled individual soil particle sizes. Scanning electron microscopy (SEM) equipped with energy disperse X-ray (EDX) and Fourier transform infrared spectroscopy (FTIR) were used for the internal morphology and qualitative elemental analysis, as well as identification of possible functional groups in soil samples and commercial HA. Batch adsorption experiments were used for sorption studies. The results revealed that the amount of PCBs sorbed by soil was found to increase with an increase in contact time reaching equilibrium within 8 h. Among the soil chemical properties, soil organic matter was observed to correlate positively and play a more significant role in the sorption of PCBs. Soil samples with highest BET surface areas were related to the soil particle grain size. The sorption of PCBs onto soil was also found to decrease with an increase in the aqueous HA concentrations, and a change in the aqueous concentration of ionic strength was found to be less significant. Other important factors found to be more significant in the sorption were the degree of chlorination as well as stereochemistry of PCB congeners. The more hydrophobic and non-ortho (planar) congeners were found to contribute more significantly to sorption relative to the less hydrophobic and more ortho-substituted (nonplanar) congeners. Moreover, a decrease in the ratio of Si: (Al + Fe) was found to contribute positively to the sorption of PCBs. The kinetic studies on the partitioning of PCBs onto the soils was found to fit best with pseudo-second order, suggesting that the partitioning process of the selected PCBs between aqueous solution and active components in soil, involved more than one-step. Logarithmic values of organic carbon normalized sorption coefficient ($\log K_{oc}$) of the selected PCBs were found to decrease with an increase in the solution pH. The partitioning of PCBs onto the soils was also said to be temperature driven, where low aqueous temperatures encouraged more

partitioning of hydrophobic PCBs onto the soil. The Gibbs free energy ($\Delta G°$) was found to be negative. Therefore, the thermodynamic studies showed that the PCB interaction with soil particle sizes was a spontaneous process. The role of initial PCB concentration on the partitioning was found to be L-type. This indicated that an increase in PCB concentration in the aqueous phase made it more difficult for PCB molecules to find a vacant site available for sorption onto the soil SOM.

ACKNOWLEDGEMENTS

I would like to thank Dr Brenda Moodley for her guidance and support throughout this PhD study; and over the past five years in which I have worked with her as a Master's student, I am indeed grateful to her for genuine and real commitment to this research.

My special thanks also go to my parents Pa Edward and Mrs Cecilia Adeyinka, and to my family for the encouragement, help and caring words, I am happy and most delighted for your supports all through the progamme. Also to my brother (Adediwura, Adeyinka) for the real love and believe you have for me, thank you and I wish to return same to you all as well.

I must say thank you to special people in my research group for your constructive criticisms during the group presentations: people like Dr Samson Akpotu, Bheki Gumbi, Deborah Ogunleye, and to my colleagues in the laboratory such as Jeremiah Oluleye, Dr Seun Oyetade, Talent, and many others thank you all for the warm and wonderful moments we had together.

Sincere appreciation to the following people for their technical support most especially for making the instrumentation part of the work more convenient for me: Mrs Anita Naidoo and Unathi Bongosa from the School of Chemistry and Physics, and Gregory Moodley (Chemistry) for his assistance in making glasswares and other useful materials available - you are all appreciated.

Finally to the School of Chemistry and Physics and the entire staff for providing the research facilities and assistance in various ways for this work, you are all equally appreciated. Also grateful to College of Agriculture, Engineering and Sciences and National Research Foundation-Knowledge Interchange Collaboration (NRF-KIC) for the travel grant to attend an International Conference in Sweden and Belgium, respectively. Also, to the University of KwaZulu-Natal, South Africa for the tution free opportunity to be one of the students in this great citadel of learning – I am so proud to be so inspired. Schimadzu Technology Students Sponsorship Programme is also acknowledged for the ChromSAAMS 2016 Conference funding.

DEDICATION

This research is dedicated to God the most high for making this degree possible. I return all praises to him alone. Also to my family, for their love, perseverance and understanding while on academic exile.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ACS – American Chemical Society

AhR – Aryl Hydrocarbon

AR – Analytical Grade

ASTM – American Society for Testing and Materials

ATSDR – Toxic Substances and Disease Registry

BC – Black Carbon

BCF – Bioconcentration Factor

BET – Brunauer-Emmet-Teller

BJH – Barrett-Joyner-Halenda

C/N – Carbon Nitrogen Ratio

$CaCl_2$ – Calcium Chloride

CEC – Cation Exchange Capacity

CI – Confidence Interval

CUCE – Cornell University Cooperative Extension

DCM – Dichloromethane

DHAs – Dissolved Humic Acids

DL – Dioxin Like

DNA – Deoxyribonucleic Acid

DOM – Dissolved Organic Matter

EC – European Commission (EC)

EDX – Energy Disperse X-ray

FA – Fulvic Acid

F_{oc} – Fraction of Organic Carbon

FTIR – Fourier Transform Infrared Spectroscopy

GC-MS – Gas Chromatography-Mass Spectrometer

GGT – Gamma Glutamyltransferase

GPS – Global Positioning System

GSH – Glutathione

HA – Humic Acid

HCL – Hydrochloric Acid

HNO_3 – Nitric Acid

HOCs – Hydrophobic Organic Contaminants

HOPDA – Hydroxylpenta-2,4-dienoate

HPLC – High Performance Liquid Chromatography

HS – Humic Substance

HSDB – Hazardous Substances Data Bank

ICES – International Council for the Exploration of the Sea

ICP – Inductively Coupled Plasma

IOM – Institute of Medicine

IPCS – International Programme on Chemical Safety

IQ – Intelligent Quotient

IUPAC – International Union of Pure and Applied Chemistry

K_d – Sediment-Water Distribution Coefficient

K_{oc} – organic carbon normalized sorption coefficient

K_{ow} – Octanol-Water Partition Coefficient

K_w – Water/Air Partition Coefficient

LOD – Limit of Detection

LOI – Loss on Ignition

LOQ – Limit of Quantification

MCL – Maximum Contaminant Level

NaOH – Sodium Hydroxide

NAP – National Academies Press

NDL – Non Dioxin Like

NFPA – National Fire Protection Association

NIP – National Implementation Plan

OC –Organic Carbon

OCPs – Organochlorinated Pesticides

OECD – Organization for Economic Corporation and Development

OES – Optical Emission Spectrometry

OM – Organic Matter

OPs – Organic Pollutants

PAHs – Polycyclic Aromatic Hydrocarbons

PCBs – Polychlorinated Biphenyls

PCCDs – Polychlorinated Dibenzodioxins

PCDFs – Polychlorinated Dibenzofurans

POP – Persistence Organic Pollutants

QSAR – Quantitative Structure-Activity Relationship

SC – Stockholm Convention

SEM – Scanning Electron Microscopy

SEPA – State Environmental Protection Administration

SIM – Selected Ion Monitoring

SOM – Soil Organic Matter

SPM – Suspended Particulate Matter

SPM – Suspended Particulate Matter

STP – Sewage Treatment Plant

TCE – Trichloroethylene

TDS – Total Dissolved Solid

TEFs – Toxic Equivalency Factor

TOC – Total Organic Carbon

UK – United Kingdom

UNEP – United Nations Environmental Programme

USA – United State of America

USEPA – United State Environmental Protection Agency

USSR – Union of Soviet Socialist Republics

UV – Ultraviolet

WHO – World Health Organization

WWTP – Waste Water Treatment Plant

XRD – X-Ray Diffractometer

CHAPTER 1

INTRODUCTION

1.1 General overview

Surface water contamination by organic pollutants because of either point or non-point sources such as surface runoff, industrial or domestic discharges as well as mobilization from soil or sediment to water body has been a serious concern to the general public. Soil contamination by persistent organic pollutants (POPs) such as, polychlorinated biphenyls (PCBs) is an environmental problem, which has drawn scientific attention globally, due to their toxic effects (Colborn *et al*., 1996). PCBs are a group of 209 synthetic chlorinated hydrocarbons with biphenyls skeletons belonging to the most persistent, bio-accumulative, and toxic pollutants, and in the past decades are extensively used in the electricity generating industry as insulating or cooling agents, in transformers and capacitors, as flame retardants, in paints as well as coatings (Eljarrat and Barcelo, 2009; Erickson and Kaley, 2011). Their usage and production in any form were banned globally through a treaty signed in 2004 by the Stockholm Convention (SC) on POPs. It is a global treaty, under the supervision of the United Nations Environmental Programme (UNEP), the institution tasked with reducing the production and preventing the use of hazardous and persistent organic chemicals, such as PCBs. They provide member countries with financial assistence in the clean-up of old storage of materials containing POPs, and protecting humans and the environment. This treaty also sensitizes the general public on the dangers of POPs (Bouwman, 2004; Xu *et al*., 2013). Because of the various anthropogenic and the chemical properties of the products, PCBs are now widely distributed globally, and measurable concentrations occur in aquatic organisms and wildlife across the globe. These pollutants are able to bio-magnify and bio-accumulate in ecosystems, as well as pose a significant threat to human health and the environment including resulting in death, birth defects, reproductive failure, liver damage, tumors, and a wasting syndrome (UNEP, 2013). They are highly hydrophobic and therefore have low water solubility but prefer to be soluble in non-polar solvents, biological tissues, lipids or fats and oils. This property enables them binding freely with water-soluble organic compounds in water, and soil humic materials thereby bio-accumulating and biomagnifying in the food chain (ATSDR, 2000; IPCS, 2003).

The sorption process plays a significant role in controlling the distribution, transportation, and fate as well as the remediation of surface waters such as streams, rivers and oceans (Morel and Gschwend, 1987). Through sorption/desorption and sedimentation/resuspension phenomena, natural sediments can act as both aquatic sources and sinks for many organic compounds. The level at which a particular organic species undergoes partitioning between sediments and the aqueous phase is determined by the physicochemical properties of that particular organic species (Chin *et al*., 1988). The equilibrium partitioning of an organic pollutant between aqueous solution and sediment is mostly described by the sediment-water distribution coefficient (K_d), which is the ratio of the equilibrium concentration of the pollutants in the sediment (q_e) to the corresponding equilibrium aqueous concentration (C_e) (Nguyen *et al*., 2005). The properties of the organic pollutants (PCBs) such as aqueous solubility, polarity and octanol-water partition coefficient (K_{ow}) (ratio of concentration of pollutant in the octanol phase over concentration in the aqueous phase) play major roles in the partitioning and mobility of the organic pollutant within environmental matrices and particularly the sediment and aqueous interface. K_{ow} is also a measure of the hydrophobicity of an organic pollutant. The higher the hydrophobic character of the pollutant, the less soluble it is, therefore the more its propensity to adsorb to soil or sediment particles (Bedient *et al*., 1994). Solubility is known to be the maximum amount of a contaminant that can dissolve in water at a given temperature, which is inversely proportional to the partitioning coefficient of the pollutant (Belfort, 1979; Chiou *et al*., 1986). Pollutant polarity is another major factor that controls the mobility of the pollutant within the environmental media. The more polar a pollutant is, the more it tends to readily dissolve in water compared to nonpolar pollutants and thereby adsorbs less to soil organic matter (SOM).

Soil or sediment is mostly a heterogeneous mixture of different constituents such as inorganic, organic like humic substances (HS), and living materials. The sorption capacity of a given sorbent (e.g soil) is largely dependent on its physicochemical properties, the chemical properties of the sorbate as well as changes in environmental parameters such as pH, temperature and electrical conductivity (Spark and Swift, 2002). Of all these properties, soil/sediment texture is a highly important parameter for the process of sorption of organic pollutants. A soil or sediment solution with mostly clay content and organic matter has a tendency for sorption of a higher amount of organic pollutant. Classification of soil based on the soil texture includes clay, silt and sand, among these, clay in most cases intermixed with the organic particulate matter, have better adsorption

properties due to its smaller particle size and high surface charge as well as the high surface area. Organic and mineral matter within the soil/sediment is also known to play some unique role in the sorption process of nonionic organic pollutants in the environmental media. Soil or sediment organic matter acts as a partitioning medium while soil mineral matter under a relatively dry condition serves as an adsorbent (Chiou *et al*., 1985; Rutherford and Chiou, 1992). The pH of the sediment aqueous phase also affects the sorption of the organic pollutant due to the solubility of the pollutants at different pH. Some pollutants dissolve better in aqueous phase under specific pH conditions. Increases in pH tend to cause an increase in the solubility of organic matter due to increasing particle dispersion (You *et al*., 1999). Also, organic acids tend to adsorb better under acidic conditions while basic pollutants, such as iopromide and carbamazepine, adsorb better under alkaline conditions (Canter and Knox, 1985; You *et al*., 1999; Carballa *et al*., 2008). Other important parameters controlling the sorption of the organic pollutants are temperature and conductivity, or salinity of the solution. The adsorption/desorption rates of organic pollutants from sediment, due to temperature changes, has been reported to have a significant effect on it concentrations in the environmental media (Zhou *et al*., 2006; Cheng *et al*., 2007). Studies have also shown that high ionic strength in aqueous phase would increase the aqueous solubility of organic pollutants and cause a significant decrease in the partitioning of the pollutants onto the soil or sediment phase (Borrirukwisitsak *et al*., 2012).

1.2 Background of the study

In recent years, the level of organic pollutants and its health effects on humans and organisms in the environment have been a cause for serious concern. Organic pollutants are found in various environmental media such as surface water, wastewater, soil and sediment, aquatic biota as well as sludge (Kanda *et al*., 2003; Loraine and Pettigrove, 2006; Joss *et al*., 2004). Based on the toxicological and health-related effects of these pollutants, information is required about their distribution, transportation as well as their fate in the environment. According to Wenia and Mackay (1999), the spread of organic pollutants in the environment was described by four building block: phase partitioning, transformation, emission, and transport. Among these key elements, sorption is one of the major driving forces controlling the transportation, fate, and remediation of organic pollutants and may also be a rate controlling step for other factors like biodegradation and photolysis within the environmental media (Bekbolet *et al*., 1999). Several studies have been

carried out on levels and bioavailability of the organic pollutants in many parts of the world much of which has been on monitoring of both polar and nonpolar persistent organic pollutants. Partitioning studies involving sorption of hydrophobic pollutants, such as, polycyclic aromatic hydrocarbons (PAHs) and few cases of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) as well as pharmaceuticals have been documented in some developed countries such as the United States of America (USA), United Kingdom (UK), China, Spain and Japan (Schwarzenbach *et al*., 2003; Stevens *et al*., 2003, Carballa, *et al*., 2008 and Yamamoto *et al.*, 2009). Qiao *et al*. (2008) studied the partitioning characteristics of PAHs between sediment and water in a shallow lake of China. The authors found that the partitioning coefficient between sediment and overlying water (log K_{oc}) for PAHs with log $K_{ow} < 5$ were positively correlated with their log K_{ow} values. Liying et al. (2009), investigated the influences of three sediment size fractions (< 63 µm, 63 – 100 µm and 100 – 300 µm) on the K_d of water-soluble organic carbon from two cross-sections of the middle Yellow River in China. The K_d of water soluble carbon was found to be highly influenced by the chemical structures of the NaOH extracted HSs in different sediment particle sizes. There was a strong correlation between K_d and the aromatic structures of HSs found particularly in the larger size fractions of 63-100 µm and 100-300 µm compared to the smaller size fraction of < 63 µm. The trend observed was suggested to be due to the lower aqueous solubility of the sediment organic carbon associated with higher concentrations of aromatic environments in the larger particle sizes. You *et al*. (1999) also studied the effects of pH and water/soil ratio on the partitioning of organic matter in soils in New Jersey, United States. The results indicated that at higher pH relative to the ratio of the UV absorbance (at 465 nm and 665 nm), there was a general increase in the humic acid / fulvic acid ratio, which shows that a greater solubility of the high molecular weight SOM at this pH. Wang *et al*. (2001) analyzed the concentrations of 16 US EPA priority PAHs in four particle size fractions (< 62 µm, 62 -125 µm, 125 - 250 µm and 250 µm) of the Boston Harbor sediments, United States. The results revealed that PAH concentrations in measured pore water were significantly lower than the concentrations predicted by equilibrium partitioning models and partition coefficients measured by sorption experiments compared to sediments. In addition, the authors noted that higher concentrations of PAHs were found in the larger size fraction of 250 µm while clay and silt fractions (< 62 µm, 62 – 125 µm) contained the least PAH concentrations for all the three sites studied. It was noted that, despite the significant differences in the concentrations within the sediment fractions, the

composition of PAHs in the four particle size fractions for all the sediments studied showed similar composition patterns dominated by PAHs with three or more ring systems. A positive correlation was found to exist between PAHs and sedimentary organic carbon for all size fractions in the sediments. Mcgroddy *et al*. (1995) noted that the relative importance of geochemistry factors influencing the partitioning of PAHs between benthic ecosystems needs further investigations. Steven *et al*. (1999) determined the proportions of PCBs from the water/sediment sorption samples from Lake Jarnson, Sweden. The reported observed K_d values at 18 days were similar for the various sediments irrespective of a congener's molecular weight or concentration. Also, Carballa *et al*. (2008) determined the K_d and K_{oc} values of 12 substances such as pharmaceuticals, estrogens and musk fragrances, in mesophilic and thermophilic digested sludge from a sewage treatment plant (STP) in Galicia in the North West of Spain. The results indicated that digested sludge was more prone to the sorption of musk fragraces and estrogen due to an elevated total suspended solids concentration while the sorption of pharmaceuticals on digested sludge was considered to be less likely. The trend observed could be attributed to the fact that, K_{ow} better describes hydrophobic interaction compared to sorption of polar and ionic compounds. Yamamoto *et al*. (2009) also studied the partitioning of eight highly consumed selected pharmaceuticals with a relatively high potential ecological risk in the aquatic environment of Tokushima City, Japan. The result showed that neutral compounds or carboxylic acids had lower K_d values compared to three amines (atenolol, ifenprodil and propranolol). The K_d values of the amines were similar to that of a four-ring PAH (pyrene). The K_{ow} values were higher for sediment or soil with higher organic content, and the log K_{oc} values showed a poor linear correlation with its respective log K_{ow} values at neutral pH. These studies also further showed that, other physicochemical parameters such as electrochemical affinity, together with hydrophobic interaction, are more significant for the sorption onto the sediment or soil at neutral pH.

There is little or no information on partitioning studies of nonpolar organic pollutants such as PCBs, OCPs and PAHs in African soil. In addition, studying the partitioning effects on different particle grain sizes is important because, studying the soil sample as a whole may not provide in-depth information on the role of each soil particle fraction and their individual significant role in the mobility and sorption of the OPs. Therefore, this study aimed at bridging this gap to further examine the role of individual soil particle grain sizes and the various environmental factors that affect adsorption of PCBs to soil/sediment, as well as kinetic, thermodynamic and adsorption

isotherms, the role of HA concentrations as well as effect of stereochemistry on the partitioning of eight selected PCB congeners between the aqueous solution/porewater and individual soil particle grain sizes as well as sediment samples. Currently, to the best of the author's knowledge, there have been no reports of soil physicochemical parameters, change in the aqueous solution of HA concentration and effect of non-ortho and ortho-substituted PCB congeners, kinetic and thermodynamic studies carried out on natural soil for partitioning studies of organic pollutants, which this research presents. Furthermore, this study reports the first scientific data on the partitioning of hydrophobic contaminants (PCBs) between aqueous solution and soil or sediment systems on South African soil taken from a sub-tropical climate, which has a different soil mineralogy component and characteristics compared to soil or sediment from other parts of the world.

1.3 Aim of the research

The aim of this research was to investigate the phase partitioning of nonpolar organic pollutants (selected PCB congeners) between the aqueous phase and various soil or sediment particle grain sizes, as well as the effects of physicochemical parameters and various environmental conditions on the partitioning of PCBs on soil or sediment from the uMngeni River of KwaZulu-Natal, South Africa.

1.4 Objectives

The objectives were to:

1. Quantitatively determine the total organic carbon content (TOC), soil organic matter (SOM), the carbon-nitrogen ratio (C/N) and cation exchange capacity (CEC) as well as the surface characteristics of the different soil particle grain sizes.

2. Determine the effects of pH, kinetic studies, temperature and ionic strength on the partitioning of the selected PCBs between the different soil particle grain sizes and aqueous solution.

3. Investigate the role of humic acid (HA) dose and thermodynamics on the sorption of PCB congeners onto the soil particle grain sizes.

4. Evaluate the effect of PCB stereochemistry such as non-ortho-substituted (planar) and ortho-substituted (nonplanar) on partitioning experiments.

5. Evaluate the partitioning of the eight selected indicator PCB congeners between the sediment and pore water system collected along five selected sites of uMngeni River of KwaZulu-Natal, South Africa.

1.5 Research scope

Generally, there are several factors influencing the partitioning of organic pollutants in the environment most especially within the aquatic ecosystem. These include parameters such as differing physicochemical properties of organic pollutants, various soil or sediment types, and the chemical properties of the soil or sediment, which are affected by the climatic and weather conditions within the catchment areas. Once organic pollutants partition to soil or sediment, their mobilisation to the surface water and leaching into the ground water is reduced. This then affects their degradation, transportation and fate in the environment. Thus, in order for remediation studies to be carried out, an understanding of the in-depth partitioning of organic pollutants in aqueous systems must first be studied. Therefore, this research focuses on the partitioning study of one group of synthetic hydrophobic organic pollutants (PCBs) within the aqueous and soil/sediment phases. Soil and porewater samples were collected at strategic locations (as described in the methodology) along the river course. Model real soil samples were extracted and spiked with the selected PCBs and their partitioning was studied based on temperature, pH, kinetics and physicochemical properties of the soil. The effect of HA concentration and pH and thermodynamic studies were undertaken as well as the effects of stereochemistry of the organic pollutants on their partitioning. Finally, real sediment samples collected along the uMngeni River were investigated to determine the partitioning of the PCBs in real samples.

1.6 Justification of study

Most POPs are recalcitrant[1] compounds that are extremely persistent in the environment.

[1] Recalcitrant organic pollutants are chemical substances which remain in the environment for extended periods of time. They can either be naturally occurring or from synthetic origins. Recalcitrant organic chemicals that are resistant to biodegradation are common surface water and soil contaminants at hazardous waste sites (Goerke *et al*., 2004; Chu *et al*., 2006; Ashraf, 2017).

Contamination of the aquatic ecosystems by hydrophobic organic contaminants (HOCs), such as PCBs, are a major environmental problem due to their long range of transportation, bio-accumulation and proven health-related effects (ATSDR, 2000; Levinson *et al*., 2008). Significant quantities of these contaminants are frequently released to the environment either through point or non-point sources originating from natural or anthropogenic sources (through industrial, domestic and WWTP discharges as well as leakage from old electronics waste). Wet deposition, surface water runoff, and remobilization of PCBs previously adsorbed onto soil and sediment SOM due to heavy rainfall as well as changes in environmental conditions such as temperature, solution pH, and salinity are also major factors controlling the distribution of pollutants in the environment.

This research work focuses on the uMngeni River located in the geographical area of KwaZulu-Natal province of South Africa. It is a major river within the province that serves many purposes, such as one of the main supplies of potable water for surrounding communities, as a recreational body of water, as well as its usefulness for irrigational purposes. This river was selected due to its wide usage and the pollution history recorded in the past by researchers. The river is polluted by many anthropogenic activities such as industrial, commercial, municipal, and domestic activities as well as runoff from agricultural activities within the surrounding environment. The river has been receiving attention within the academic community in recent years ranging from microbiological to chemical studies but as yet there is no information about the sorption/distribution and remediation studies of the organic pollutants reported on this river. Preliminary investigations on the concentration levels of PCBs along this river by Gakuba *et al*. (2015) showed that there were significant concentrations of PCBs in the surface water and its sediment, with trace levels at some sites along the river. Although the production and usage of these pollutants have been long prohibited in the world including South Africa, due to the long half-lives of the pollutants, persistence and hydrophobic properties, they tend to partition more onto the soil and sediment for a longer period. They are then able to remobilize into the water phase once environmental parameters such as pH and temperature as well as particulate matter in the water body changes. To understand the mechanisms, transportation as well as best possible remediation approach of the pollutants in the environment, detailed sorption studies need to be carried out. Therefore, the outcome of this research is expected to provide knowledge on how the pollutants (PCBs) partition themselves between the aqueous and soil or sediment phases. This will provide information or enable an understanding of transportation of pollutants, the role of soil

physicochemical properties, the effect of changes in environmental conditions, the mechanisms of partitioning of PCBs and their fate in the environment as well as their availability to humans and animals who consume water directly from the river.

1.7 Overview of thesis

This thesis is put together as a series of papers together with an introduction, literature review and methodology. The introduction (Chapter 1) gives a background to the study and presents the aims and objectives as well as the research scope and justification of the study. The literature review (Chapter 2) describes work that has been carried out in this field of study by other researchers and highlights the main focus areas of this work. The methodology found in Chapter 3 provides the experimental details of the study, sampling and analytical protocols used and the instrumentation used for the analysis of the samples. Chapter 4 describes the results obtained for the effect of soil physicochemical parameters and environmental parameters such as pH, temperature, ionic strength and kinetic studies on the partitioning of the selected PCBs to aqueous systems. Chapter 5 describes the effect of HA concentration, pH, temperature and isotherm studies that gives an understanding of the mechanism of partitioning. Chapter 6 describes the effect of stereochemistry of the PCBs (ortho and non-ortho substituted) on partitioning and Chapter 7 presents the results of PCB partitioning on real samples collected from the uMngeni River. Chapter 8 gives the general conclusions of this study and future recommendations.

REFERENCES

ATSDR, Agency for Toxic Substances and Disease Registry (2000). Toxicological Profile for Polychlorinated Biphenyls (PCBs). Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Atlanta, Georgia.

Ashraf, M. A., (2017). Persistent organic pollutants (POPs): a global issue, a global challenge. *Environ. Sci. Pollut. Res*. **24**: 4223–4227. doi 10.1007/s11356-015-5225-9.

Bedient, P. H., Rifai, H. S., and New ell, C. J., (1994). Ground water contamination: Transport and remediation, prentice hall, Englewood Cliffs, New Jersey, United State. 1994.

Belfort, G., (1979). Selective adsorption of organic homologues onto activated carbon from dilute aqueous solutions. Solvophobic interaction approach and correlations of molar adsorptivity with physicochemical parameters. *Environ. Sci. Technol.* **13**, (8): 939-946

Bekbolet, M., Yenigun, O., and Yucel, I., (1999). Sorption studies of 2, 4-D on selected soils. *Water Air Soil Pollut*. **111**: 75–88.

Borrirukwisitsak, S., Keenan, H. E., and Lindsay, C. G., (2012). Effects of salinity, pH and temperature on the octanol-water partitioning coefficient of bisphenol A. *I. J. E. S. D*. **3**: 460-464.

Bouwman, H., (2004). South Africa and the Stockholm convention on persistent organic pollutants. *S. Afr. J. Sci.* **100**: 323-328.

Burton, E.D., Phillips, I.R.., Hawker, D.W., (2004). Sorption and desorption behaviour of tributyltin with natural sediments. *Environ. Sci. & Technol.* **38**: 6694-6700.

Canter, L. W. and Knox, R. C., (1985). Ground water pollution control, Lewis Publishers, Michigan, United State of America. pp 149-164.

Carballa, M., Fink, G., Omil, F., Lema, M. J., and Ternes, T., (2008). Determination of the solid-water distribution coefficient (K_d) for pharmaceuticals, estrogens and musk fragrances in digested sludge. *Water Res*. **42**: 287-295

Cheng, J. P., Wu, Q., Xie, H. Y., Gu, J. M., Zhao, W. C., Ma, J., and Wang, W. H., (2007). Polychlorinated biphenyl (PCBs) in PM_{10} surrounding a chemical industrial zone in Shanghai, China. *Bull. Environ. Contam. Toxicol.* **79**: 448-453.

Chin, Y-P., Peven, C. S., and Weber, W. J., (1988). Estimating soil/sediment partition coefficients for organic compounds by higher performance reverse phase liquid chromatography. *Environ. Sci Technol*. **39**: 913-924

Chiou, C. T., Shoup, T. D., Porter, P. E., (1985). Mechanistic roles of soil humus and minerals in the sorption of nonionic organic compounds from aqueous and organic solutions: *Organic Geochem.* **8**: 9-14.

Chiou, T. C., Chlou, Malcolm, R. L., Brlnton, T. I., Kile, D. E., (1986). Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environ. Sci. Technol*. **20**: 502-508.

Chu, W., Wong, M., Zhang, J., 2006. Accumulation, distribution and transformation of DDT and PCBs by phragmites Australis and Oryza sativa L.: II. Enzyme study. *Environ. Geochem. Health.* **28**, (1): 169–181.

Colborn, T., Dumanoski, D., Myers, J. P., (1996). Our Stolen Future Ed. 1996; New York, USA: Dutton.

Eljarrat, E. and Barceló, D., (2009). Chlorinated and brominated organic pollutants in contaminated sediments. The Handbook of Environmental Chemistry. pp 21–56.

Erickson, M. D., and Kaley, R. G., II (2011). Applications of polychlorinated biphenyls. *Environ. Sci. Pollut. Res.* **18**: 135-151.

Gakuba, E., Moodley, B., Ndungu, P., Birungi, G., (2015). Occurrence and significance of polychlorinated biphenyls in water, sediment pore water and surface sediments of uMngeni River, KwaZulu-Natal, South Africa. *Environ. Monit. Assess*. **187**: 568, doi 10.1007/s10661-015-4790-1.

Goerke, H., Weber, K., Bornemann, H., Ramdohr, S., Plotz, J., (2017). Increasing levels and biomagnification of persistent organic pollutants (POPs) in Antarctic biota. *Marine Poll. Bull*. **48**: 295-302. doi:10.1016/j.marpolbul.2003.08.004.

IPCS, Concise International Chemical Assessment Document 55 (2003). Polychlorinated biphenyls: Human health aspects. Geneva, Switzerland: World Health Organization; pp 1–60. Available from: http://whqlibdoc.who.int/publications/2003/9241530553.pdf. *Accessed,* 14/07/ 2017.

Joss, A., Andersen, H., Ternes, T., Richle, P.R., Siegrist, H., (2004). Removal of estrogens in municipal wastewater treatment under aerobic and anaerobic conditions: consequences for plant optimization. *Environ. Sci. Technol*. **38**: 3047–3055.

Kanda, R., Griffin, P., James, H.A., Fothergill, J., (2003). Pharmaceuticals and personal care products in sewage treatment works. *J. Environ. Monit.* **5**: 823–830.

Levinson, J., Channsluszny, S., Yasman, Y., Butalov, V., Schetcher, I., (2008). Detector for particulate PAHs in water. *Anal. Bioanal. Chem*. **381**: 1884-1591.

Liying, S., Weiling, S., Jinren, N.I., (2009). Partitioning of water soluble organic carbon in three sediment size fractions: Effect of the humic substances. *J. Environ. Sci.* **21**: 113-119.

Loraine, G. A. and Pettigrove, M. E., (2006). Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in Southern California. *Environ. Sci. Technol*. **40**: 687–695.

Mcgroddy, S. E. and Farrington, J. W., (1995). Sediment pore water partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Barbor, Massachusetts. *Environ. Sci. Technol*. **29**: 1542-1550.

Morel, F. M. M. and Gschwend, P. M., (1987). In aquatic surface chemistry: Chemical process at the particle – water interface*;* Stumm, W., Ed.; Wiley: New York. pp 405-422.

Nguyen, H. T., Goss, K. U., and Ball, W. P., (2005). Polyparameter linear free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments. *Environ. Sci. Technol*. **39**: 913-924.

Qiao, M., Huang, S., Wang, Z., (2008). Partitioning characteristics of PAHs between sediment and water in a shallow lake. *J. Soils Sediments*. **8**: 69-73.

Rutherford, D W. and Chiou, C., (1992). Effect of water saturation in soil organic matter on the partition of organic compounds. *Environ. Sci. Technol*. **26**, (2): 336-340.

Spark, K. M., Swift, R. S., (2002). Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total Environ*. **298**: 147-161

Steven, B. H., Bjorklund, E., Bowadt, S., Mathiasson, L., (1999). Determining PCB sorption/desorption behavior on sediments using selective supercritical fluid extraction. 3. Sorption from water. *Environ. Sci. Technol*. **33**: 3152-3159

Stevens, J. L., Northcott, G. L., Stern, G. A., Tomy, G. T., Jones, K. C., (2003). PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musk's and polychlorinated n-alkanes in UK sewage sludge: survey results and implications. *Environ. Sci. Technol.* **37**: 462–467.

Schwarzenbach, R. P., Gschwend, P. M., Imboden, D. M., (2003). Environmental organic chemistry. Wiley, New York, Chichester, Brisbane, Toronto, Singapore. pp 376.

UNEP, United Nations Environment Programme, on POPs, (2013). Results of the global survey on the concentrations in human milk of persistent organic pollutants by the United Nations Environment Programme and the World Health Organization. UNEP/POPs/COP.6/INF/33. *Accessed,* 26/09/ 2017.

Wang, X-C., Zang, Y-X., and Chen, R. T., (2001). Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. *Mar. Pollut. Bull*. **42**: 1139-1149.

Wania, F., and Mackay, D., (1999). The evolution of mass balance models of persistent organic pollutant fate in the environment. *Environ. Pollut.* **100**: 223-240.

Xu, F.L., Kong, X.Z., He, W. and Qin, N., (2013). Distributions, sources, andecological risks of hexachlorocyclohexanes in the sediments from Haihe Plain, Northern China. *Environ Sci Pollut Res*. **20**, (4): 2009-2019.

Yamamoto, H., Nakamura, Y., Moriguchi, S., Nakamura, Y., Honda, Y., Tamura, I., Hirata, Y., Hayashi, A., and Sekizawa, J., (2009). Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments. *Water Res*. **43**: 351-362.

You, S-J., Yin, Y., Allen, H. E., (1999). Partitioning of organic matter in soils: effects of pH and water/soil ratio. *Sci. Total Environ*. **227**: 155-160

Zhou, R., Zhu, L., Yang, K. and Chen, Y. (2006). Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. *J. Hazard. Mater.* **137**: 68-75.

CHAPTER 2

LITERATURE REVIEW

2.1 Polychlorinated biphenyls (PCBs)

2.1.1 Introduction

Polychlorinated biphenyls (PCBs) are a class of aromatic chemical compounds which constitute an important class of persistent organic pollutants (POPs) with some or all hydrogen atoms on the phenyl rings substituted by chlorine atoms (m + n = 1–10). PCBs have a general chemical formula of $C_{12}H_{(10-m-n)}Cl_{(m+n)}$, where (m+n) corresponds to the number of chlorine atoms on the two phenyl rings (Ballschmiter and Zell 1980). Theoretically, there are 209 PCB congeners made up of differing number and position of the chlorine atoms on the phenyl rings ranging from mono-chlorinated isomers to the fully chlorinated deca-chlorobiphenyl isomer. The carbon positions are numbered 1 to 6 on one ring, and 1′ to 6′ on the other. The positions 2,2′,6, and 6′ are called "ortho", positions 3,3′,5 and 5′ are named "meta" and positions 4 and 4′ are called "para" (Schulte and Malisch, 1983; Ballschmiter *et al*., 1992). The general chemical structure of a PCB is shown in **Fig**. 2.1

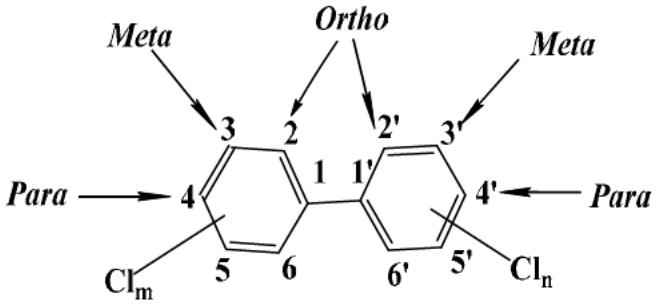


Figure 2.1: General structure of polychlorinated biphenyls (PCBs) (Ballschmiter and Zell, 1980; Schulte and Malisch, 1983; Ballschmiter *et al*., 1992)

2.1.2 Sources and production of PCBs

There are no known natural sources of PCBs; they are mainly of industrial origin that have found wide application in industries since the 1930s. Consequently, PCBs have been listed among the class of priority pollutants as implemented by some agencies in developed countries such as, US Environmental Protection Agency (USEPA), European Commission (EC) and the State Environmental Protection Administration (SEPA) in China (Bi *et al*., 2002). Developed countries have since phased out their use but developing countries still have application for them to this present day. The first production of PCBs dates back to 1881 and its usage in the industry began in 1929 (Tanabe, 1988). During this period, Monsanto Co. under the trade name Aroclor produced almost half of all the PCBs manufactured in North America with the other 38% from Germany, the USSR, France, and the UK (Breivik *et al*., 2007). In addition, Geneva Industries production of PCBs was reduced during the period 1972 to 1974 (EPA, 2008b). In China, the production of PCBs started in 1965 but stopped by the 1980s. Preliminary investigations and analysis revealed that about 7 000 – 10 000 tons of PCBs were produced in China from 1965 to 1974, with 9 000 tons as PCB_3 (similar to Aroclor 1242) and 1 000 tons as PCB_5 (similar to Aroclor 1254) (Xing *et al*., 2005; NIP China, 2007). Both tri and penta PCBs are two major industrial PCB mixtures produced in China. PCB_3 has been identified as being close to Aroclor 1242 (with a reported breakdown of congeners of: mono-CB 1%, di-CB 17%, tri-CB 52%, tetra-CB 25%, penta-CB 5% and hexa-CB < 1% (Albro and Parker, 1979). PCB_5 has been identified as being close to Aroclor 1254 (a commercial European mixture, containing approximately tetra-CB 21%, penta-CB 48%, hexa-CB 23%, and hepta-CB 6%; Jiang *et al*., 1997) in composition (Wang *et al*., 1981). PCB_3 contains a relatively higher percentage of low-chlorinated congeners, and PCB_5 contains a relatively high abundance of high-chlorinated congeners. Aroclor 1242, a chlorinated biphenyl was once widely used as a commercial congener mixture and as a dielectric medium in transformers and capacitors with an average chlorination of three chlorine atoms per molecule (tri-chlorinated PCBs). The Chinese technical PCB_5, with similar composition to Aroclor 1254 has been widely used in industry in heat-transfer fluids, hydraulic lubricants, dielectric fluids, and transformer oil. Aroclor mixtures have a code made up of four numbers, for example, (Aroclor 1252) where the first two numbers identify the type of compound (12 = chlorinated biphenyl) and the last two numbers (52) provides information about the percent chlorine by weight (Hutzinger *et al*., 1974; Kalmaz and

Kalmaz 1979). Aroclor 1016 was an exception in this category, because it is produced from Aroclor 1242 and therefore has 41% percent chlorine instead of 42% (Safe 1994). Aroclor that has low chlorine content is a clear, less viscous oil, while the high chlorine mixtures are more viscous with a waxy appearance (Hutzinger *et al*., 1974; Pal *et al.,* 1980; Addison, 1986). The trade names of some commercial PCB mixtures manufactured in other countries are Clophen (Germany), Fenclor (Italy), Kanechlor (Japan), and Phenoclor (France) (De Voogt and Brinkman, 1989). The composition of commercial Clophen A-60 and Phenoclor DP-6 is similar to Aroclor 1260, and that of Kanechlor 500 is similar to Aroclor 1254. Fenclor contains 100% deca-chlorobiphenyl (De Voogt and Brinkman 1989). Of all PCBs manufactured and used as industrial chemicals, over 30% find their way back into the environment. Production of PCBs has decreased drastically from over 39 008 tons in 1970 to 15 892 tons in 1977. The current presence of PCBs in the environment, even though it has been phased out by EPA in 1979, could be attributed to the remobilization of the PCBs from soil into the aqueous phase and volatization to the gaseous phase and back to soil by the wet deposition process. Other sources of PCBs into the environment include leachate from landfills, combustion of municipal refuse and sewage sludge, and illegal or improper disposal of waste materials, such as old transformer fluid, and old electronics in municipal landfills (UNEP, 2001; UNEP, 2009; Hu and Hornbuckle, 2010; UNEP, 2011). The key sources of POPs into the aquatic environment is represented in **Fig**. 2.2.

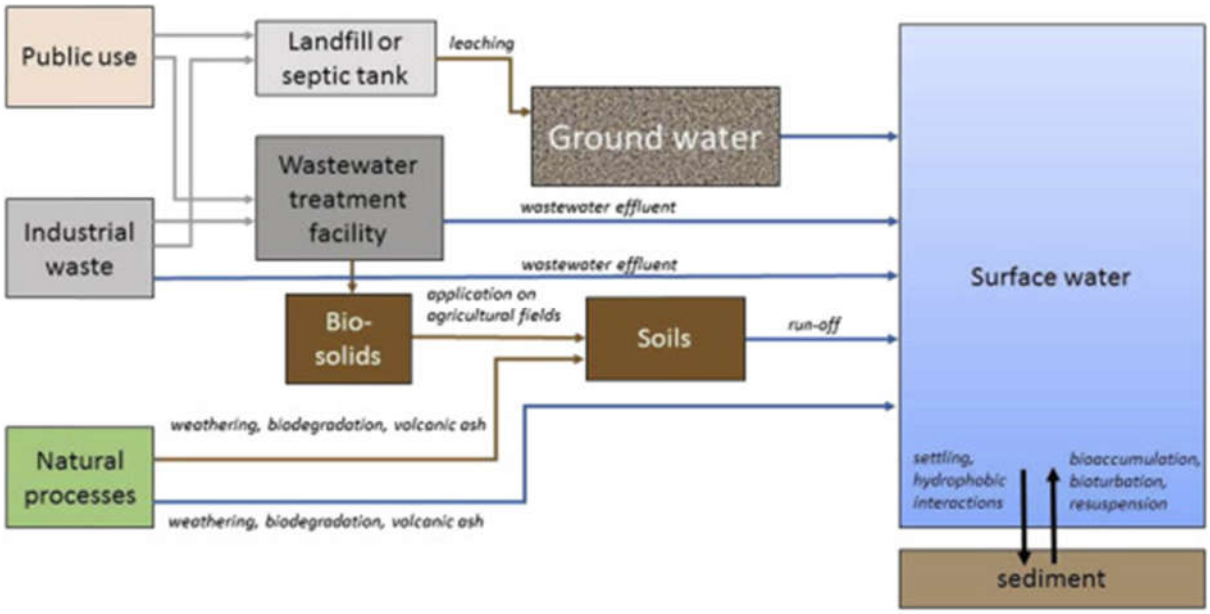


Figure 2.2: Sources of contaminants and transport to environmental reservoirs through water (Hannigan *et al*., 2018)

2.1.3 Uses and application of PCBs

The choice of PCB for industrial usage is dependent on its properties, such as, degree of chemical inertness, its ability to resist heat, its non-flammability potential, vapour pressure as well as its dielectric constant. Due to these properties, PCBs found many industrial applications such as as paint additives in carbonless copy paper and in plastics, dielectrics in transformers and large capacitors and as heat exchange fluids (Erickson 1997, 2001; Johnson *et al*., 2006). In China, PCB_3 (similar to Aroclor 1242) was primarily used in power capacitors for generating and distributing electricity, while PCB_5 (similar to Aroclor 1254) was mainly used as a paint additive.

PCBs were mostly used as mixtures containing several congeners and were rarely used as individual PCBs. However, in order to achieve specific properties, they were mixed with other compounds, for example, the PCB product Sovol was mixed with α-nitro naphthalene to enhance its vapour pressure and was sold as Nitrosovol (UNEP, 1988). Combining PCBs with asbestos produced a product called Galveston that was used on galvanized steel and galvanized corrugated sliding panels that found many uses in the defence force. After PCB production and use was phased out, obsolete PCB-containing materials such as transformer oils were withdrawn from circulation and stored for disposal (Xing *et al*. 2005). A large proportion of this old equipment was made up of capacitors (NIP China, 2007). Other uses of PCBs include sealants and flame-retardant coatings, inks, adhesives, dyes used for carbonless duplicating paper, lubricants for conveyor belts, rubber products, paints, additives in pesticide formulations, plasticizers, supports for catalysts, immersion oil for microscopes, cutting and lubricating oils, surface and metal coatings, and wire insulators (ATSDR, 2000; Erickson, 2001; Erickson & Kaley, 2011).

2.1.4 PCB congeners and homologs

Generally, the word “congeners” is used as the common term to describe all the possible 209 PCB compounds. The degree of chlorination plays an important role in classifying PCBs. The term

"homolog" is used to refer to all PCBs with the same number of chlorine atoms (e.g., trichlorobiphenyls). Homologs with different substitution patterns are referred to as isomers. For example, the tetrachlorobiphenyl homolog has four chlorine substituents and contains 42 isomers, they all belong to the same homolog group but their molecular arrangements do not necessarily need to be identical. The stereochemistry of PCBs is dependent on the position of chlorine atoms on the phenyl rings such as *ortho*, *meta* or *para* positions. If the PCB molecule has a larger chlorine atom at the *ortho* position instead of a smaller hydrogen atom, it results in the PCB molecule taking on a nonplanar configuration. PCBs may assume a planar configuration when the phenyl ring is substituted with chlorine atoms at non-*ortho* positions or mono-*ortho* substituted position and are commonly referred to as planar or coplanar congeners. The substitutions of the phenyl rings with chlorine atoms at both *ortho* positions will make it more difficult for congeners to assume a planar conformation more easily (ATSDR, 2000).

The number and position of the chlorine atoms affect the toxicology of PCBs, because the chlorine atom in the *ortho* position inhibits the free movement of the benzene rings along its axis. Planar PCB congeners with four or more chlorine atoms at *para* and *meta* positions have been found to be more toxic than their corresponding congeners with the chlorine atoms at *ortho* positions (Safe, 1984; USEPA, 2012). A toxic equivalency factor (TEF) is used to describe the potential toxicity of planar halogenated hydrocarbons. This is done by comparing the calculated TEF values to the most toxic compound in this class which is 2,3,7,8-tetrachloro dibenzo-*p*-dioxin. TEFs for planar PCB congeners range from 5×10^{-4} for PCB 77 to 0.1 for PCB 126 while nonplanar PCB 105 and 180 has a TEF of 3×10^{-5} and 1×10^{-5}, respectively (Safe 1994; Eisler and Belisle, 1996; Hoffman *et al*., 1996). The toxicity of planar PCBs may be due to its binding to the aryl hydrocarbon receptor (AhR) thereby producing dioxin-like effects, which are similar to that found with nonplanar PCBs (e.g. tumor promoter).

2.1.5 Physical and chemical properties of PCBs

PCB congeners are mostly colourless or slightly yellowish, and in most cases odourless, crystalline compounds. However, commercial products are viscous liquid mixtures of these compounds with viscosity increasing as the degree of chlorination increases, resulting in a light yellow to a dark

coloured liquid. Aroclor 1242 for example, is known to be a liquid while Aroclor 1260 has a characteristic sticky resin texture (Erickson, 2001). Generally, the water solubility ranges between 1 x 10^{-5} to 1.21 mg/L and vapour pressure of 3 x10^{-5} to 0.9 Pa at 25ºC decreases as the degree of chlorine substitution increases, with lipid solubility increasing with increasing chlorine substitution. Due to the general inertness of PCBs, they resist acids, alkalis and oxidants and their high flash-points make them useful as a fire-retardant (IPCS, 2003). Because of their excellent dielectric (insulating) properties, they have a wide variety of applications, such as dielectric fluids in transformers and capacitors, heat-transfer fluids and lubricants.

The physical properties of PCBs are important in understanding their analytical and physiological properties, and their environmental behaviour. Due to the increase in the log K_{ow} values from log K_{ow} 4.3- 8.3 for monochlorobiphenyl and decachlorobiphenyl in the environmental media, PCBs are more likely to interact with soil or sediment organic components, biological tissues, or with organic materials in aquatic systems. Also, the range of log K_{ow} values of 4.3 to 8.3 signify that high partition ratios of about 10^4 to about 10^8 are possible for PCBs in the environment (Wania and Mackay 1999). The volatilization rate of PCBs from water surfaces relative to their vapour pressure is dependent on their degree of hydrophobicity. Thus, the gas-particle phase transfer of PCBs may play an important role in their transportation and distribution in the atmosphere. PCBs are combustible liquids, and its combustion by-products are in most cases more hazardous than the parent material itself. Its by-products of combustion include hydrogen chloride, polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) (NFPA, 1994). Physical and chemical properties of Aroclors are presented in **Table** 2.1, and **Table** 2.2 presents the homolog groups of PCB congeners.

Table 2.1:

Physical and chemical properties of Aroclor mixtures

Property Aroclor	Molecular weight (g/mol)	Physical state	Melting point, ºC	Boiling point, ºC	Density, g/cm^3 at 25ºC	Solubility: Water, mg/L	Partition coefficients: Log K_{ow}	Vapor pressure, mm Hg at 25ºC	Conversion factors Air (25ºC)	Flashpoint, ºC
1016	257.9	Oil	No data	325–356	1.37	0.42 (25ºC)	5.6	4.0 x 10^{-4}	1 mg/m^3=0.095 ppm	170
1221	200.7	Oil	1	275–320	1.18	0.59 (24ºC)	4.7	6.7 x 10^{-3}	1 mg/m^3=0.12 ppm	141–150
1232	232.2	Oil	No data	290–325	1.26	0.45 (25ºC)	5.1	4.06 x 10^{-3}	1 mg/m^3=0.105 ppm	152–154
1242	266.5	Oil	No data	325–366	1.38	0.34 (25ºC)	5.6	4.06 x 10^{-4}	1 mg/m^3=0.092 ppm	176–180
1254	328	Viscous liquid	No data	365–390	1.54	0.057 (24ºC)	6.5	7.71 x 10^{-5}	1 mg/m^3=0.075 ppm	No data
1260	357.7	Sticky resin	No data	385–420	1.62	0.08 (24ºC)	6.8	4.05 x 10^{-5}	1 mg/m^3=0.065 ppm	No data
1262	389	No data	No data	390–425	1.64	0.052 (24ºC)	No data	No data	1 mg/m^3=0.061 ppm	195
1268	453	Viscous liquid	No data	435–450	1.81	0.300 (24ºC)	No data	No data	1 mg/m^3=0.052 ppm	195

Source: USEPA, 1985; HSDB, 2000; ATSDR, 2000; USEPA, 2003.

Table 2.2:

The homolog groups of PCB congeners

Property / Homolog	CAS NO	Molecular Weight	Melting point, ºC	Boiling point, ºC	Solubility: Water, mg/L (25ºC)	Partition coefficients: Log K_{ow}	Approximate bioconcentration factor in fish	Approximate evaporation at 25ºC (g/m^2 /h)	Vapour pressure (Pa) at 25ºC
Monochlorobiphenyl	27323-18-8	188.7	25 - 77.9	285	1.21-5.5	4.3 - 4.6	2 .5 x 10^3	2.5 x 10^{-1}	0.9-2.5
Dichlorobiphenyl	25512-42-9	223.1	24.4 - 14	312	0.06-2.0	4.9 - 5.3	6.3 x 10^3	6.5 x 10^{-2}	0.008-0.60
Trichlorobiphenyl	25323-68-6	257.5	28 – 87	337	0.015-0.4	5.5 - 5.9	1.6 x 10^4	1.7 x 10^{-2}	0.003-0.22
Tetrachlorobiphenyl	26914-33-0	292.0	47 - 180	360	0.0043-0.010	5.6 - 6.5	4.0 x 10^4	4.2 x 10^{-2}	0.002
Pentachlorobiphenyl	25429-29-2	326.4	76.5 - 124	381	0.004-0.02	6.2 - 6.5	1.0 x 10^5	1.0 x 10^{-3}	0.0023-0.05
Hexachlorobiphenyl	26601-64-9	360.9	77 - 150	400	0.0004-0.0007	6.7 - 7.3	2.5 x 10^5	2.5 x 10^{-4}	0.0007-0.012
Heptachlorobiphenyl	28655-71-2	395.3	122 -149	417	0.000045	6.7 – 7	6.3 x 10^5	6.2 x 10^{-5}	0.00025
Octachlorobiphenyl	55722-26-4	429.8	159 - 162	432	0.0002-0.0003	7.1	1.6 x 10^6	1.5 x 10^{-5}	0.0006
Nonachlorobiphenyl	53742-07-7	464.2	183 - 206	445	0.00018-0.0012	7.2 - 8.16	4.0 x 10^6	3.5 x 10^{-6}	-
Decachlorobiphenyl	2051-24-3	498.7	306	456	0.00001	8.26	1.0 x 10^7	8.5 x 10^{-7}	0.00003

Source: ATSDR, 2000; USEPA, 2003.

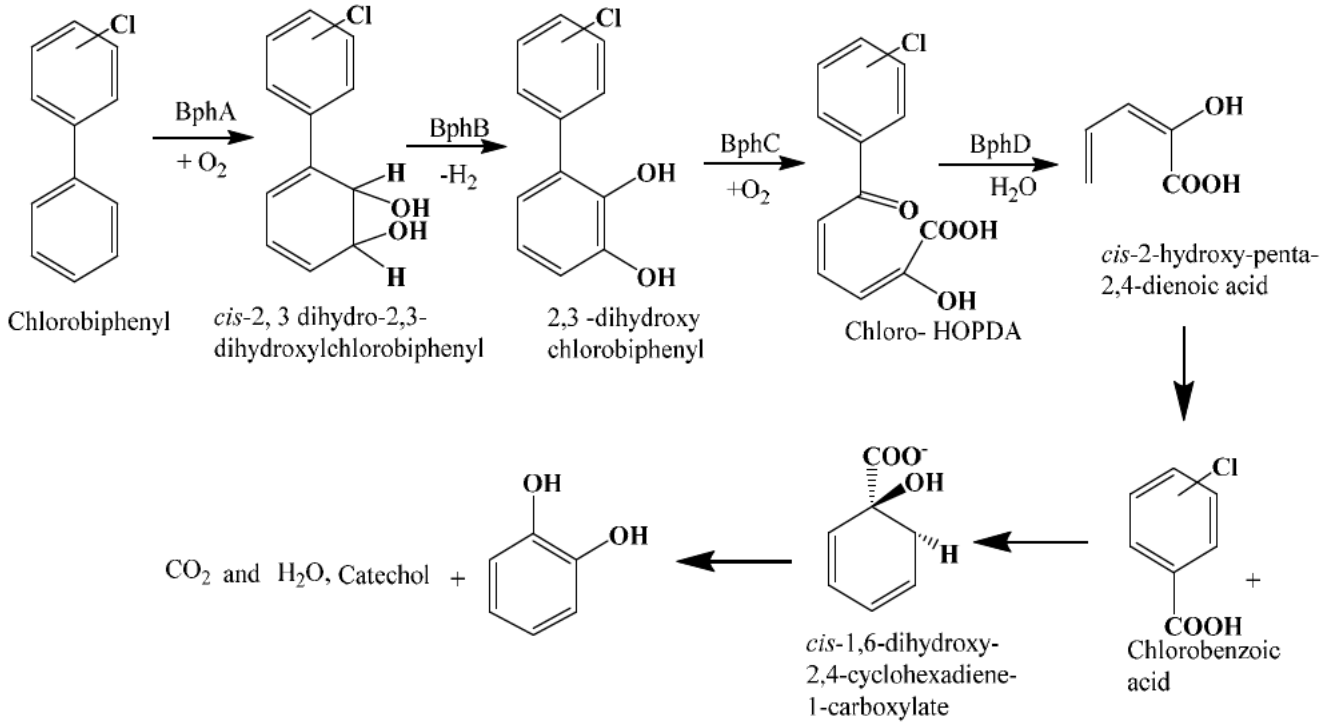
2.1.6 The fate of PCBs in the environment

PCBs are more likely to be susceptible to biodegradation in the environment *via* two major routes, that of aerobic and anaerobic conditions. Less chlorinated PCBs are usually susceptible to aerobic degradation, which occurs *via* two pathways. The initial stage involves the addition of O_2 at positions 2 and 3 by a dioxygenase enzyme to form intermediate toxic metabolites of 2,3 dihydroxychlorobiphenyl and chloro-HOPDA which subsequently metabolizes to chlorobenzoic acid and *cis*-2-hydroxypenta-2,4-dienoate. The final stage of aerobic biodegradation takes place through general metabolism to less toxic products such as catechol and carbon dioxide, water, chlorine, and biomass (Gan and Berthouex 1994; Bedard, 2003; Pieper, 2005) (**Fig** 2.3a).

However, microbial reductive dechlorination of highly chlorinated PCBs occurs under anaerobic conditions. In this case, the dechlorination process involves the loss of *meta* and *para* chlorine atoms resulting in depletion of more chlorinated PCB congeners, leaving the biphenyl nucleus untouched with the formation of less toxic *ortho* chlorinated PCB congeners. The preferential loss of *meta* and *para* chlorines by anaerobic action has been shown to result in a significant decrease in the amounts of coplanar and dioxin-like PCB congeners (Quensen *et al*., 1992). Thermal degradation of *ortho* PCB (penta-CB) in the presence of air at 600ºC for 60 seconds was found to involve four major processes with six different byproducts. The first mechanism involved the loss of two *ortho* chlorines. Mechanism two takes place *via* the loss of HCl and a 2,3 chloride shift while mechanism three occurs through the loss of HCl and the last process involves the loss of H_2 molecule (Buser and Rappe, 1979). Details of aerobic oxidative biodegradation of PCB and thermal degradation processes of 2,2',4,5,5'- penta-CB are shown in **Fig**. 2.3 a and b, respectively.

Both the hydrophobic and stereochemistry characters of PCB are the major factors controlling the rate of microbial activities decomposition of PCBs (Eisler 1986). Generally, the microbial degradation rate of PCBs in soils decreases as the number of chlorine atoms on the phenyl rings increases (Furukawa 1982).

a


Cl
BphA
+ O_2
H
OH
OH
H
BphB
-H_2
OH
OH
BphC
+O_2
O
COOH
OH
BphD
H_2O
OH
COOH
Chlorobiphenyl
cis-2, 3 dihydro-2,3-dihydroxylchlorobiphenyl
2,3 -dihydroxy chlorobiphenyl
Chloro- HOPDA
cis-2-hydroxy-penta-2,4-dienoic acid
CO_2 and H_2O, Catechol +
OH
OH
COO^-
OH
H
cis-1,6-dihydroxy-2,4-cyclohexadiene-1-carboxylate
Cl
COOH
+
Chlorobenzoic acid

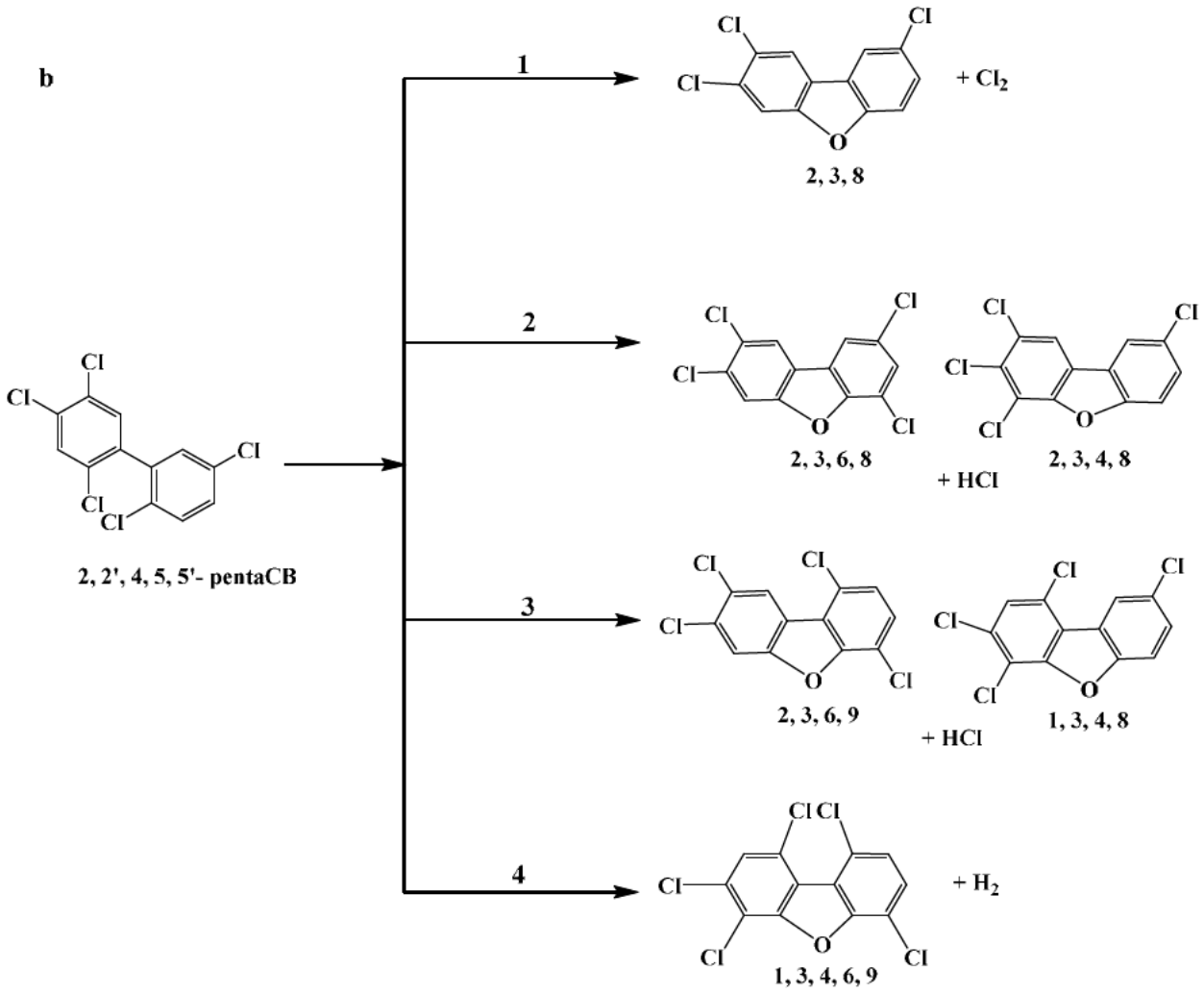


Figure 2.3: (a) Aerobic oxidative biodegradation of chlorobiphenyl and (b) thermal degradation processes of 2,2',4,5,5'- penta-CB in the environment (Furukawa, 2000; Bedard, 2003; Pieper, 2005)

2.1.7 Health related effects of PCBs

PCBs have been associated with many health-related effects in both animals and humans. The first human health effects of PCBs reported were the incidents of *Yusho* and *Yucheng*. The *Yusho* incident occurred in Japan in 1968, which involved more than 1 600 people ingesting rice oil contaminated with PCBs (NAP, 2001). The health effect associated with PCB exposure has been linked to two major important areas depending on the level and duration of exposure. The first category is the short-term effect: according to the EPA this is associated with PCBs, which are capable of causing potential health impacts on people who are exposed to concentrations

that are higher than the expected maximum contaminant level (MCL) for a short period of time. The associated effects are lesions that look like acne, discolouration of the skin, hearing and vision problems, as well as spasms[2] (Klanova *et al*., 2007; ATSDR, 2000). The second category is referred to as 'long-term effects'. In this case, PCBs are capable of causing various health challenges as a result of a lifetime of exposure at levels above the MCL. Effects such as acute poisoning, nose irritation, throat and gastrointestinal tract problems (such as severe abdominal pain, nausea, vomiting and diarrhea), endocrine disruption, reproductive and immune dysfunction, and learning disorders in children were observed. In addition, neurobehavioral disorders (headache, dizziness, depression, and nervousness, muscle and joint pain), and changes in liver functioning (symptoms are nausea, vomiting, weight loss, jaundice, edema, and abdominal pain) as well as cancer were found to be associated with this category (Katsoyiannis and Samara, 2005; USEPA, 2012). Some of the environmental and biological health related issues of PCBs are discussed below.

2.1.8 Environmental related effects of PCBs

PCBs are very persistent in the environment and bioaccumulate in all environmental media and animals such as soil and sediments, suspended particulate matter in water and air, in wildlife and the fatty tissue of animals and probably humans. Research into their break-down products is limited and only microbial degradation has been studied (Schwarzenbach *et al*., 1993; Muir *et al*., 1996). Human exposure to PCBs are mostly *via* ingestion of contaminated food since PCBs are lipophilic and accumulate in the food chain, and fatty tissues of animals. Exposure may also be through inhalation and dermal absorption (ATSDR, 2000; IOM, 2003). Research has shown that farmed salmon fed with concentrated fishmeal or fish oil containing significant amounts of PCBs resulted in elevated concentrations of PCBs (Hites *et al*., 2004). The most common PCBs found in food are higher chlorinated congeners. This is due to their lower volatility and more biological persistence in plants and animals than the lesser chlorinated congeners. Inhalation is another important route of PCB exposure however, it is difficult to determine the significance of inhalation compared with ingestion. Johansson *et al.* (2003) noted that PCBs may be bound to indoor dust, and possibly either ingested or inhaled. Their finding

[2]A spasm is a sudden involuntary contraction of a muscle, a group of muscles, or a hollow organ such as the heart. Spasms occur mostly in skeletal muscles and result because of excessive use of the muscle resulting in it becoming tired and sometimes dehydrated. Spasm may occur suddenly and may be painful but is usually short-lived. It may be relieved by gently stretching the muscle.

further established that individuals who spend sufficient time in the presence of volatile PCBs might possibly be continuously exposed to it, which is not accounted for in studies of "total" PCB exposure (ATSDR, 2000). This is due to rapid metabolism and excretion by the human body of less chlorinated PCB congeners. To further establish the exposure level of PCBs due to inhalation, blood samples were analysed for PCBs from individuals living in houses where a PCB-containing sealant was used. Dermal absorption of PCBs had also been reported by Wester *et al.* (1987, 1993) to occur primarily in the workplace, most commonly *via* contact with contaminated sediments or physical handling of PCB solutions without adequate protection. Studies also showed that PCB congeners with fewer chlorine atoms are more readily absorbed through the skin compared to congeners containing more chlorine atoms (Garner & Matthews, 1998). As noted by Patterson *et al.* (2009), human health effects from PCBs may possibly not be related to any pattern found in commercial PCB products. The general public may often be exposed to multiple sources of PCBs, and only rarely to a single commercial product. This reason could be as a result of any of the following factors.

i) Environmental matrices, biological organisms including humans may be exposed to PCBs through more than one path.
ii) The degree of dechlorination varies in sediments, soils, water and air. During this process the volatile commercial PCBs with low chlorine atoms are lost.
iii) PCBs that are consumed by aquatic species and animals may be broken down to less chlorinated and hydroxylated congeners. Thus, the PCBs found in these species, which eventually are consumed as food, may have a different congener profile as compared to commercial PCBs.
iv) If the main route of exposure is inhalation, then there may be selective exposure to volatile congeners or those that have a lower degree of chlorination and are less persistent.
v) Genetically, differences in individuals may lead to variations in metabolic breakdown or selective metabolism of specific congeners.

Due to their hydrophobic nature and relatively moderate vapour pressure, PCBs can sorb to soils or volatilize, and in most cases leach less to groundwater (Buckley-Golder, 1999). An already contaminated aquatic sediment system with PCBs may lead to remobilization of PCBs back into the surface water, bioaccumulate in fatty tissues of aquatic life and suspended particulate matter in water and thereby cause potential health effects to aquatic life and humans that consume the water (**Fig**. 2.4).

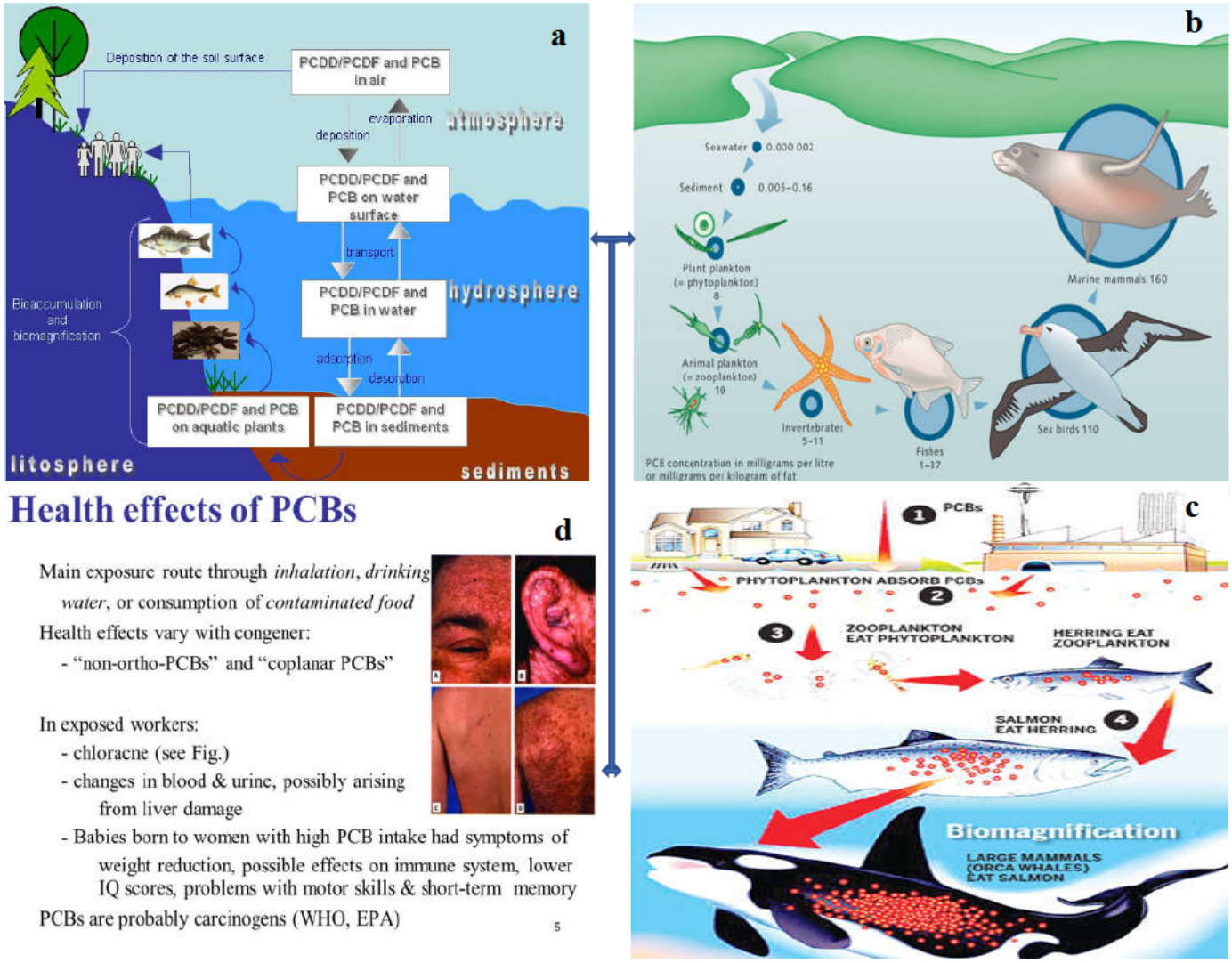


Figure 2.4: Diagram showing transportation (a) bioaccumulation, biomagnification (b-c) and health related effects of PCB in marine organisms and humans (d). Adapted from http://worldoceanreview.com/en/wor-1/pollution/organic-pollutants/: Date accessed 29/02/2018

2.1.9 Biological related health effects of PCBs

2.1.9.1 Carcinogenicity and genotoxicity effects

Several experiments studying the dietary administration of PCBs in mice and rats to examine the carcinogenic effect of PCBs have been carried out (Silberhorn *et al*., 1990). Stomach and lung tumours have been recently reported apart from the liver tumours, which in the past had been the most frequent tumours observed after PCB exposure. In order to validate information in some of the bioassays for liver cancer, an evaluation has been used by a panel of pathologists

(Schaeffer, 1984; Norback and Weltman, 1985). The results showed that more chlorinated PCB mixtures, (Aroclor 1260 and Clophen A60), gave a possible hepatocarcinogenic response (liver tumour related issue). However, results of many other studies showed that there were more incidences of hepatocellular proliferative lesions in both male and female rats, which were found to be associated with ingestion of other PCB mixtures such as Aroclor 1254, Clophen A30. Tumour initiation caused by various PCB mixtures and individual congeners was assessed by Hayes *et al.* (1985), in a bid to initiate the formation of a liver-related enzyme (gamma glutamyltransferase) positive foci[3] in F344 rats[4]. Gamma glutamyltransferase (GGT) is a membrane enzyme, which has a very crucial role in glutathione (GSH)[5] metabolism. The outcome of their experiment indicated that none of the PCBs generated GGT-positive foci, whilst other known initiators showed positive formation of the liver tumour (PCB mixtures themselves do not have any adverse effects or altered the antioxidant membrane-bound enzymes towards the cells initiation of liver tumour on the assay system used). In addition, the potential of PCBs to form tumours was studied extensively in two-stage carcinogenesis models in rat liver, and in mouse lung and skin. The administration of PCB mixtures, such as Aroclor 1254 (Preston, *et al*., 1981), Kanechlor 400 (Kimura *et at*., 1976), Clophen A50 (Oesterle *et al*., 1984), and Kanechlor 500 (Nishizumi, 1976; Tatematsu *et al*., 1979) to rats with different initiating agents (different Aroclor of PCB mixtures) has demonstrated an increase in the number and size of altered hepatic foci, which is an early sign of liver tumour. Aroclor 1254 has also been reported to initiate tumour promotion in liver and lung in mice (Anderson *et al*., 1994). Promotion effects have been documented for nearly all the individual PCB congeners investigated thus, both DL-PCB and NDL-PCBs have been linked to tumour promotion.

There is insufficient evidence at present that suggest PCBs cause point mutations, either in *Salmonella typhimurium* (Ames test) or in V79 Chinese hamster cells (Ahlborg *et al*., 1992; WHO, 1993). The results of most assays on cytogenetic effects were found to be negative and some reports indicated a significant increase in chromosomal abnormalities in mammalian cells, such as chromatid breaks and rearrangement (Ahlborg *et al*., 1992; WHO, 1993). PCBs have been reported to bind to DNA both in *vivo* and in *vitro* and DNA regeneration have been

[3] Foci is a small group of cells produced in the liver which are different to the surrounding tissue. This indicates the start of a lesion, which may result in nodules forming or eventually lead to heptacellular carcinomas.
[4] F334 rats are the experimental animals used for the study
[5] Glutathione is a marker for apoptotic balance, which is produced during normal metabolism and it is important for protecting cells against oxidants, removal and detoxification of carcinogens (Whitfield, 2001). However, any alterations to glutathione pathway can have a profound effect on cell survival (Hanigan, 1995; Dominici *et al*, 1999; Hanigan *et al*, 1999; Whitfield, 2001).

observed in mammalian cells in *vitro* (Ahlborg *et al*., 1992; WHO, 1993). However, low chlorinated PCB congeners may cause mutagenicity and DNA damage. The proposed possible mechanism for the genotoxicity effect of PCBs involved its metabolic process to arene oxide intermediates, which are able to alkylate critical cellular macromolecules (Safe, 1984; 1990). Studies have also shown that several PCB mixtures and certain selected PCB congeners are capable of inducing oxidative stress in the liver such as lipid peroxidation and oxidative DNA damage in laboratory animals, effects on vitamin A metabolism and intercellular communication and consequently promoting liver tumours (Glauert *et al*., 2001; Robertson and Hansen, 2001; Fadhel *et al*., 2002; Tharappel *et al*., 2008). More importantly, the International Agency for Research on Cancer also classified PCBs as a human carcinogen based on evidence of malignant melanoma and direct association with breast cancer as well as cancer originating in white blood cells (IARC, 2016b). Some selected PCB congeners and highly chlorinated commercial PCB mixtures such as PCB 126, PCB 118 and Araclor 1260, Araclor 1254, and Kanechlor 500 with dioxin-like and AhR related activities have been reported to show strong positive correlations with cancer-associated effects such as tumour promotion and estrogen activity (IARC, 2016b). Breast cancer was also reported at an elevated level in men who had previously been exposed to combinations of PCBs and dioxins at higher concentrations (Villeneuve *et al*., 2010).

2.1.9.2 Carcinogenic effects

Few cases of epidemiological studies of PCB exposure in animals and humans have been linked to a possible cause of cancer, which has caused concern about their potential carcinogenicity (USEPA, 2012). In a case study of victims of the *Yusho* PCB outbreak in Japan due to the previous occupational exposure to PCBs, results indicated an increased incidence of liver and biliary tract cancer, which could be traced to a possible association of PCBs with brain cancer as revealed by data of human carcinogenicity status (Sinks *et al*., 1992; ATSDR, 2000). Studies on workers in an electrical capacitor manufacturing plant in New York and Massachusetts were found to develop cancer, which resulted in death in some cases. The cause of this was shown to be exposure to PCBs found in the electrical components (Brown and Jones, 1981; Brown, 1987b). A study of 2 222 men working between 1946 and 1975 at a transformer-manufacturing plant in Manitoba, Canada, where PCBs were used to fill large transformers, showed an increased incidence of cancer and mortality related issues (Yassi *et al*., 2003). The result

indicated a high risk for cancer of the digestive tract, in particular cancers of the stomach and pancreas, among workers in the transformer-assembly department. Increased risk of cancers of the gallbladder and pancreas were also observed among all workers, and a higher incidence of cancer of the pancreas was reported among workers in the transformer-assembly department (Yassi *et al*., 2003). Similarly, a study was conducted in Bergamo, Italy, among 471workers who were involved in building of transformers between 1950 and 1988, using PCBs until 1980 and mineral oils thereafter, as well as those who repaired transformers from 1988 until the early 1990s. The mortality from cancer of the intestine was found to be high among the workers (standardized mortality ratio (SMR), 2.6; 95% confidence interval (CI), 1.6–3.5; 11 deaths), but mortality from cancer of the stomach or liver or leukemia was not reported (Caironi *et al*., 2005). De Guire *et al.* (1988, 1992) found an increased incidence of mortality from malignant melanoma among 9 590 employees of a telecommunications company in Montreal, Canada, who had been employed for 6 months or more between 1976 and 1983 who might have probably been exposed to PCBs.

However, there are inconsistencies in cancer-related studies with many having setbacks such as a small number of samples used, a short period of investigation, possible contamination with other chemicals and some other unexpected factors. In all the cases investigated, PCB mixtures were found to be likely contaminated with PCDFs, which may have affected the results.

2.1.9.3 Neurological and immunological effects

Associated effects of PCBs in relation to neurological imbalance in animals and humans have been thoroughly investigated. Studies on laboratory animals have shown that PCBs are able to cause negative neurological effects in both infants and adult animals. Reasonable data have shown that PCBs play a role in neurobehavioral alterations observed in infants and young children of women exposed to low PCB concentrations. The neurobehavioral study was conducted by exposing rats to Aroclor 1254. The results indicated that the memory of rats undergoing maze experiments were affected when they were exposed to Aroclor 1254 prior to and just after birth (Corey *et al*., 1996). Rats exposed to PCBs were found to make more mistakes going through the maze than control rats inrespective of whether the pups continued to be fed the PCBs or feeding had stopped. Research showed that month old offsprings from rats that were fed approximately 1 mg Aroclor 1254/kg/day during pregnancy and

breastfeeding stages made more errors than control rats in a Morris water maze during trials (Provost *et al*., 1999).

In a bid to test the effect of PCBs in humans, a series of epidemiological investigations were conducted in a general population who consumed fish from Lake Michigan in the United States. Studies were later conducted on 242 pregnant women who consumed a moderate to high amount of contaminated fish from Lake Michigan. The control for this study was a group of 71 pregnant women who did not consume fish (Fein, 1984). The outcome of epidemiological studies revealed that the intake of fish correlated positively to the PCB levels in maternal serum and milk, and also to the cord serum concentrations of the pregnant women who were exposed to the PCBs. There were equal proportions of PCB concentration levels in the fat of maternal serum and breast milk as well as in cord serum of mother to infant pair (Jacobson, 1983). On the other hand, the relationship of intake of fish and cord serum PCB levels with gestational age, birth weight, head circumference, and size were noted to be inversely proportional. Furthermore, delayed infant autonomic maturity and unusually poor reflexes were also found to be associated with fish intake as reported (Jacobson, 1984). Investigations conducted on the infants at 7 months of age, revealed that, there was an inverse relationship between the cord blood PCB level and visual recognition (Jacobson *et al*., 1985). At the age of 4 years, the findings showed that there was an association between cord serum level of PCB and under performance in verbal and numerical memory tests on the children as revealed by McCarthy memory scale (Jacobson *et al*., 1990). These children were also found to perform below average in other tests of cognitive development and sustained attention (Jacobson *et al*., 1992). Prenatal exposure to PCBs was found to be associated with lower body weight at 4 years of age (Jacobson *et al*., 1990). Therefore, these effects were found to be more associated with prenatal rather than postnatal exposure to PCBs. However, composite activity rating at 4 years were found to be inversely associated with the concentration of PCBs in breast milk, how long children were breast-fed, and the concentration of PCBs in serum.

Epidemiological investigations conducted on newborn babies and children in the Lake Michigan area exposed to levels of PCBs prior to birth and shortly after birth, showed they had weak verbal and memory skills, poor reflexes and deficiencies in memory, learning and intelligent quotient (IQ) (Jacobson *et al*., 1990a; Jacobson and Jacobson, 1996; Lanting *et al*., 1998c; Patandin *et al*., 1999).

Rhesus monkeys exposed to prolonged low concentrations of Aroclor 1254 showed significant effects on immunological parameters (Tryphonas *et al*., 1991). Immunological studies in monkeys and other animals revealed a number of serious effects on the immune system when exposed to both chronic and low-level exposure to Aroclor 1254. The effects include a visible decrease in the size of the thymus gland in infant monkeys and rhesus monkey immune systems by altering their T-cells; reductions in sheep red blood cells leading to reduced response of the sheep immune system, and decreased resistance to the Epstein-Barr virus and other infections in animals exposed to PCBs (ATSDR, 2000; Ritter *et al*., 2005; USEPA, 2012). Studies on the victims exposed to PCBs in the *Yu-Cheng* incident reported them to have weak immune systems resulting in the easy onset of various infections (ATSDR, 2000).

2.1.9.4 Reproductive and developmental effects

Research has shown that people who were exposed to PCBs had reproductive dysfunction. Female victims tend to have associated effects such as disorders of the reproductive organs, menstrual disturbances, and an increased risk of miscarriage and stillbirth as well as reduced lactation, which was also found to be associated with increased levels of PCBs in maternal breast milk. Associated effects on male fertility was also attributed to certain levels of exposure of male victims to PCBs (ATSDR, 2000). Studies were conducted on workers who were directly exposed to Aroclors during the manufacturing process for at least 1 year before the birth of an infant, and workers with low levels of exposure where Aroclors were not directly used. The results of the investigation on PCB exposure found that women who had previously worked with PCBs gave birth to babies having low birth weight and as the level of PCB exposure increased, slow foetal development was observed (USEPA, 2012). *Yusho* and *Yu-Cheng* PCB exposure incidences of 1970 were investigated in the affected patients; the result indicated that irregular menstrual cycles and unusual normal body temperature patterns were observed in female *Yusho* patients (Kusuda, 1971). Fertility history, sperm counts, and testicular abnormalities have been investigated using physical examination of men who have historical occupational contact with PCBs and those without. The results indicated that 55 transformer repairmen who had formally been exposed to PCBs were found to be normal compared to 56 unexposed workers who were similar in age, race, and marital status (Emmett *et al*., 1988a, 1988b). Furthermore, the effect of PCBs of *Yusho* incidence on males was also investigated. The result of the investigation showed that there was a delay in sexual maturation,

and testicular and scrotal development was said to be unaltered in boys born to *Yu-Cheng* women, although the exposed boys had significantly shorter genitals (Guo *et al*., 1993). Among the 74 children born to *Yu-Cheng* women during or after the *Yusho* poisoning incidence, the sex ratio of boys to girls was unaltered (Rogan *et al*., 1999). Evaluation of 137 live births occurred between 1978 and 1985, of which 69 were girls and 68 were boys.

Toxicity of PCBs on the reproductive organs of animals has been documented. A well-established investigation on the oral exposure to low doses of PCBs on minks was found to cause reproductive failure. Six months before minks mated, they were exposed to 0.4 mg/kg/day of Aroclor 1254 for 39 weeks, and the offspring were terminated at 4 weeks. Only two of seven mated females were able to conceive and give birth producing a total of two kids (one alive and one dead) (Aulerich and Ringer, 1977). Intermediate-duration studies of low doses of commercial PCB mixtures on the reproductive effects in female monkeys have been demonstrated. Exposure to 0.8 mg/kg/day Aroclor 1248 for 2 months caused a reduction in conception rate in monkeys (Allen *et al*., 1974a). However, conception was not found in two of five monkeys that were bred 3 months after treatment, miscarriage was also noticed in two out of the three pregnant monkeys, and the two non-pregnant monkeys were reported to rebreed twice again during the subsequent 5 months without any success being recorded (Allen *et al*., 1974a, b). Steinberg *et al*. (2008) investigated the effect of PCB mixtures Aroclor 1221 on pregnant Sprague-Dawley rat. The concentration of PCBs were varied at 0, 0.1, 1 or 10 mg/kg which were administered during late pregnancy to evaluate whether it would compromise reproductive physiology in both the fetally-exposed female offspring (F1 generation) and their female offspring (F2 generation). Both the body cells and reproductive development, which include ages of eye opening, pubertal landmarks, and serum reproductive hormones of F1 and their F2 female offspring were monitored during the study. The outcome of their investigation indicated that, low doses of Aroclor 1221 administered during the critical period of neuroendocrine development was found to cause differential effects of Aroclor 1221 on F1 and F2 female rats. Other effects noticed on the F1 generation includes, a significant alteration of serum luteinizing hormone (LH) in the 1 mg/kg Aroclor 1221 group. The F2 generation was also noticed to show more profound alterations, particularly with respect to fluctuations in hormones and reproductive tract tissues across the estrous cycle. Similar observations were reported by Chung *et al*., (2001); Salama *et al*., (2003) and Steinberg *et al*., (2007) on the effect of PCB Aroclor mixtures on the laboratory animals used for their studies.

2.2 Fate of the organic pollutants in the environment

Evaluating the behaviour and distributions of organic pollutants such as PCBs requires critical assessment of the key processes controlling their fate such as volatilization, diffusion, degradation, leaching, plant uptake, bioaccumulation, sorption (adsorption, absorption, and partitioning processes), run-off and persistence in the environment. These factors will help in determining the extent of environmental exposure to these chemicals. Organic pollutants tend to undergo one form of these processes or the other within the environmental media such as biotic or abiotic degradation, or volatilization of low molecular weight hydrophobic organic pollutants while high molecular weight HOCs may be sorbed and accumulate onto the soil organic matter (Schwarzenbach *et al*., 1993; Semple *et al*., 2003). The key processes controlling the fate of organic pollutants in the environment are shown in **Fig**. 2.5 and are briefly discussed below.

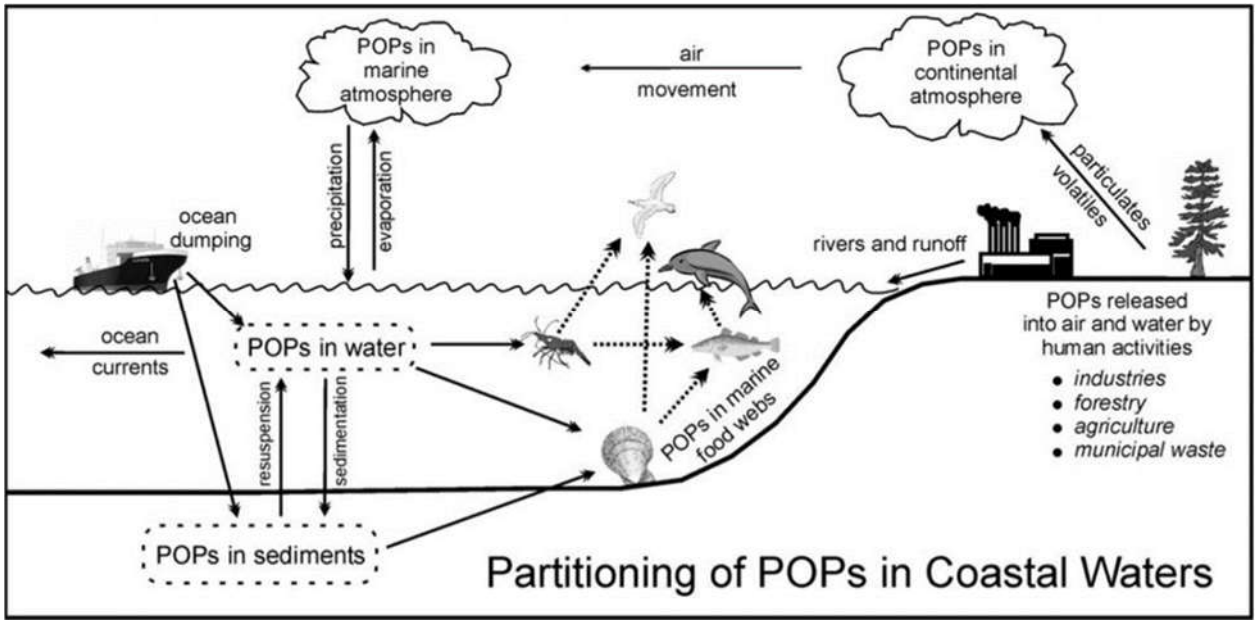


Figure 2.5: Transportation, distribution, and partitioning of the persistent organic pollutants in the environment. Adapted from www.bofep.org: Date accessed, 19/02/2018

2.2.1 Volatilization

The transportation process by which organic pollutants transfer from one environmental compartment such as the surfaces of plants, soil, and water into the vapour phase in the

atmospheric compartment is called volatilization. The movement of the organic pollutant between different compartments is an important mass-transfer phenomenon (Wolters *et al*., 2004). Understanding volatilization rates is critical to determine the amount of pollutant that enters the air phase as well as a change in the concentration of the pollutant from the source compartments. The transfer process (volatilization rates) from the source of contamination (water body, sediments, soil, and plants) to the atmosphere is highly dependent on the physicochemical properties of the organic pollutant itself, the presence of other pollutants that may hinder the volatilization rates, the physicochemical properties of the environmental matrices, and the atmospheric conditions. The volatility of pollutants is a vital parameter for evaluating its hazardous level. More importantly, Henry's law constant (H) is commonly used to measure the extent of the partitioning rate of the organic pollutant between air and water at equilibrium (Schwarzenbach *et al*., 1993). The relative tendency of an organic pollutant to volatilize from the aqueous phase to the gaseous phase is based on competition between its vapour pressure and water solubility.

This parameter is important in determining the potential for intermediate transport into the air. As an example of its application, its concentration in gas phase is related to its concentration in an underlying aquifer by equation 2.1.

$$H = \left(\frac{C_a}{C_w}\right) RT \qquad 2.1$$

where:

C_a = concentration of the organic pollutant in air (mg/m^3)

C_w= concentration of the chemical in groundwater (µg/L)

H = Henry's law constant (atm-m^3/mol)

R = gas constant (8.314 Pa /m^3.mol.K)

T = absolute temperature (K)

Values of H > 10 indicate very high air affinity and values of H < 10^{-4}, very low air affinity.

If Henry's law constant value of a pollutant is low, the pollutant will tend to partition more into the aqueous phase and will therefore, move more slowly to the gaseous phase than pollutants with high H values. As a general guideline, when H values are in the range of 10^{-7} – 10^{-5} atm-m^3/mol volatilization tends to be low, for H between 10^{-5} and 10^{-3} atm-m^3/mol volatilization is not rapid but possibly significant, and for H > 10^{-3} atrn-m^3/mol volatilization is rapid (Lyman

et al., 1990). The soil surface volatilization is a complex process, due to the partitioning of its molecules between three phases *viz*, solids, water-filled pores and gas-filled pores, which may not necessarily be in equilibrium due to slow rates of diffusion within, or transfer between the phases. Soil conditions, such as soil water content, as well as weather conditions like temperature and wind speed, might possibly influence the rates of volatilization by up to two orders of magnitude (Ahangar *et al*., 2008).

2.2.2 Vapour pressure

The pressure exerted by the vapour of an organic pollutant in equilibrium with its solid or liquid form at any given temperature is called vapour pressure. It is a relative measure of the volatility rate of an organic pollutant (OP) in its pure state, thereby determining the rate of volatilization of OPs in the environment. It is important to estimate the volatilization rate of a pollutant or its Henry's law constant value, particularly for those OPs with a low water solubility (Lyman *et al*., 1990). Generally, the higher the vapour pressure, the more likely an OP may exist in significant amounts in the gaseous phase. Thus, OPs with high vapour pressure are more likely to migrate from groundwater to soil and remobilise to surface water and eventually be transported by air.

Water/Air Partition Coefficient (K_w)

The water/air partition coefficient (K_w) relates the distribution of organic pollutants between water and air. The expression relates to the inverse of Henry's law constant (H), given by equation 2.2.

$$K_w = \left(\frac{C_{water}}{C_{air}}\right) = \frac{1}{H} \qquad 2.2$$

where, C_{air} is the concentration of the OP in air (mg/m^3) and C_{water}, the concentration of the OP in water (mg/L)

2.2.3 Degradation and biodegradation

Degradation is the half-life of OPs usually measured in days, which may occur *via* biological, physical, or chemical processes in the environmental media. It is usually expressed as the time it takes for one-half of a given amount of an OP to be degraded. Half-lives are normally used to measure the persistence rate of an OP since they indicate how long it will remain in various

environmental media. Long half-lives, usually greater than a month or a year, signifies a persistent OP in the environment. (USEPA, 1987). Generally, the greater the half-life, the more persistent a chemical is likely to be.

However, biodegradation is an important environmental process that controls the breakdown of organic compounds. The degradation process produces enzyme-catalyzed transformation products from organic constituents, and the degrading organism is primarily microorganisms. Two conditions are important for biodegradation of pollutants to occur: pollutants must be bioavailable and they must be readily biodegradable (Reid *et al*., 2000; Christopher *et al*., 2002).

During transformation (biodegradation process) some chlorinated pollutants tend to become harmless to both their targeted organisms and the rest of the environment. However, in some cases, contaminants may degrade into metabolites that are more toxic than the parent compound (Gavrilescu, 2005). The ultimate fate of a constituent introduced into several environmental systems (e.g., soil, water. etc.) may be the degradation of the parent compound to metabolites that may be more toxic or less toxic than the parent compound. For example, trichloroethylene (TCE) biodegrades to produce 1,2-dichloroethylene (1,2-DCE), vinyl chloride, and other compounds. In this case, the metabolite, 1,2-DCE is less toxic whereas the other metabolite vinyl chloride is more toxic than TCE.

Degradation *via* biological processes may lead to other chemical reactions such as depletion of oxygen levels in microbial degradation processes, which then results in an anaerobic environment, as well as the onset of redox potential-related reactions. The biodegradation potential should therefore, be carefully evaluated in the design of monitoring programs as degradation may cause the dissipation of PCBs from soils and plants. Pollutants may degrade at different rates in the environment depending on the chemical structures of the pollutants, the activity of the degrading microorganisms, and the population of the degrading microorganisms as well as the availability of pollutants to microorganisms (Semple *et al*., 2003). It may take some soil organisms a few days to degrade a pollutant whereas, other pollutants might take several years to degrade (Nash, 1967; Kerle, 1996). Degradation/biodegradation gives structural transformation of pollutants and results in a change of its pattern of movement in the environment.

2.2.4 Leaching

The process of preferential movement of OPs through soil compartments rather than over soil surfaces is called leaching. Leaching of OPs is a serious environmental concern due to their tendencies to reach the water table and therefore contaminate the groundwater. The possibility of OPs reaching the groundwater or not depends either on its movement through soil or disappearance from soil (Edgehill and Fin, 1983; Waldman and Sheval, 1993). OPs will tend to pose no environmental problem if the rate of degradation is adequately faster than the rate of leaching, therefore, an OP will disappear prior to reaching the groundwater. Evaluation of soil leaching rates of OPs is vital because it gives an idea of how long an OP will remain in the topsoil before undergoing degradation or dissipation (Kjaer *et al*., 2001; Tiktak *et al*., 2003).

Leaching is associated with two major phenomena:

i) Preferential flow, which is a process whereby water and OPs (solutes) migrate faster through soil macropores, bypassing many of the soil matrices. Preferential flow allows OP molecules to travel faster through a compartment in the soil, with a low probability that the molecules will remain in soil particles or be degraded by microbes. This is characterized by rapid flows of water *via* wormholes, root channels, and gaps in the soil created by the root growth. Factors such as soil particle grain size, soil geometry, and macropore distribution of the soil affect the preferential flow (Kjaer *et al*., 2001).

ii) Matrix flow is another leaching phenomenon, and in this case, water and OPs move slowly through the soil. An OP migrates slowly with water into small pores in the soil and as a result has longer contact time with the soil particles.

The most important parameters that control OP leaching include among others: the degradation potential of the OP (how persistent pollutants are in the environment), its sorption behaviour, and its ability to remobilise to the aqueous solution once it is sorbed. Weakly sorbed and less degraded OPs by soil are more prone to be leached to groundwater than those that strongly bind to soil. An OP with low K_{oc} values and high-water solubility have a higher tendency to be leached than those with higher values (Regitano *et al*., 2005). Another factor found to enhance the leachability of organic pollutants is the presence of dissolved humic substances in the soil, which is capable of increasing the solubility of organic pollutants (Lassen *et al*., 1997).

2.2.5 Uptake and bioconcentration factor (BCF)

Uptake is a process whereby pollutants migrate from the water or soil compartment into plants or animals. Uptake of pollutants depends on factors such as physicochemical properties of the pollutants and soil/sediments as well as environmental conditions such as pH, and temperature. Most importantly, factors such as plant species, growth stage and intended use of plants were also found to influence the uptake (Finlayson and MacCarthy, 1973). Soil characteristics such as moisture, SOM, clay fraction, soil particulate matter, soil pH and temperature were also found to influence the uptake of pollutants (Finlayson and MacCarthy, 1973; Kaufman, 1983). Pesticide type, formulation, mode of action and application have been documented to affect the uptake of the pollutant (Kaufman, 1983).

Bioconcentration factor (BCF) is the ratio of concentration of chemical constituents in organisms or some parts of animal tissues or the whole body to the concentration in water at equilibrium (equation 2.3) (Hamelink, 1977). BCF provides information on the accumulation of a pollutant in the fatty tissue of an aquatic organism thereby interfering with background concentrations of the pollutant in water. BCF is determined by dividing the concentration of the pollutant in the biological organism by the concentration of the pollutant in the water, for either hydrophobic or hydrophilic pollutants. The BCF values (equation 2.3) in the environmental media is an important parameter in evaluating the degree of bioaccumulation as well as predicting its significance for sampling of biota during the evaluation of a particular site.

$$BCF = \frac{Concentration\ in\ biota\ (C_A)}{Concentration\ in\ surrounding\ medium\ (C_W)} \qquad 2.3$$

BCF can also be used to describe the absorption and elimination rates of pollutants in biota as given by equation 2.4. Typically, plants are seldom used to evaluate the BCF for soil. Zhang *et al*. (2004) suggested that leafy vegetables sometimes act as an indicator of human exposure to PAHs. The result of their investigation suggested that total PAH concentrations in Chinese vegetables were found between the ranges of 8.6 to 111 µg/g (dry weight), corresponding to BCFs of 18 to 871, which according to the EPA guideline of 1987, have the potential to cause serious threat to human health (USEPA, 1987; Zhang *et al*., 2004).

$$BCF = \frac{k_1}{k_2} \qquad 2.4$$

where, k_1 and k_2 are uptake and elimination rate constants for the pollutants, respectively; and C_A (ug/kg) and C_W (ug/L) are the concentrations of the pollutant in the organism and water at steady state, respectively.

BCF is an important determinant factor for human exposure to pollutants *via* the food web. Values of BCF are usually in the range of 1 to over 10^6. Constituents having a BCF greater than 1.0 are said to be bioaccumulative, but if a constituent exhibits a BCF greater than 100, it has the potential to cause serious environmental problems (USEPA, 1987). There are several different methods for determining this parameter, such as the bioaccumulation of pollutants in plants, highlighted by Lyman *et al*. (1990). Other methods available to estimate BCF includes fugacity models, octanol-water partition coefficient (K_{ow}), driven mass balance or chemical mass balance models (USEPA, 2011).

2.2.6 Sorption

Sorption is a process that occurs in different phase compartments, and results in OPs becoming associated with soils and sediments. It is a key process determining the distribution of pollutants in the environment (Huang *et al*., 2003). The process is referred to as adsorption, if the molecules bind to a two-dimensional surface, or the attraction is between the outer surfaces of a solid particle and the OP. Absorption or partitioning is the process involved if the molecule enters a three-dimensional matrix or uptake of OPs is from the aqueous phase into the physical structure of the solid (Chiou, 2002; Hassett and Banwart, 2002). Due to the heterogeneous and complex nature of soils, the two processes (adsorption and absorption) may occur simultaneously and it is almost impossible to differentiate between the two processes. In order to avoid ambiguity between adsorption and absorption of the OPs within the environmental matrix, sorption process is commonly used in environmental situations involving the uptake of the OPs by soil or sediment (Chiou, 2002, Schwarzenbach *et al*., 2003). The sorption process in aquatic environments control the distribution, transport, and transformation of organic pollutants between the aqueous phase and soil or sediment, and can therefore, limit the remediation as well as biological uptake and microbial degradation of OPs (Oliver and Charlton 1984). Hence, a better understanding of sorption of OPs is important, for evaluating various health problems that organic pollutants may pose in the environment.

The distribution of OPs among different compartments is dependent on some properties such as (i) compound properties like hydrophobicity and aqueous solubility (K_{ow}), partition coefficient (K_d), organic carbon adsorption normalize coefficient (K_{oc}), molecular size, polarity and functional group present and branching; (ii) sorbent characteristics like organic matter content, clay mineralogy, and surface area as well as secondary environmental factors such as pH and temperature.

2.2.5.1 Hydrophobicity and aqueous solubility (K_{ow})

This is commonly referred to as the octanol-water partitioning coefficient (K_{ow}) which is defined as the ratio of a chemical's concentration in the octanol phase (organic) to its concentration in the aqueous phase of a two-phase octanol/water system as indicated by equation 2.5 (Lyman *et al*., 1990)

$$K_{ow} = \frac{Concentration\ in\ octanol\ phase}{Concentration\ in\ aqueous\ phase} \qquad 2.5$$

K_{ow} gives information on the concentration of chemical in the octanol phase to its concentration in the aqueous phase of a two phase system at equilibrium. It has been positively correlated with environmental fate and transport parameters such as K_{oc} and BCF and therefore is often used to estimate values for these two parameters. The higher the K_{ow} the more the organic pollutant will partition to the soil or sediment.

Generally, pollutants with low K_{ow} (< 10) values may be considered relatively hydrophilic, whereas those with high K_{ow} (>10^4) values are considered highly hydrophobic. The hydrophilic pollutants are more soluble in water and have low soil or sediment adsorption coefficients with a low degree of bioaccumulation in aquatic life. High K_{ow} values are generally an indication of a pollutant's ability to accumulate in fatty tissue and therefore bioaccumulate in the food chain.

2.2.5.2 Soil-water partition coefficient (K_d)

The adsorption ratio K_d (L/g), is the ratio of the amount of a chemical adsorbed by a soil or sediment (solid phase q_e indicated also as x/m, where x is the amount of compound sorbed on

the mass m of soil) (mg/g), to the amount of chemical in the solution (aqueous phase C_e) (mg/L), at equilibrium as represented in equation 2.6

$$K_d = \frac{Concentration\ of\ adsorbed\ \ chemical\ in\ soil\ q_e}{Concentration\ of\ adsorbed\ chemical\ in\ aqueous\ solution\ C_e} \qquad 2.6$$

Both the physicochemical characteristics of the soil and the extent to which the soil material will retain, or adsorb the pollutant greatly influence the mobility of the pollutant in soil or sediment system. In addition, the chemical properties of both the pollutant and the soil influences the degree of adsorption of the pollutant on the soil. The K_d value can be evaluated based on the soil total organic matter and dissolved organic matter contents which are denoted by F_{oc} (the fraction of organic carbon in the soil). The higher the value of K_d the less mobile is the contaminant. Thus, most of the pollutant is immobile and therefore binds to soil organic materials as a result of high sorption affinity. Therefore, the higher the K_d the more likely a pollutant will bind to soil or sediment than remain in the water.

The soil organic carbon-water partitioning coefficient (K_{oc}) is the ratio of the amount of chemical adsorbed per unit weight of organic carbon (OC) in the soil or sediment to the concentration of the chemical in solution at equilibrium (L/kg). K_{oc} is a measure of the tendency for organic chemicals to be adsorbed by soil or sediment, which is K_d normalized unit of soil humus and is expressed by **equation** 2.7.

$$K_{oc} = \frac{K_d}{F_{oc}} \qquad 2.7$$

where, F_{oc} is the humus fraction in a weighted fraction of organic carbon relative to the mass of soil in the solid phase.

The K_{oc} value is specific to different chemicals and is not influenced by the soil/sediment physicochemical properties. The tendency of a constituent to be adsorbed to soil, however, is a function of its property and is influenced by the organic carbon content of the soil or sediment. The K_{oc} value is a measure of the hydrophobicity of a chemical. Values of K_{oc} typically range from 1 to 10^7; the higher the $K_{oc,}$ the more likely a chemical will bind to the soil or sediment than remain in the water.

2.2.5.3 Sorbate polarity

The functional groups present in the organic compound (contaminant) will determine its aqueous solubility and the type of interaction involved in the sorption of OPs. A polar compound with a permanent electric dipole will have a tendency to increase its water solubility and hence decrease its tendency to sorb onto the SOM. However, some neutral organic compounds, (those with neither a basic nor an acidic functional group) such as PCBs, can be easily adsorbed by soil through hydrophobic interactions. In addition, acidic or basic compounds can be ionized which in turn could strongly affect their sorption onto soil (Kah and Brown, 2006).

The type of interaction depends on the nature of the sorbent as well as the physicochemical characteristics of the sorbate i.e its hydrophobic or hydrophilic characteristics (Hamaker and Thompson, 1972). Weber *et al*. (1991) classified the possible interactions involved between sorbate and sorbent into three major categories of sorption such as physical, chemical, and electrostatic. The physical sorption process is due to interactions between dipole (permanent or induced) moments of sorbate and sorbent molecules. Since the hydrophobic pollutants have a low affinity for water, the weak physical bond that results is now much greater. Chemical interactions were found to involve covalent bonding and hydrogen bonding. Lastly, electrostatic interactions were noted to involve both ion–ion and ion–dipole forces. The interaction types were assigned with approximate energy values associated according to Von Oepen *et al*. 1991. These were van der Waals interactions (4–8 kJ/mol), hydrophobic bonding (4 kJ/mol), hydrogen bonding (2–40 kJ/mol), charge transfer, ligand-exchange and ion bonding (40 kJ/mol), direct and induced ion–dipole and dipole– dipole interactions (2–29 kJ/mol), and chemisorption (covalent bond) (60–80 kJ/mol).

2.2.5.4 Molecular size

The size of a molecule is one of the fundamental factors affecting the sorption of organic pollutants. This is related to the relative surface area and molecular volume of a compound (Calvet, 1989). Sabljic (1984) noted that the London-van der Waals force is dependent on the surface area of the molecule involved in the sorption process. The water solubility of a compound is a function of its molecular volume, which in turn can affect the sorption of the organic compound (Lambert, 1967). Generally, the larger the size of a molecule or the higher

its molecular weight, the less soluble it tends to be in aqueous solutions. As the molecular weight increases, so does the proportion of the hydrocarbon character in the organic pollutant increase. Therefore, the importance of hydrogen bonding and dipole–dipole interactions in the molecule decreases, while the importance of London dispersion forces increases, which will ultimately lead to progressively fewer favourable electrostatic interactions with water and reduced solubility.

2.2.5.5 Organic matter content

It has been established by various researchers that soil organic matter is the most important soil component that plays a key role in the sorption of non-ionic pollutants such as PCBs, OCPs, and PAHs onto soils (Goring, 1962; Hamaker and Thompson, 1972; Chiou, 1989; Wauchope *et al*., 2002). The extent to which non-ionic pollutants bind onto the soil is strongly dependent on the content of the SOM (Huang and Weber, 1997; Karapanagioti *et al*., 2001), even in soils containing less than 0.1% of organic carbon content (Ball and Roberts, 1991). The higher the content of the SOM in the soil, the higher the binding constant of the non-ionic pollutants onto the soil. The distribution of soil humic substances also play a major role in the partitioning of the pollutants. A relatively low SOM content in the soil will encourage the microstructure of the soil particles to be the dominant factor in the sorption process (Chiou *et al*., 1983). SOM is heterogeneous in nature; in addition, the physicochemical nature of SOM is dependent on the origin, age, weathering, and maturation period of soil, as well as soil depth (Zech *et al*., 1997; Chefetz *et al*., 2000; Xing, 2001; Song *et al*., 2002). Due to the physicochemical characteristics, SOM is made up of both hydrophilic and hydrophobic substituents for sorption of HOCs in soil. Song *et al*. (2002) and Accardi-Dey and Gschwend, (2002) reported that soils and sediments not only contain polymeric humic substances but also contain some particulate kerogen and black carbon containing substances in varying proportion that exhibit no sorption characteristics. As a result, of the heterogeneous nature of SOM, it has been suggested that non-ionic organic contaminants would sorb mostly to the amorphous polymethylene structures in humic materials (Hu *et al*., 2000). Thus, the more amorphous material present, the more the sorption affinity of the pollutant to the SOM. This was supported by Lin *et al.* (2007) who noted that the role of amorphous polymethylene structures served as a major sorption site for HOCs and found that phenanthrene adsorbed more on the hydrophobic constituents of tea leaves.

2.2.5.6 Clay mineralogy

Clay minerals can be considered as a good sorbent for nonionic HOCs. Due to the promising sorption properties of clay such as small particle size, large surface area, and unique charge characteristics, clay minerals have been reported to sorb a wide range and variety of HOCs (Yildiz *et al*., 2004; Li *et al*., 2004; Chappell *et al*., 2005; Yuan *et al*., 2013). Bradley (1945) and Hoffmann *et al.* (1960) hypothesized that the methylene groups of the aliphatic chain in the clay are more likely to form hydrogen bonds with clay mineral (Ca-montmorillonite) having the structure C–H••••O–Si. Therefore, the degree of sorption is dependent on the activity of the methylene groups as well as the chain length (Hoffmann *et al*., 1960). Also, Brindley *et al.* (1963) studied the sorption of acetoaceticethylester and β,β-oxydipropionitrile on clay minerals such as gibbsite, kaolinite, Ca and Na-montmorillonite. The authors noted the decreasing order of sorption per unit of surface of clay minerals was gibbsite > kaolinite > montmorillonite. The surface area of gibbsite and half the surface area of kaolinite has hydroxide substituents, which results in higher adsorption compared to montmorillonite which has oxygen substituents and half the surface area of kaolinite. It is therefore thought that sorption occurs through hydrogen bonding between the hydroxide substituents and the oxygen atoms in the organic molecules. However, for montmorillonite, its hydroxides prefer to hydrogen bond with water instead resulting in less sorption of organic molecules by hydrogen bonding with the montmorillonite's hydroxide. In addition, the exchangeable cations of montmorillonite, Ca and Na, may react with water and form complexes that block a large part of the surface involved in sorption. Exchangeable cations on kaolinite are thought to be relatively smaller in the total sorption surface area, while gibbsite may probably have no cations. Therefore, it is expected that montmorillonite will have lower surface sorption than gibbsite and kaolinite. In addition, due to the abundant, inexpensive and environmentally congenial characteristics, clay minerals have found wider applications in different environmental remediation processes (Churchman *et al*., 2006; Gates *et al*., 2009; RuizHitzky *et al*., 2010; Gupta and Bhattacharyya, 2012; Zhu *et al*., 2015).

2.2.5.7 Surface area

Surface area is one of the most important soil characteristics affecting the sorptive behaviour of HOCs by clay materials. Sorption of HOCs have been reported to be influenced by surface area of the adsorbents, where sorption is dominated by surface adsorption, sorption increase as

the surface area increases (Chiou, 2002; Chappell *et al*., 2005; Yuan *et al*., 2013). Natural soil is primarily composed of clay, silt, sand, water, and a variable amount of natural organic carbon (Piwoni and Keeley, 1990). All of these characteristics and components affect the sorption of pollutants on soil. For example, silts and clays have a much higher surface area than sand; generally have a negative surface charge and have a high natural organic matter content, and therefore they adsorb organic pollutants much more than sand (Piwoni and Keeley, 1990). Li and Gupta, (1994) noted that the affinity (K_f values) of organic compounds such as benzene, toluene and xylenes, was lower towards kaolinite than for montmorillonite or illite, which has a lower specific surface area. A similar trend was previously reported by Bailey and White (1970) who found that montmorillonite with a 2:1 expandable lattice clay and illite with a nonexpendable 2:1 clay, with higher surface areas of 8 x 10^6 m^2/kg and 10^5 m^2/kg, respectively, had better adsorption of organic pollutants compared to kaolinite. Kaolinite is a clay with 1:1 structure, comprising an octahedral aluminium layer overlying tetrahedral silicon sheets with smaller surface area of 3 x 10^4 m^2/kg. The ratio represents the amount of silicon to aluminium sites in the clay, and in the case of kaolinite, the ratio implies an equal abundance of Si and Al sites in the clay. Qi and Zhang, (2015) studied the sorption-desorption of testosterone on three soil particle fractions. Their investigations showed that clay had the highest sorption capacity for testosterone followed by silt and then sand, which had the least sorption capacity for this pollutant. This was attributed to the larger BET surface areas found in clay and silt (52.21 and 23.30 m^2/g) compared to the smaller surface area exhibited by sand (2.23 m^2/g).

2.2.5.8 pH

The aqueous phase pH is one of the major environmental parameters that affects the distribution and transportation of pollutants in the aqueous environment. The pH value influences sorption mostly *via* the charge of the adsorbent and the surface electrical properties of the adsorbate, which in turn affects the electrostatic interaction and sorption affinity between them (Xiong *et al*., 2015). The sorption of organic compounds having a wide range of chemical characteristics is dependent on the degree of water solubility, the dissociation constant of the sorbate, and the pH of the clay system (Delle Site, 2001). The main effect of solution pH on sorption affinity is through effects on the surface charge of soil organic matter and aqueous composition, which could be characterized by hydrophobic interactions. An increase in solution pH could lead to deprotonation resulting in both organic matter and soil inorganic solid surfaces having a

negative charge (You *et al*., 1999). A relatively low solution pH value could cause a small molecule of organic matter to bond with the oxygen atoms on mineral surfaces and thus form large aggregates. This would then lead to adsorption of organic pollutants. An increase in the solution pH will destroy the organic polymer or increase the dissociation/ionisation of the functional groups on SOM, which could lead to an increase in the charge of the SOM structure and cause a disappearance of the hydrophobic sites in the soil. The affinity of hydrophobic pollutants in the soil will then be released into the aqueous phase, which could lead to a decrease in the sorption capacity of soil (Yang *et al*., 2013). Qi and Zhang, (2015) reported a decrease in the sorption capacity of sand, silt and clay from 0.49 to 0.33 ng/g, from 1.1 to 1.05 and from 1.34 to 1.20 ng/g, respectively, as the pH of the solution increased from 3 to 11. The trend was attributed to the fact that the electrostatic attraction of the hormone sorption onto the soil was affected by surface charge, which changed with solution pH. The interaction between dissolved humic acids (DHAs) and PAHs was studied by Pan *et al.* (2007). The authors reported that for nonpolar organic compounds such as PAHs, hydrophobic interaction is primarily responsible for binding with DOM with sorption of PAHs on DHAs decreased as pH increased. This was attributed to the fact that carboxyl and hydroxyl substituents of organic matter are deprotonated as the solution pH increases, leaving the molecules with an overall negative charge at pH 7 and 11 (neutral and alkaline conditions). This then results in stretching and opening of molecules due to inter- or intra-molecular repulsion. However, the tangled nature of the polymeric structure of humic acid and its internal nonpolar nature may still present hydrophobic areas but some of the hydrophobic sites may be too small to allow PAHs to bind. In addition, the polar groups of the humic acid may also prevent sorption of PAHs thus leading to a reduction in the sorption of PAHs (Chien *et al*., 1997). Zhu *et al.* (2004) observed an increase in the sorption capacity of SOM at low pH values. The reason was due to the π-π electron donor-acceptor interactions that were more favoured at low pH values (acidic environment), causing a significant change in the conformation of organic matter leading to a more favourable π-π interaction environment.

2.2.5.9 Temperature

Sorption/desorption rate, transportation, and distribution of the HOCs in the environment is a temperature driven process (Hulscher and Cornellissen, 1996; Delle Site 2001). A change in the solution temperature could lead to surface adsorption and a change in the aqueous solubility

of the HOCs, thereby affecting the adsorption efficiency of the HOCs onto the sorbent (Peiyu *et al*., 2016). Sorption of HOCs on a solid sorbent occurs in most cases when the free energy (ΔG) of the sorptive exchange is negative (equation 2.8) (Hulscher and Cornelissen 1996; Delle Site, 2001). An increase in the sorption capacity could be an exothermic process if the equilibrium constant decreases with an increase in the temperature (Schwarzenbach *et al*., 1993).

$$\Delta G = \Delta H - T\Delta S \qquad 2.8$$

where, $\Delta G°$ (kJ/mol), $\Delta H°$(kJ/mol), and $\Delta S°$ (kJ/mol.K) are Gibbs free energy change, enthalpy change, and entropy change in the sorption process, respectively, T (K) is the temperature and R is the ideal gas constant (J/mol.K). $\Delta H°$ represents the enthalpy change that occurs during sorption. Thus, there are two forces that play a role in the sorption process and these are enthalpy-related and entropy-related forces (Hamaker and Thompson, 1972). The enthalpy term describes the affinity of a chemical for the absorbing surface relative to its affinity for the solvent. Hydrophobic bonding is an example of an entropy-driven process. In this bonding the sorbate transfers from the aqueous phase to the soil with London dispersion forces (instantaneous dipole-induced dipole) involved in the interaction between the sorbate and the soil resulting in large entropy changes (Delle Site, 2001). In general, K_d decrease with an increase in solution temperature. Smaranda *et al.* (2014) studied the effect of temperature on the sorption of pentachlorophenol (PCP) in soil at three different aqueous solution temperatures, 10, 25 and 50ºC. The results of their investigation revealed that over the studied temperature range, an increase in the sorption capacity occurred with an increase in the temperature range of 10 to 25ºC, but the amount of PCP adsorbed decreased sharply as the temperature increased to 50ºC. The result was best described to be an exothermic process over 25ºC. The sorption of PCP in soil was noted to be favoured at low temperature. A similar result was reported by Marouf *et al*. (2006) on the sorption of PCP onto dolomite, where a decrease in the sorption of PCP was noticed as the temperature increased from 25 to 50ºC. This could be attributed to the fact that an elevated temperature may affect the bond between soil and PCP if the sorption process is based on the functional groups interacting. Podoll *et al.* (1989) also reported that the K_d value of naphthalene on soil decreased when temperature increased from 15 to 50°C and isosteric enthalpy[6] of adsorption was said to be an exothermic process. Other

[6] The standard enthalpy of adsorption at a fixed surface coverage. Also known as the isosteric heat or the isosteric heat of adsorption.

researchers reported an inverse relationship for organic compounds between K_d and solubility. Research has shown that for compounds that become more soluble at elevated temperatures, their K_d values decrease when temperature increases. However, compounds that become less soluble at elevated temperatures have higher sorption at high temperature (Choiu *et al*., 1979).

2.3 Adsorption kinetics

Kinetic studies investigate changes in chemical properties with time and are concerned especially with rates of change. Understanding the sorption kinetics is important as it provides vital information on the reaction processes as well as the mechanism of sorption, which is important when planning batch adsorption systems. In addition, the kinetics describes the rate at which the sorbent takes up the pollutant, which in turn controls the time taken by the sorbate to interact favourably with the sorbent at the solid–solution boundary (Ho and Mckay, 1998). McKay (1984) noted that the adsorption process involved three major steps: (i) film resistance; which involves movement of the pollutant from the bulk solution, passing through a liquid boundary layer, to the external surface of the solid material (sorbent); (ii) intraparticle resistance, which is the transfer of the pollutant from the solid sorbent surface to the intraparticle active sites and (iii) reaction resistance; which is the interaction of the pollutant with the available sites on both the external and internal surfaces of the solid material (sorbent). In addition, the sorption kinetic model provides information on the interaction between sorbent and aqueous interface for the determination of the mechanism of the adsorption processes. The mechanism could best be explained by the pseudo first-order, pseudo second-order rate equation (Ho and Chiang, 2001), and intraparticle diffusion models (Wang and Zhu, 2008). A correlation coefficient (R^2) value close to 1 suggests that the experimental results will be similar to that obtained by the theoretical model. Therefore, the knowledge of the rate at which the pollutants are removed from aqueous solution helps in the designing of suitable wastewater treatment plants that are capable of removing pollutants.

2.3.1 Types of adsorption models

Adsorption can be categorized into two major types depending on the nature of forces that exist between the sorbate molecules and sorbent.

2.3.1.1 The pseudo-first order model

The sorption kinetics may be described by a pseudo-first order, which follows the Lagergren rate equation (Lagergren, 1898).

$$\log(q_{e-}q_t) = \frac{k_1}{2.303}t \qquad 2.9$$

where, k_1 is the Lagergren rate constant of pseudo-first-order adsorption (min^{-1}), and q_t and q_e are the amounts of HOCs (mg/g) at contact time t and at equilibrium, respectively. From the plot of log (q_e-q_t) *versus* t (equation 2.9), the values of k_1 (rate constant) and q_e (adsorption quantity) at equilibrium can be evaluated from the slope and intercept, respectively. The correlation coefficient (R^2) values from the plot will indicate the linearity for the pseudo-first order kinetic model. The correlation between the calculated q_e and observed q_e can also be used to predict whether the sorption of HOCs obeys the pseudo-first-order kinetic model or not. The pseudo-first order model assumes that the sorption process involves only one-step (unimolecular reaction) or is inclined towards physisorption.

2.3.1.2. The pseudo-second order model

The pseudo second-order adsorption kinetic rate equation is expressed by the following equation (Ho *et al*., 2000):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad 2.10$$

where, k_2 is the rate constant of the pseudo-second-order adsorption (g/mg.min), and q_e and q_t are the adsorbed amounts of the HOCs in mg/g of adsorbate at equilibrium and time t, respectively. The q_e calculated can be evaluated from the inverse of the slope and the partitioning rate constant k_2 which can be obtained from the intercept of a plot of t/q_e *versus* t. The agreement between the calculated q_e and experimental q_e, and the linearity of the observed correlation coefficient (R^2) values from all the data at different concentrations could be used to predict if the adsorption kinetics of HOCs follows the pseudo-second order (Rodrigues *et al*., 2010). The pseudo-second order is used to predict if the reaction process involves more than one-step, which may be determined by bimolecular interactions between the sorbents and the active sites on the sorbate, which is then characterized as a chemisorption process (Ho *et al*., 2000).

2.3.1.3. The intraparticle diffusion model

Intraparticle diffusion is related to the particle size of the adsorbent. The intraparticle diffusion model using the Weber and Morris model equation predicts the mechanism and rate-controlling step in the adsorption process of HOCs (Weber and Morris, 1963; Wu, 2007). The rate constant of intraparticle diffusion (k_{id}) can be determined by using equation 2.11.

$$q_t = k_{id}\, t^{\frac{1}{2}} + C \qquad 2.11$$

where, q_t is the number of chlorinated hydrocarbons adsorbed at time t, $t^{1/2}$ (hr) is the square root of the time required to reach equilibrium, C (unitless) is the intercept referring to the thickness of the boundary layer. If the intercept is a large value (> 1), the kinetic mechanism follows intraparticle diffusion. In addition, if intraparticle diffusion occurs, then q_t *versus* $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, the plot exhibits a multi-linear rate where there are two or more steps involved and some other mechanisms along with intraparticle diffusion are possible in the sorption process and the adsorption mechanism is more likely to be a very complex one (Tan *et al*., 2009; Alhooshani, 2015: Cunha *et al*., 2010).

2.4 Adsorption isotherms

Adsorption isotherms are a study of adsorption of the adsorbate at different concentrations with changes in pH, time and temperature. Various isotherm models were previously used for the investigation of adsorption capacity in the adsorption of HOCs from aqueous solution. Sorption isotherm models can offer vital information regarding the physicochemical processes involved in the sorption. There are various equations developed to describe sorption isotherms. Some are derived based on consideration of the sorption processes involved, while others are based on empirical points of view. Some factors must be considered when selecting the best model equation to use while fitting data on sorption isotherms. One such factor is that the equation should clearly provide a good fit of the data, and the number of fitted parameters must also provide their physical meaning. Adsorption processes involve the adsorbate being adsorbed onto the adsorbent. According to Le-Chatelier's principle, the direction of equilibrium would shift in such a way to relieve the stress of the system during the sorption process. Sorption isotherms are in most cases nonlinear.

$$\text{Sorbate + sorbent} \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} \text{sorption}$$

2.4.1 Langmuir adsorption isotherm

Irving Langmuir developed a model in 1916 to show the relationship between the pressure of a gas above a surface, and its surface coverage, all at a constant temperature. (Langmuir, 1916). The model suggests that adsorption on a uniform solid surface, which has specific active sites and energies occurs *via* a single layer of the pollutant (Langmuir, 1916; Hameed *et al*., 2006; Deng *et al*., 2009). The Langmuir linear equation is given in equation 2.12.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \qquad 2.12$$

where, b is the Langmuir equilibrium constant (L/mg), and q_m (mg/g) is the monolayer adsorption capacity, which can be evaluated from a plot of C_e/q_e *versus* C_e.

2.4.1.1 The Langmuir model is based on the following assumptions:

- There is a monolayer of pollutants covered on the adsorbent surface;
- The energy of sorption for each ion is homogeneous and independent of the number of active sites on the solid material
- The sorption occurs only on targeted sites and involves no interactions between sorbed ions (no phase transition);
- The rate of sorption after equilibrium is reached is insignificant in comparison with the initial rate of sorption.

2.4.1.2 Limitations of the Langmuir adsorption isotherm are

- The Langmuir adsorption isotherm assumes that the surface is capable of adsorbing one molecule thick layer. However, in reality, there are chances of multilayer formation. Because it ignores the possibility that the initial monolayer may act as a substrate for further physical adsorption and hence is not applicable in the case where a multilayer is formed.

- According to this theory, when adsorption has reached equilibrium, temperature should no longer have an effect on the adsorption. However, experiments have shown that equilibrium maximum value decreases with an increase in temperature.
- The theory holds good only at low pressure.
- The Langmuir equation describes chemisorption and a type I isotherm but fails to treat general physical adsorption and the other types II – VI isotherms. In case of chemisorption, the adsorbate molecules will be localized only at the active sites, leaving an unspecified area around each chemosorbed molecule so the value of q_m will be strongly affected. Whereas in physisorption the type I isotherm is associated with condensation in the micropores with no clearly defined region of monolayer coverage.

2.4.2 Freundlich adsorption isotherm

Freundlich described the variation of the amount of the gas adsorbed per unit mass of the adsorbent with pressure at constant temperature. The Freundlich adsorption isotherm equation describes the relationship between the quantity of the pollutant adsorbed and the aqueous concentration of the pollutant at equilibrium. The model is often used to describe the adsorption by a heterogeneous surface of an adsorbent (equation 2.13) (Freundlich, 1906). The Freundlich model is generally applicable to most experimentally determined data (Schwarzenbach *et al*., 1993).

$$lnq_e = lnK_f + \frac{1}{n}C_e \qquad 2.13$$

where, q_e is the concentration of pollutants adsorbed on the soil phase (mg/g), C_e is the aqueous phase concentration after sorption equilibrium (ng/mL); K_f is Freundlich sorption constant (L/mg), and 1/n is Freundlich intensity parameter, (an indicator of sorption linearity). The plot of log q_e *versus* log C_e has a slope equal to 1/n, and an intercept equal to log K_f. The following assumptions were used for the types of processes involved in the adsorption. If the values of 1/n = 1, it means the adsorption is linear, 1/n > 1 means a physical process (weak bond) is predominant in the adsorption and represents a favourable adsorption condition, 1/n < 1, then adsorption is a chemical process (strong bond) (Treybal, 1968; Poots and Healy, 1978; Ho and McKay, 1984: Desta, 2013; Qi *et al*., 2016). The linearity of the graph (R^2) provides information as to which model is most suitable for the observed adsorption process.

2.4.2.1 Limitation of Freundlich's adsorption isotherm

- Freundlich’s equation is not confirmed by any theory and is purely based on experimental observations.
- The equation can only be used up to a specific pressure and thereafter is invalid.
- The values of constant K_f and n varies with temperature.
- Freundlich’s adsorption isotherm becomes invalid at high adsorbate concentrations.

2.4.3 Types of adsorption

2.4.3.1 Physical adsorption (physisorption)

This is also referred to as van der Waals forces. This type of force is very weak and the desorption can easily occur when heat is applied to the system or the pressure is decreased.

2.4.3.2 Chemical adsorption (chemisorption)

The force of attraction that exists between sorbate and sorbent in chemisorption processes have similar strength with chemical bonds. It is also referred to as Langmuir adsorption. The force of attraction in chemisorption forms a very strong bond; therefore, this system does not easily undergo desorption.

Table 2.3:

Comparison between physisorption and chemisorption

Physisorption	Chemisorption
Low heat of adsorption (enthalpy) usually 5-50 kJ/mol	The high heat of adsorption (enthalpy) in the range of 40-800 kJ/mol
Mostly involves Van der Waal's forces	Forces of attraction form strong chemical bonds
It usually occurs at low temperature and the reverse process occurs at high temperature	It occurs at high temperature
Desorption occurs easily	Desorption does not occur or occurs to a limited extent
It results in easy liquefaction of a gas	The extent of adsorption does not lead to easy liquefaction of the gas
It is not very specific	It is highly specific
The saturation is multilayer in nature (heterogeneous surface)	It forms monomolecular layers (homogeneous surface)
It does not require any activation energy (exothermic process)	It requires activation energy (endothermic process)

REFERENCES

Accardi-Dey, A., Gschwend, P.M., (2002). Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environ. Sci. Technol*. **36**: 21–29.

Addison, R.F., (1986). PCBs in perspective. Can. Chem. News 38 (Feb.):15–17.ATSDR (Agency for Toxic Substances and Disease Registry). 1995. Toxicological profile for polychlorinated biphenyls: Draft for public comment (update). U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA

Ahangar, A. G., Smernik, R. J., Kookana, R. S., Chittleborough D. J., (2008). Separating the effects of organic matter-mineral interactions and organic matter chemistry on the sorption of diuron and phenanthrene. *Chemosphere* **72**: 886-890.

Ahlborg, U.G., Hanberg, A. & Kenne, K., (1992). Risk assessment of polychlorinated biphenyls (PCBs). Nordic Council of Ministers, Nord 1992:26.

Albro, P.W., Parker, C.E., (1979). Comparison of the compositions of Aroclor 1242 and Aroclor 1016. *J. Chromatogr*. **169**: 161–166.

Alhooshani, K.R. (2015). Adsorption of chlorinated organic compounds from water with cerium oxide activated carbon composite. *Arab. J. Chem*. dio.org/10.1016/j.arabjc.2015.04.013.

Allen J.R., Carstens, L. A., Barsotti, D. A., (1974a). Residual effects of short-term, low-level exposure of nonhuman primates to polychlorinated biphenyls. *Toxicol Appl Pharmacol* **30**:440-451.

Allen, J. R., Norback, D. H., Hsu I. C., (1974b). Tissue modifications in monkeys as related to absorption, distribution, and excretion of polychlorinated biphenyls. *Arch. Environ. Contam. Toxicol.* **2**: 86-95.

Anderson, L.M., Logsdon, D., Ruskie, S., Fox, S.D., Issaq, H.J., Kovatch, R.M., Riggs, C.M., (1994). Promotion to polychlorinated biphenyls of lung and liver tumours in mice. *Carcinogenesis*. **15**: 2245–2248.

ATSDR, Toxicological Profile for Polychlorinated Biphenyls (Update) (2000). Atlanta (GA): US Department of Health and Human Services, Public Health Service, Agency for

Toxic Substances and Disease Registry. Available from: http://www.atsdr.cdc.gov/ToxProfiles/ tp17.pdf. Accessed 10/09/2017.

Aulerich, R. J., Ringer, R. K., (1977). Current status of PCB toxicity to mink, and effect on their reproduction. *Arch. Environ. Contam. Toxicol*. **6**: 279-292.

Bailey, G. W., White, J. L., (1970). Factors influencing the adsorption, desorption, and movement of pesticides in soil. *Residue Rev*. **32**: 29-92.

Ball, W. P., Roberts, P. V. (1991). Long-term sorption of halogenated organic chemicals by aquifer materials. 2: Intra particle diffusion. *Environ. Sci. Technol*. **25**: 1237-1249.

Ballschmiter, K., Bacher, R., Mennel, A., Fischer, R., Riehle, U., Swerev, M., (1992). The determination of chlorinated biphenyls, chlorinated dibenzodioxins, and chlorinated dibenzofurans by GC-MS. *J. High Resolut. Chromatogr*. **15**,(4): 260–700. doi:10.1002/jhrc.1240150411

Ballschmiter, K., and Zell, M., (1980). Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography: composition of technical Arochlor- and Clophen-PCB mixtures. *Fresenius J. Anal. Chem*. **302**,(1): 20–31.doi:10.1007/BF00469758.

Bedard, D.L., (2003). Polychlorinated biphenyls in aquatic sediments: environmental fate and outlook for biological treatment. In: Haggblom, M.M., Bossert, I. D. (Eds.), Dehalogenation: Microbial Processes and Environmental Applications. Kluwer Academic Publishers, Boston, MA. pp 443-465.

Bi, X. H., Chu, S. G., Meng, Q. Y., Xu, X. B., (2002). Movement and retention of polychlorinated biphenyls in a paddy field of WenTai area in China. *Agr. Ecosyst. Environ*. **89**, (3): 241-252.

Bradley, W F., (1945). Molecular association between montmorillonite and some polyfunctional organic liquids. *J. Am. Chem. Soc*. **67**: 975-981.

Brindley, G. W., Bender, R., Ray, S., (1963). Sorption of non-ionic molecules from aqueous solutions on clay minerals. Clay–organic studies VII. *Geochim. Cosmochim. Acta.* **27**: 1129-1137.

Breivik, K., Sweetman, A., Pacyna, J. M., Jones, K. C., (2007). Towards a global historical emission inventory for selected PCB congeners–a mass balance approach 3. An update.

Sci. Total. Environ. **377**, (2–3): 296–307. doi:10.1016/j.scitotenv.2007.02.026 PMID:17395248

Brown, D. P., (1987b). Mortality of workers exposed to polychlorinated biphenyls -An update. *Arch Environ Health.* **42**, (6): 333-339.

Brown, D. P. and Jones, M., (1981). Mortality and industrial hygiene study of workers exposed to polychlorinated biphenyls. *Arch Environ. Health.* **36**: 120-129.

Buckley-Golder D., (1999). Compilation of EU Dioxins Exposure and Health Data. Summary Report for European Commission DG Environment and the UK Department of the environmental transport and the regions. Available from: http://www.greenpeace.se/ files/file_72.pdf. Accessed 23/06/2017.

Buser. H-R. and Rappe, C., (1979). Thermal decomposition of PCB (2, 2' 4, 5, 5'pentaCB). *Chemosphere*. **8**, (3): 157.

Caironi, M., Olivari, L., Sampietro, G., Mandelli, G., Mosconi, G., (2005). Preliminary results of a mortality study in 471 ex-exposed workers to PCBs. *G Ital Med Lav Ergon*. **27**, (3): 279–81.

Calvet, R., (1989). Adsorption of organic chemicals in soils. *Environ. Health Persp*. **83**: 145-177.

Chappell, M. A., Laird, D. A., Thompson, M .L., Li, H., Teppen, B. J., Aggarwal, V., Johnston, C. T., Boyd, S. A., (2005). Influence of smectite hydration and swelling on atrazine sorption behaviour. *Environ. Sci. Technol*. **39**: 3150-3156.

Chefetz, B., Chen, Y., Clapp, C. E., Hatcher, P. G., (2000). Characterization of organic matter in soils by thermochemolysis using tetramethylammonium hydroxide (TMAH). *Soil Sci. Soc. Am. J.* **64**, (2): 583–589.

Chiou, C. T., (2002). Partition and Adsorption of Organic Contaminants in Environmental Systems, John Wiley &Sons. Inc: Hoboken, N. J., New York. pp 257.

Chiou, C. T., (1989). Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. Reactions and movement of organic chemicals in soils; Sawhney, B. L., Brown, K.Eds. (Madison, WI: Soil Science Society of America, SSSA special publication No. 22, 1989). pp 1–29.

Christopher, J. A., Kirk M., Semple, K. T., (2002). The adaptation of two similar soils to pyrene catabolism. *Environ. Pollut*. **119**: 357-364.

Churchman, G. J., Gates, W. P., Theng B. K. G., Yuan, G., (2006). Clays and clay minerals for pollution control. In: Handbook of Clay Science (Bergaya, F., Theng, B. K. G., and Lagaly, G., editors). Elsevier, Amsterdam. pp 625-676.

Corey, D. A., Juarez de Ku, L. M., Bingman, V. P., (1996). Effects of exposure to polychlorinated biphenyl (PCB) from conception on growth, and development of endocrine, neurochemical, and cognitive measures in 60-day old rats. *Growth Dev Aging.* **60**: 131-143.

Chung, Y. W., Nunez, A. A., Clemens, L. G., (2001). Effects of neonatal polychlorinated biphenyl exposure on female sexual behavior. *Physiol. Behav*. **74**: 363–370.

Cunha, G. C., Romao, L. P., Santos, M., Arau´ jo, B., Navickiene, S., Pa´ dua, V., (2010). Adsorption of trihalomethanes by humin: Batch and fixed bed column studies. *Bioresource Technol*. **101**: 3345–3354.

De Guire, L., Cyr, D., Thériault, G., Provencher, S., Iturra, H., Case, B. W., (1992). Malignant melanoma of the skin among workers in a telecommunications industry: mortality study 1976–83. *Br J Ind Med*. **49**, (10): 728–31.

De Guire, L., Cyr, D., Thériault, G., Provencher, S., Iturra, H., Case, B. W., (1988). Increased incidence of malignant melanoma of the skin in workers in a telecommunications industry. *Br J Ind Med*. **45**, (12): 824–8.

Delle Site, A., (2001). Factors affecting sorption of organic compounds in natural sorbent/water system and sorption coefficients for selected pollutants. A review. *J. Phys. Chem*. Ref. Data. **30**, (1): 187-253.

Deng, H., Yang, L., Tao, G., Dai, J. (2009). Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—application in methylene blue adsorption from aqueous solution. *J. Hazard. Mater*. **166**: 1514–1521.

de Voogt, P. and Brinkman, U. A. T., (1989). Production, properties and usage of polychlorinatedbiphenyls. In: Kimbrough, J., editors. Halogenated biphenyls,

terphenyls, naphthalenes, dibenzodioxins and related products. Amsterdam, the Netherlands: Elsevier Science Publishers. pp 3–43.

Edgehill, R U. and Fin, R. K., (1983). Microbial treatment of soil to remove pentachlorophenol. *Appl. Environ. Microbiol*. **45**: 1122-1125.

Eisler, R. and Belisle, A. A., (1996). Planar PCB hazards to fish, wildlife and invertebrates: A synoptic review. Contaminant Hazard Reviews Report No. 31. U.S. Department of the Interior, National Biological Service, Washington, DC. Available on: http://www.pwrc.usgs.gov/infobase/eisler/chr_31_planar_pcbs.pdf. *Accessed 10/11/2017*.

Emmett, E. A., Maroni, M., Jeffery, J. S., (1988b). Studies of transformer repair workers exposed to PCBs: II. Results of clinical laboratory investigations. *Am. J. Ind. Med.* **14**: 47-62.

Emmett, E. A., Maroni, M., Schmith, J. M., (1988a). Studies of transformer repair workers exposed to PCBs: I. Study design, PCB concentrations, questionnaire, and clinical examination results. *Am. J. Ind. Med*. **13**: 415-427.

Erickson, M. D. and Kaley, R G., (2011). Applications of polychlorinated biphenyls. E*nviron. Sci. Pollut. Res. Int*. **8**: 135-151. doi 10.1007/s11356-010-0392-1

Erickson, M. D., (1997). Analytical Chemistry of PCBs. 2nd ed. Boca Raton: Lewis Publishers. pp 667.

Erickson, M. D., (2001). Introduction to PCB properties, uses, occurrence and regulatory history. In: Robertson, L. W., Hansen, L. G, editors. PCBs, recent advances in environmental toxicology and health effects. The University press of Kentucky. pp 11-30

Fadhel, Z., Lu, Z., Robertson, L.W., Glauert, H. P., (2002). Effect of 3,3',4,4'-tetrachlorobiphenyl and 2,2',4,4',5,5'-hexachlorobiphenyl on the induction of hepatic lipid peroxidation and cytochrome P-450 associated enzyme activities in rats. *Toxicol*. **175**: 15–25.

Finlayson, D. D. and MacCarthy, H. R., (1973). Pesticides residues in plants, in Environmental Pollution by Pesticides (Ed: C.E. Edwards), Plenum Press, New York. pp 57-86.

Freundlich, H. M. F., (1906). Over the Adsorption in Solution (adsorption in solution). *J. Phys. Chem*. **57**: 384–470.

Furukawa, K., (1982). Microbial degradation of polychlorinated biphenyls (PCBs). In: Biodegradation and detoxification of environmental pollutants, Chakrabarty, A.M., ed. CRC Press, Boca Raton, Florida. pp 33-57.

Gan, D. R. and Berthouex, P. M., (1994). Disappearance and crop uptake of PCBs from sludge-amended farmland. *Water Environ. Res*. **66**: 54–69.

Garner, C. E. and Matthews H. B., (1998). The effect of chlorine substitution on the dermal absorption of polychlorinated biphenyls. *Toxicol Appl Pharmacol*. **149**, (2): 150–8. doi:10.1006/taap.1998.8370 PMID:9571983.

Gates, W. P., Bauazza, A., Churchman, G. J., (2009). Bentonite clay keeps pollutants at bay. *Elements*. **5**: 105-110.

Gavrilescu, M., (2005). Fate of pesticides in the environment and its bioremediation. *Eng. Life Sci*. **5**: 497-526.

Glauert, H. P., Robertson, L. W, Silberhorn, E. M., (2001). PCBs and tumour promotion. In: Robertson LW, Hansen LG, editors. PCBs: Recent Advances in Environmental Toxicology and Health Effects. University Press of Kentucky; Lexington, Kentucky. pp 355–371.

Goring C. A. I., (1962). Control of nitrification by 2-chloro-6(trichloromethyl) pyridine. *Soil Science*. **93**: 211-218.

Guo, Y. L., Lai, T. J., Ju, S. H., Chen, Y. B., Hsu, C. C., (1993). Sexual development and biological findings in *Yucheng* Children. "Presented at Dioxin '93, 13th International Symposium on chlorinated dioxins and related compounds, Vienna, Austria, 20-24 September, (1993). **14**: 235–238.

Gupta, S. S., and Bhattacharyya, K. G., (2012). Adsorption of heavy metals on kaolinite and montmorillonite: a review. *Phys. Chem. Chem. Phys*. **14**: 6698-6723.

Hamaker, J. W. and Thompson, J. M., (1972). In Organic chemicals in the soil environment, edited by Goring, C. M., Hamaker, J. W. (Marcel Dekker, New York). pp 49–143.

Hameed, B. H., Mohd Din, A. T., Ahmad, A. L., (2006). Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. *J. Hazard. Mater*. **141**: 819–825.

Hamelink, J. L., (1977). Current bioconcentration factor test and theory. In aquatic toxicology and hazard evaluation, ASTM STP 634. (Eddicted by Mayer, F. L., Hamelink, J. L.,) Eds., ASTM, Philadelphia, Pennsylvania. pp 149-161.

Hanigan, M. H., (1995). Expression of gamma-glutamyl transpeptidase provides tumour cells with a selective growth advantage at physiologic concentrations of cyst(e)ine. *Carcinogenesis*. **16**: 181–185.

Hannigan, R. E., Genest, D. M., Robinson, W. E., (2018). Chemistry of Natural Waters. In Green Chemistry. Elsevier, University of Massachusetts, Boston, United States. pp 235-359.

Hassett, J. J. and Banwart, W. L., (2002). The sorption of nonpolar organics by the soils and sediments. Partition and adsorption of organic contaminants in environmental systems. Chiou, C. T. John Wiley and Sons, Hoboken, New Jersey. pp 31-45.

Hayes, M. A., Safe, S. H., Armstrong, D., Cameron, R. G., (1985). Influence of cell proliferation on initiating activity of pure polychlorinated biphenyls and complex mixtures in resistant hepatocyte in vivo assays for carcinogenicity. *J. Natl. Cancer Inst*. **74**: 1037–1041.

Hites, R. A., Foran, J. A., Carpenter, D. O., Hamilton, M. C., Knuth, B. A., Schwager, S. J., (2004). Global assessmentof organic contaminants in farmed salmon. *Science*. **303**, (5655): 226–9. doi:10.1126/science.1091447 PMID:14716013.

Ho, Y.S. and Chiang, C.C., (2001). Sorption studies of acid dye by mixed sorbents. *Adsorption.* **7**: 139–147.

Ho, Y.S. and McKay, G., (1998). Sorption of dye from aqueous solution by peat. *Chem. Eng. J*. **70**, (2): 115-124.

Ho, Y. S., Wase, D. A. J., Foster, C. F., (2000). Study of the sorption of divalent metal ions on to peat. *Adsorpt. Sci. Technol*. **18**: 639–650.

Hoffman, D. J., Rice, C. P., Kubiac, T. J., (1996). PCBs and dioxins in birds. In: Beyer, W N., Heinz, G H., Redmon, A W,. (eds) Environmental contaminants in wildlife: interpreting tissue concentrations. CRC/Lewis Publishers, Boca Raton, Florida. pp 165–207.

Hoffmann, R. W. and Brindley, G. W., (1960). Adsorption of non-ionic aliphatic molecules from aqueous solutions on montmorillonite. *Geochim. Cosmochim. Acta.* **20**: 15-29.

Hu, D. and Hornbuckle, K. C., (2010). Inadvertent polychlorinated biphenyls in commercial paint pigments. *Environ. Sci. Technol*. **44**,(8): 2822–2827 doi:10.1021/es902413k PMID:19957996.

Huang, W., Peng, P., Yu Z., Fu, J., (2003). Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *App. Geochem*. **18**: 955-972.

Huang, W. and Weber Jr., W. J., (1997). A distributed reactivity model for sorption by soils and sediments. 10: Relationships between sorption, hysteresis, and the chemical characteristics of organic domains. *Environ. Sci. Technol*. **31**: 2562–2569.

Hulscher, T. E. M. T. and Cornelissen, G., (1996). Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants- a review. *Chemosphere*. **32**, (4): 609- 626.

Hutzinger, O., Safe, S., Zitko, V., (1974). The chemistry of PCBs. CRC Press, Cleveland, OH. IOM, Institute of Medicine (2003). Dioxins and dioxin-like compounds in the food supply. Washington (DC): The National Academies Press. pp 769–879.

IARC, International Association on Research and Cancer (2016b). Monographs on the Evaluation of Carcinogenic Risks to Humans, volume 107: Polychlorinated Biphenyls and Polybrominated Biphenyls. International Agency for Research on Cancer, Lyon, France. ⟨http://monographs.iarc.fr/ENG/Monographs/vol107/mono107.pdf⟩. *Accessed 04/12/2018*.

IOM; Institute of Medicine (2003). Dioxins and dioxin-like compounds in the food supply. Washington (DC): The National Academies Press.

IPCS, The International Programme on Chemical Safety (2003). Concise international chemical assessment document 55. Polychlorinated biphenyls: human health aspects.

Geneva, Switzerland: World Health Organisation; pp. 1–60. Available from: http://whqlibdoc.who.int/publications/2003/9241530553.pdf. *Accessed 10/11/2017*.

Jacobson, S. W., Jacobson, J. L., Fein, G. G., Schwartz, P. M., (1983). Intrauterine exposure of human newborns to PCBs: Measures of exposure. In: PCBs: Human and Environmental Hazards. F.M., D'Itri and Kamrin M. (eds.): Boston: Butterworth. pp 311–343.

Jacobson, J. L., (1984). Prenatal exposure to an environmental toxin: A test of the multiple effects model. *Dev. Psychol.* **20**: 523–532.

Jacobson, J. L. and Jacobson, S. W., (1996a). Intellectual impairment in children exposed to polychlorinated biphenyls in utero. *N Engl. J Med.* **335**, (11): 783-789.

Jiang, K., Li, L., Chen, Y., Jin. J., (1997). Determination of PCDD/Fs and dioxin-like PCBs in Chinese commercial PCBs and emission from a testing PCB incinerator. *Chemosphere.* **34**: 941–950.

Johnson, G. W., Quensen, J. F., III, Chiarenzelli, J. R., Hamilton, M. C., (2006). Polychlorinated biphenyls. In: Morrison RD, Murphy BL (eds) Environ forensics contaminant specific guide. Elsevier, New York. pp 187–225

Johansson, N., Hanberg, A., Wingfors, H., Tysklind, M. (2003). PCB in building sealant is influencing PCB levels in blood of residents. *Organohalogen Compd*. **63**: 381–4.

Kah, M., C. D. and Brown, C. D., (2006). Adsorption of ionisable pesticides in soils. *Rev. Environ. Contam. Toxicol*. **188**: 149-218.

Kalmaz, E.V. and Kalmaz, G. D., (1979). Transport, distribution and toxic effects of polychlorinated biphenyls in ecosystems: Review. *Ecol. Model*. **6**: 223–251.

Karapanagioti, H. K., Childs, J., Sabaini, D., (2001). Impacts of heterogeneous organic matter on phenanthrene sorption: different soil and sediment samples. *Environ. Sci. Technol*. **35**: 4684–4698.

Kaufman, D. D., (1983). Fate of toxic organic compounds in land-applied wastes, in land treatment of hazardous wastes (Eds: J.F. Parr, P.B. Marrsh, J.M.Kla), Noyes Data Corp., Park Ridge, New York. pp 171.

Kerle, E. A., Jenkins, J. J., Vogue, P. A., (1996). Understanding pesticides persistence and mobility for ground water and surface water protection. Report EM 8561, Oregon State University Extension Service.

Kimura, N.T., Kanematsu, T., Baba, T., (1976). Polychlorinated biphenyl(s) as a promotor in experimental hepatocarcinogenesis in rats. *Z. Krebsforsch*. **87**: 257–266

Kjaer, J., Olsen, P., Sjelborg, P., Fomsgaard, I., Mogensen, B., Plauborg, F., (2001). The Danish pesticides leaching assessment programme, GESU report. Geology survey of Denmark and Greenland, Copenhagen.

Klanova, J., Matykieiczova, N., Zdenek, M., Prosek, P., Laska, K., Klan, P., (2007). Persistent organic pollutants in soil and sediment from James Ross Islands. *Antarctica Environ. Pollut.* **152**: 416-423.

Kusuda, M., (1971). A study on the sexual functions of women suffering from rice-bran oil poisoning. *Sanka to Fujinka* **38**: 1062-1072.

Lagergren, S., (1898). About the theory of so-called adsorption of solution substances, Kungliga Svenska Vetenskapsakademiens. Handlinga. pp 1–39.

Langmuir, I., (1916). The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc*. **38**: 2221–2295

Lanting, C. I., Patandin, S., Fidler, V., Weisglas-Kuperus, N., Sauer, P. J. J., Boersma, E. R., (1998c). Neurological condition in 42-month-old children in relation to pre- and postnatal exposure to polychlorinated biphenyls and dioxins. *Early Hum Dev*. **50**: 283–292.

Lassen, P., Poulsen, M. E., Stuer-Lauridsen, F., Carlsen, L., (1997). Leaching of selected PAHs and hetero analogues from an organic matrix into synthetic ground water. Influence of dissolved humic material. *Chemosphere*. **34**: 335-344.

Li, Y. and Gupta, G., (1994). Adsorption/desorption of hydrocarbons on clay minerals. *Chemosphere.* **29**, (3): 627-638.

Li, H., Teppen, B. J., Johnston, C. T., Boyd, S. A., (2004). Thermodynamics of nitroaromatic compounds adsorption from water by smectite clay. *Environ. Sci. Technol*. **38**: 5433-5442.

Lin, D., Pan, B., Zhu, L., Xing, B., (2007). Characterization and phenanthrene sorption of tea leaf powders. *J. Agric. Food Chem*. **55**, (14): 5718–5724.

Lyman, W.J., Reeh1, W. F., Rosenblatt, D. H., (1990). Handbook of chemical property estimation methods: Environmental behaviour of organic compounds. America Chemical Society, Washington, D.C. U.S. Department of energy office of scientific and technical information. https://trove.nla.gov.au/work/17999773. *Accessed 05/10/2017.*

Marouf, R., Khelifa, N., Marouf-Khelifa, K., Schott, J., Khelifa, A., (2006). Removal of pentachlorophenol from aqueous solutions by dolomite sorbents. *J. Colloid Interface Sci*. **297**: 45-53.

McKay, G., (1984). The adsorption of basic dye onto silica from aqueous–solution solid diffusion-model. *Chem. Eng. Sci*. **39**: 129–138.

Muir, D.C.G., Omelchenko, A., Grift, N.P., Savoie, A., Lockhart, W.L., Wilkinson, P., Brunskill, G. J., (1996). Spatial trends and historical deposition of polychlorinated biphenyls in Canadian midlatitude and Arctic lake sediments. *Environ. Sci. Technol*. **30**: 3609-3617.

NAP, The National Academies Press (2001). A risk management strategy for PCBs-contaminated sediments. National Academy Press. 2101 Constitution Ave., NW Box 285 Washington, DC 20055 800–624–6242 202–334–3313 (in the Washington metropolitan area) http://www.nap.edu. *Accessed 05/11/2017.*

Nash, R. G. and Woolson, E. H., (1967). Persistence of chlorinated hydrocarbon insecticides in soil. American Association of the Advancement of Science. *Science*. **157**: 924-927. doi: 10.1126/science.157.3791.924

NIP, National Implementation Plan China (2007). The People's Republic of China National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants. Available from: http://chm.pops.int/Implementation/NIPs/ NIPSubmissions/tabid/253/Default.aspx. *Accessed 10/09/2017.*

Nishizumi, M., (1976). Enhancement of diethylnitrosamine hepatocarcinogenesis in rats by exposure to polychlorinated biphenyls or phenobarbital. *Cancer Letters*. **2**: 11–16.

NFPA, National Fire Protection Association (1994). Fire Analysis and Research Division, Quincy, Massachusetts. 1980-1992 NFIRS, NFPA Survey.

Norback, D. H. and Weltman, R. H., (1985). Polychlorinated biphenyl induction of hepatocellular carcinoma in the Sprague-Dawley rat. *Environ. Health Perspect*. **60**: 97–105.

Oliver, B. G. and Charlton, M. N., (1984). Chlorinated organic contaminants on settling particulates in the Niagara River vicinity of Lake Ontario. *Environ. Sci. Technol*. **18**: 903-908.

Oesterle, D. and Deml, E., (1984). Dose-dependent promoting effect of polychlorinated biphenyls on enzyme-altered is lands in livers of adult and weanling rats. *Carcinogenesis*. **5**: 351–355.

Pal D., Webber, J. B., Overcash, M. R.., (1980). Fate of polychlorinated biphenyls (PCBs) in soil- plant systems. *Residue Rev*. **74**: 45–98.

Pan, B., Ghosh, S., Xing, B., (2007). Nonideal binding between dissolved humic acids and polyaromatic hydrocarbons. *Environ. Sci. Technol*. **41**, (18): 6472–6478.

Patandin, S., Lanting, C. I., Mulder, P. G. H., Boersma, E. R., Sauer, P. J. J., Weisglas-Kuperus, N., (1999). Effects of environmental exposure to polychlorinated biphenyls and dioxins on cognitive abilities in Dutch children at 42 months of age. *J. Pediatr*. **134**: 33–41.

Patterson, D. G., Jr, Wong, L. Y., Turner, W. E., Caudill, S. P., Dipietro, E. S., McClure, P. C., (2009). Levels in the U.S. population of those persistent organic pollutants (2003–2004) included in the Stockholm Convention or in other long range transboundary air pollution agreements. *Environ Sci Technol*. **43** (4), 1211–8. doi:10.1021/es801966w PMID:19320182

Peiyua, L., Luping, X., Hui, X., Wen, X. 2016. Research of adsorption on PCBs: Isotherm modeling and influencing factors. MATEC Web of Conferences. **67**: 06030

Pieper, D.H., (2005). Aerobic degradation of polychlorinated biphenyls. *Appl. Microbiol. Biotechnol.* **67**: 170-191.

Piwoni, M. D. and Keeley, J. W., (1990). Basic concepts of contaminant sorption at hazardous waste sites. In EPA/EPRI Workshop on Leachate Testing Methods in Houston, Texas, in January 1989. *Accessed, 22/02/2018.*

Podoll, R. T., Jaber, H. M., Mill, T., (1986). Tetrachlorodibenzodioxin: rates of volatilization and photolysis in the environment. *Environ. Sci. Technol*. **20**: 490-492.

Poots, G. M. V. J. P., Healy, J. J., (1978). Removal of basic dye from effluent using wood as an adsorbent. *J. Water Pollut. Contr, Fed*. **50**: 926–935.

Preston, B D., Van Miller, J P., Moore, R W., Allen, J R. (I981). Promoting effects of polychlorinated biphenyls (Aroclor 1254) and polychlorinated dibenzofuran-free Aroclor I254 on diethylnitrosamine-induced tumorigenesis in the rat. *J. Natl. Cancer Inst*. **66**, (509): 5-16.

Provost, T. L., Juarez, De Ku L. M., Zender, C., (1999). Dose- and age-dependent alterations in choline acetyltransferase (ChAT) activity, learning and memory, and thyroid hormones in 15- and 30-day old rats exposed to 1.25 or 12.5 ppm polychlorinated biphenyl (PCB) beginning at conception. *Prog. NeuroPsychopharmacol. Biol. Psychiat*. **23**: 915-928.

Qi, Y. and Zhang, T. C., (2015). Sorption and desorption of testosterone at environmentally relevant levels: Effects of aquatic conditions and soil particle size fractions. *J. Environ. Eng*. **142**: 1-9.

Qi, Y. and Zhang, T.C., (2016). Sorption and desorption of testosterone at environmentally relevant levels: Effects of aquatic conditions and soil particle size fractions. *J. Environ. Eng*. **142**: 1-9.

Quensen, J., Boyd, S. A., Tiedje, J. M., Lopshire R. F., Enke, C. G., (1992). Expected dioxin-like toxicity reduction as a result of the dechlorination of Aroclors. In: General Electric Company Research and Development Program for the Destruction of PCBs, Eleventh Progress Report. Schenectady, NY: General Electric Corporate Research and Development. pp 189-196.

Regitano, J. B., W. S. da Rocha, W. S., Alleoni, L. R., (2005). Soil pH on mobility of imazaquin in oxisols with positive balance of charges. *J. Agric. Food Chem*. **53**: 4096-4102.

Reid, B. J., Jones, K. C., Semple, K. T., (2000). Bioavailability of persistent organic pollutants in soils and sediments-a perspective on mechanisms, consequences and assessment. *Environ. Poll*. **108**: 103-112.

Ritter, L., Solomon, K. R., Forget, J., (2005). Persistent organic pollutants: An assessment report on DDT, aldrin, dieldrin endrin, chlordane, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, dioxins and furans. Report for the International Programme on Chemical Safety (IPCS) within the frame work of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC). pp 44.

Rogan W. J., Gladen B. C., Guo Y-L. L., (1999). Sex ratio after exposure to dioxin-like chemicals in Taiwan. *Lancet*. **353**: 206-207.

Ruiz-Hitzky, E., Aranda, P., Darder, M., Rytwo, G., (2010). Hybrid materials based on clays for environmental and biomedical applications. *J. Mater. Chem*. **20**: 9306-9321.

Sabljic, A., (1984). Prediction of the nature of strength of soil sorption of organic pollutants by molecular topology. *J. Agric. Food Chem*. **32**: 243-246.

Safe, S., (1984). Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs): Biochemistry, toxicology and mechanism of action. *Crit. Rev. Toxicol*. **13**: 319–395.

Safe, S. H., (1994). Polychlorinated biphenyls (PCBs): Environmental impact, biochemical and toxic responses, and implications for risk assessment. *Crit. Rev. Toxicol*. **24**, (2): 87–149.

Salama, J., Chakraborty, T. R., Ng, L., Gore, A. C., (2003). Effects of polychlorinated biphenyls on estrogen receptor-beta expression in the anteroventral periventricular nucleus. *Environ. Health. Perspect*. **111**: 1278–1282.

Schaeffer, E., Greim, H., Goessner, W., (1984). Pathology of chronic polychlorinated biphenyl (PCB) feeding in rats. *Toxicol. Appl. Pharmacol*. **75**: 278-288.

Schulte, E. and Malisch, R., (1983). Calculation of the real PCB content in environmental samples. *Fresenius J. Anal. Chem*. **314**,(6):545–51. doi:10.1007/BF00474844.

Schwarzenbach, R. P., Gschwend, P. M., Imboden, D. M., (1993). Environmental organic chemistry. New York, Wiley. pp 45-69.

Semple, K. T., Morriss, A. W. J., Paton, G. I., (2003). Bioavailability of hydrophobic organic contaminants in soils: Fundamental concepts and techniques for analysis. *Eur. J. Soil Sci*. **54**: 809-818.

Silberhorn, E. M., Glauert, H. P., Robertson, L. W., (1990). Carcinogenicity of polyhalogenated biphenyls: PCBs and PBBs. *Crit. Rev. Toxicol*. **20**: 440-496.

Sinks T., Steele, G., Smith, A. B., Watkins, K., Shults, R. A., (1992). Mortality among workers exposed to polychlorinated biphenyls. *Am. J. Epidemiol*. **136**: 389–398.

Smaranda, C., Bulgariu, D., Malutan, T., Gavrilescu, M., (2014). The evaluation of factors affecting sorption of pentachlorophenol in soil. *Lucrari Stiintifice*. **57**, (2): 133-138.

Song, J., Peng, P. A., Huang, W., (2002). Black carbon and kerogen in soils and sediments. 1. Quantification and characterization. *Environ. Sci. Technol*. **36**, (18): 3960–3967.

Steinberg, R. M., Walker, D. M., Juenger, T. E., Woller, M. J., Gore, A. C (2008). Effects of perinatal polychlorinated biphenyls on adult female rat reproduction: Development, reproductive physiology, and second generational effects. *Biol. Reprod*. **78**,(6): 1091–1101.

Steinberg, R. M., Juenger, T. E., Gore, A. C., (2007). The effects of prenatal PCBs on adult female paced mating reproductive behaviours in rats. *Hormones and Behavior*. **51**: 364–372.

Tan, I., Ahmad, A., Hameed, B. 2009. Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2, 4, 6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *J. Hazard. Mater*. **164**: 473–482.

Tanabe, S., (1988). PCB problem in the future: Foresight from current knowledge. *Environ. Pollut.* **50**: 5–28.

Tatematsu, M., Nakanishi, K., Murasaki,G., Mujatia, Y., Hirose, M., Ito, N., (1979). Enhancing effect of inducers of liver microsomal enzymes on induction of hyperplastic liver nodules by N-2-fluorenyl-acetamide in rats. *J. Natl. Cancer Inst*. **63**: 1411–1416.

Tharappel, J. C., Lehmler, H-J., Srinivasan, C., Robertson, L. W., Spear, B. T., Glauert, H. P., (2008). Effect of antioxidant phytochemicals on the hepatic tumour promoting activity of 3, 3', 4, 4'-tetrachlorobiphenyl (PCB-77). *Food Chem. Toxicol.* **46**: 3467–3474.

Tiktak, A., Pineros Gatcet, J. D., deNie, D. S., Vanclooster, M., Jones, A., (2003). Assessment of pesticides leaching at the pan-European level using a spatially distribution model,

Proc. of the Diffuse Pollution and Basin Management Conf., Dublin, Aquatic Ecology and Dangerous Substances Section, 17-22 August 2003.

Tryphonas, H., Luster, M. I., Schiffman, G., Dawson, L. L., Hodgen, M., Germolec, D., Hayward, S., Bryce, F., Loo, J. C., Mandy, F., (1991). Effect of chronic exposure of PCB (Aroclor 1254) on specific and nonspecific immune parameters in the rhesus (Macaca mulatta) monkey. *Fundam. Appl. Toxicol.* **16**: 773–786.

UNEP, United Nation Environmental Programme (2009). Sustainable Innovation and Technology Transfer Industrial Sector Studies: Recycling – From E-waste to Resources. United Nations Environment Programme. Available from: http://www.unep.org/pdf/Recycling_From_e-waste_to_resources.pdf. *Accessed* 24/06/2017.

UNEP, United Nation Environmental Programme (2001). Text of the Stockholm Convention on Persistent Organic Pollutants and implementation activities; amended 2009. United Nations Environment Programme Available from: http://chm.pops.int/ The Convention/Overview/Text of the Convention/ tabid/2232. *Accessed* 24/06/2017.

UNEP, United Nation Environmental Programme (2011). The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal. United Nations Environment Programme. Available from: http://www.basel.int/Portals/4/Basel%20Convention/docs/text/BaselConventionText-e.pdf. *Accessed* 24/06/2017.

UNEP, United Nations Environment Program (1988). Polychlorinated biphenyls. International Register of Potentially Toxic Chemicals (IRPTC). Scientific Reviews of Soviet Literature on Toxicity and Hazards of Chemicals No. 107. Moscow, Russian Federation: United Nations Environment Program; pp. 56.

USEPA, United State Environmental Protection Agency (1985). Drinking Water Criteria Document for Polychlorinated Biphenyls (PCBs). EPA-560/5-85-026. Final Draft, US Environmental Protection Agency, Office of Toxic Substances. Washington DC 20460 USA. pp 14-20

USEPA, United State Environmental Protection Agency (1987). Health assessment document for chlorinated benzenes. EPA 600/8-84-015F. Final report, US Environmental Protection Agency, Cincinnati, Ohio, USA. pp 6-14.

USEPA, United State Environmental Protection Agency (2012). Polychlorinated biphenys, health effects of PCBs, http://www.epa.gov/osw/hazard/tsd/pcbs/pubs/uffects/htm. *Accessed* on 10/09/2017.

USEPA, United State Environmental Protection Agency (2008b). Third Five-Year Review Report for the Geneva Industries Superfund Site, Houston, Harris County, Texas. United States Environmental Protection Agency. Available from: http://www.epa.gov/region6/6sf/texas/geneva/tx_geneva_3rd-5yr_review_09-23-2008.pdf. *Accessed* 24/02/2018.

USEPA, United State Environmental Protection Agency (2011). Estimation of fish bioconcentration factor (BCF) from depuration data. Environment Agency, Horizon House, Deanery Road, Bristol, BS1 5AH. Available from: http://publications.environmentagency.gov.uk, August 2011. *Accessed* 10/11/2018.

Villeneuve, S., Cyr, D., Lynge, E., Orsi, L., Sabroe, S., Merletti, F., (2010). Occupation and occupational exposure to endocrine disrupting chemicals in male breast cancer: a case-control study in Europe. In: *Occup. Environ. Med*. **67**: 837–844.

Von Oepen, B., Kördel, W., Klein, W., (1991). Sorption of nonpolar compounds to soils: Processes, measurements and experience with the application of the modified OECD-Guideline 106. *Chemosphere*. **22**: 285-304.

Waldam, M. and Shevah, Y., (1993). Biodegradation and leaching of pollutants: monitoring aspects. *Pure and Appl. Chem*. **65**: 1595 – 1603.

Wang, J. D., Chen, R. L., Jiang, K., Zhuang, Y. H., (1981). A study on analytical methods for polychlorinated biphenyls (PCBs). II. Identification of Chinese standard PCBs [in Chinese]. Huan Jing Ke Xue Cong Kan **2**: 7–11.

Wang, S. B. and Zhu, Z. H., (2008). Characteristics of coal fly ash and adsorption application. *Fuel*. **87**: 3469–3473.

Wania, F. and Mackay, D., (1999). The evolution of mass balance models of persistent organic pollutant fate in the environment. *Environ. Pollut*. **100**: 223-240.

Wauchope, R. D., S. Yeh, J. B. H. J., Linders, R., Kloskowski, K., Tanaka, B., Rubin, A., Katayama, W., Kordel, Z., Gerstl, M., Lane Unsworth, J. B., (2002). Pesticides soil sorption parametesr: theory, measurements, uses, limitations and reliability. *Pest Manag. Sci*. **58**: 419-445.

Weber, W. J. and Morris, J. C., (1963). Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng*. **89**: 31–60.

Weber, Jr., W. J., McGinley, P M., Katz, L E., (1991). Sorption phenomena in subsurface systems: Concepts, models and effects on contaminant fate and transport. *Water Res*. **25**: 499-528.

Wester, R. C., Maibach, H. I., Sedik, L., Melendres, J., Wade, M., (1993). Percutaneous absorption of PCBs from soil: in vivo rhesus monkey, in vitro human skin, and binding to powdered human stratum corneum. *J. Toxicol. Environ. Health*. **39**, (3): 375–82. doi:10.1080/15287399309531758.

Wester, R. C., Mobayen, M., Maibach, H. I., (1987). In vivo and in vitro absorption and binding to powered stratum corneum as methods to evaluate skin absorption of environmental chemical contaminants from ground and surface water. *J. Toxicol. Environ. Health*. **21**, (3): 367– 74. doi:10.1080/15287398709531025 PMID:3108517.

Whitfield, J. B., (2001). Glutamyl transferase. *Crit. Rev. Clin. Lab. Sci*. **38**: 263–355.

WHO, World Health Organization (1993). Polychlorinated biphenyls and terphenyls, 2nd ed. Geneva, (Environmental Health Criteria, No. 140).

Wolters, A., Kleinb, M., Vereecken H., (2004). An improved description of pesticide volatilization: Refinement of the pesticide leaching model (PELMO). *J. Environ. Qual*. **33**: 1629-1637.

Wu, C.-H., (2007). Adsorption of reactive dye onto carbon nanotubes: equilibrium, kinetics and thermodynamics. *J. Hazard. Mater*. **144**: 93–100.

Xing, Y., Lu, Y., Dawson, R. W., Shi, Y., Zhang, H., Wang, T., (2005). A spatial temporal assessment of pollution from PCBs in China. *Chemosphere*. **60**, (6): 731–9.doi:10.1016/j. chemosphere.2005.05.001 PMID:15964056.

Xing, B., (2001). Sorption of naphthalene and phenanthrene by soil humic acids. *Environ. Pollut*. **111**, (2): 303–309.

Xiong, C., Yi-yang, W., Hui-xin, L., Ming-xiang, L., Li, X., (2015). Biosorption and biodegradation mechanisms of trichlorobiphenyl by Ensifer adhaerens. *China Environ. Sci.* **35**: 1423-1428.

Yang, F., Wang, M., Wang, Z., (2013). Sorption behavior of 17 phthalic acid esters on three soils: Effects of pH and dissolved organic matter, sorption coefficient measurement and QSPR study. *Chemosphere*. **93**: 82−89.

Yassi, A., Tate, R. B., Routledge, M., (2003). Cancer incidence and mortality in workers employed at a transformer manufacturing plant: update to a cohort study. *Am J Ind Med*. **44**, (1): 58–62.

Yildiz, N., Erol, M., Aktas, Z., and Calimli, A., (2004). Adsorption of aromatic hydrocarbons on BTEA-bentonites. *Adsorp. Sci. Technol*. **22**: 145-154.

You, S-J., Yin, Y., Allen, H.E., 1999. Partitioning of organic matter in soils: effects of pH and water/solution ratio. *Sci. Total Environ*. **227**: 155-160.

Yuan, G. D., Theng, B. K. G., Churchman, G. J., Gates, W. P., (2013). Clays and clay minerals for pollution control. In: Handbook of Clay Science, Part B, 2nd edition (Bergaya, F., G. Lagaly, G., editors). Elsevier, Amsterdam. pp 587-644.

Zech, W., Senesi, N., Guggenberger, G., Kaiser, K., Lehmann, J., Miano, T. M., Miltner, A. Schroth, G., (1997). Factors controlling humification and mineralization of soil organic matter in the tropics. *Geoderma*, **79**: 117–161.

Zhang, Z. L., H. S. Hong, J. L. Zhou Yu, G., (2004). Phase association of polycyclic aromatic hydrocarbons in the Minjiang River Estuary China. *Sci. Total Environ*. **323**: 71-86.

Zhu, R., Zhou, Q., Zhu, J., Xi, Y., He, H., (2015). Organo-clays as sorbents of hydrophobic organic contaminants: sportive characteristics and approaches to enhancing sorption capacity. *Clay Clay Miner*. **63**,(3): 199–221

CHAPTER 3

GENERAL METHOD AND MATERIALS

This chapter focuses on the general experimental procedures used in this research. The chapter outlines the details of the reagents and chemicals used, treatment of model soil samples, and the real sediment samples collected at five different sites along uMngeni River of KwaZulu-Natal, South Africa. Detailed experimental techniques used for the sorption studies as well as data treatment are described. The significance of each technique for every step is highlighted.

Materials and methods

3.1 Reagents and chemicals

All reagents and chemicals were of HPLC/analytical-grade and the eight-selected PCB standards were purchased from Sigma Aldrich® (South Africa). The PCB standard stock solution mixture (50 µg/mL) was prepared using *n*-hexane and stored in the refrigerator at 4°C. The lower working concentrations for the PCB standards were prepared by appropriate dilution in *n*-hexane. Details of chemicals used are presented in **Table** 3.1

Table 3.1:

Chemicals and suppliers

Chemical	KCl	$CaCl_2$, 4-8 mesh	$MgCl_2$	$AlCl_3.6H_2O$	$BaCl_2$	$(NH_4)_2Fe(SO_4)$, CP	H_2SO_4, s.g 1.84	H_2O_2, 34%	$(C_{12}H_{10}NO_3S)_2Ba$
Supplier	Merck	B/M Scientific	B/M Scientific	Saarchem. Ltd	Associated Chemicals	BDH Laboratory	Promark Chemicals	Merck	General Chemical and Pharmaceutical Ltd.
Country	South Africa	South Africa	South Africa	South Africa	South Africa	England	South Africa	South Africa	Canada

All the glassware was baked in the oven at approximately 130°C prior to use. All chemicals and reagents were used as received.

3.2 Modeled soil

A modeled soil sample used in this research was collected from Blue Lagoon site which is the exit point of the uMngeni River to the India Ocean located North of Durban, KwaZulu-Natal, (**Fig**. 3.1) South Africa. The field soil sample was chosen as a modeled soil in order to replicate the environmental field matrix on the sorption behaviour of organic contaminants such as

PCBs. More information about the river is enumerated below (study site and sample collection). The treatment of the modeled soil and sediment samples is discussed in chapters 4 and 7, respectively. Briefly, the soil was air dried and fractionated into five different particle grain sizes (<75, 100, 200, 300 and 425 μm) using a mechanical sieves method. These selected soil particle grain sizes were chosen in this study to represent different soil particle sizes such as clay, silt, fine sand, medium sand and coarse sand (USEPA, 2008). Each fraction of soil particle size was extracted in triplicate using both *n*-hexane and dichloromethane as well as methanol to remove the targeted OPs of interest (PCBs), resulting in a model soil sample free of PCBs. To ensure that the soil samples used for the batch adsorption experiments did not contain any PCBs, the extracted soils were re-extracted and the extract analyzed using GC-MS. The chromatograms were found to contain no evidence of PCB peaks compared to the standards.

3.2.1 Soil characterization

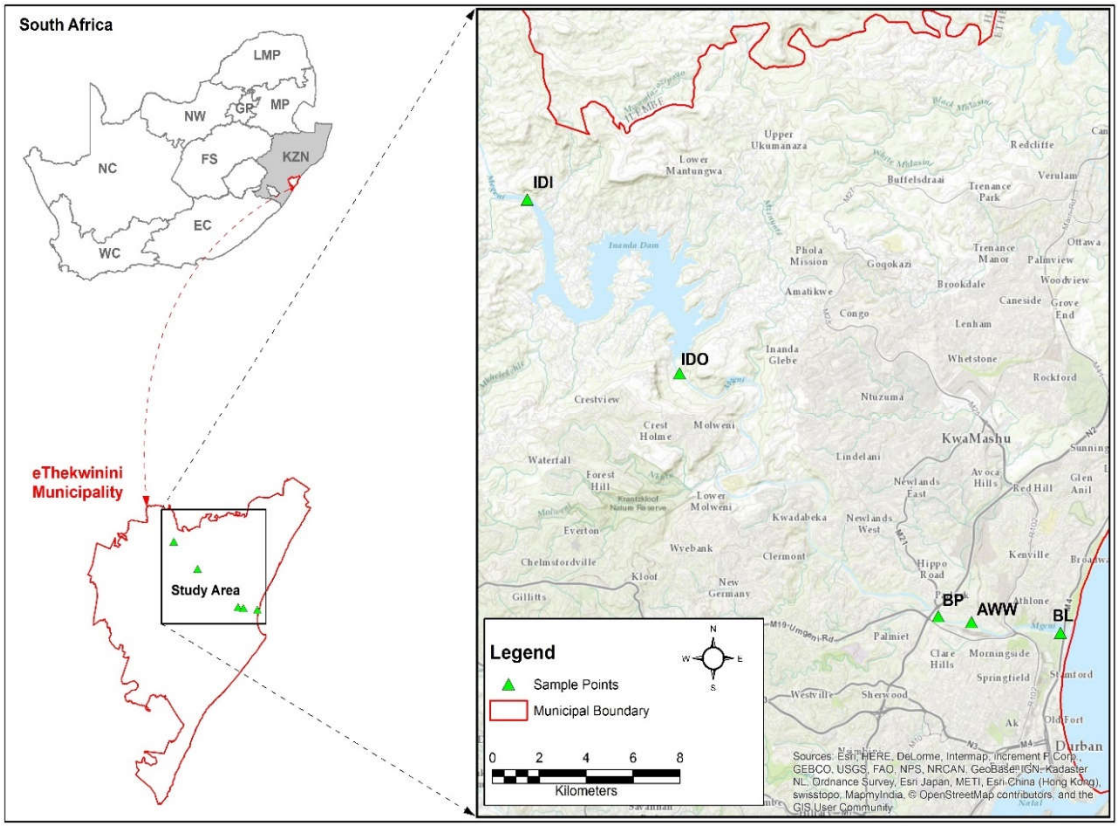
The surface areas, pore volumes and pore size distributions of each soil fraction were measured using the Brunauer-Emmet-Teller (BET) method with the initial degassing temperature set at 90°C for 2 h, raised to 200°C and held at that temperature for a further 6 h under vacuum. The results were obtained through N_2 adsorption-desorption at 77.35 K using TriStar II 3020, Autosorb Automated gas sorption system analyzer (2012 surface area and porosity Micrometritics, USA). BET surface area was evaluated from the BET plot using single point surface area at $P/Po = 0.2998$. The pore volume was measured at a single point adsorption with total pore volume of pores less than 264.59 nm diameter at $P/Po = 0.993$. Pore-size distributions were obtained using Barrett-Joyner-Halenda (BJH) from the plot with adsorption average pore width of 4V/A by BET.

The functional groups of each fraction of soil particle grain size were determined using Fourier transform infrared spectroscopy (FTIR) (Precisely spectrum 100 Perkin Elmer, USA). Details of the results are discussed in chapter 4.

3.3 Study sites and sample collection

The study area in this research is the uMngeni River, one of the major rivers in South Africa and the largest river in KwaZulu-Natal province. It is approximately 232 kilometres (144 miles) long with a catchment area of 4,432 square kilometres (1,711 sq miles) on a coordinate of 29°48′36″S 31°02′08″E. This river serves as a major source of water to the people of the

Durban area. Details about this river have been enumerated in chapter 1. Sediments used in this study were collected from five locations along uMngeni River in September 2017. The sampling map is shown in **Fig**. 3.1. The sediment samples have a varying amount of physicochemical characteristics such as differences in the level of clay, organic matter content and water pH. River sediments were collected from the selected sites based on the results of past studies, most especially on the selected eight PCB congeners. These sites were identified by Global Positioning System (GPS). River sediment samples containing appropriate pore water were collected using a stainless-steel corer into a 1 L amber glass bottle whose cap was lined with aluminium foil. The sample bottles were treated using the standard method, washed with soap, rinsed with tap water and distilled water and finally with HPLC grade acetone and *n*-hexane. Prior to the sample collection, bottles were finally rinsed with the river water to be collected. The physicochemical parameters of the river water were measured onsite as shown in **Table** 3.2. The bottles were stored in a cooler box containing ice to maintain a relatively low temperature during transportation to the laboratory.



IDI = Inanda Dam Inlet, IDO = Inanda Dam Outlet, BP = Business Park, AWW = After Waste Water Treatment Plant, BL = Blue Lagoon

Figure 3.1: Sampling site in uMngeni River, KwaZulu-Natal, South Africa. (Created using ArcMap10.4 version)

Table 3.2:

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

Site code	Sample coordinates		Physicochemical parameters				Description of the sampling site
	Latitude	Longitude					
IDI	29° 39'05.20"	30° 48'06.24"	5.51	21.40	274.00	4.89×10^2	Domestic activities and surface runoff.
IDO	29° 42'55.74"	30° 52'07.69"	6.36	21.20	195.40	3.47×10^2	Agricultural runoff and domestic activities.
BP	29° 48'19.05"	30° 58'58.08"	6.01	21.10	301.50	5.22×10^2	Domestic and commercial activities.
AWW	29° 48'27.01"	30° 59'51.05"	5.77	21.90	771.20	1.38×10^3	Effluent of treated wastewater discharged to the river
BL	29° 48'41.03"	31° 02'12.05"	5.95	20.90	28 350	5.07×10^4	Domestic and recreational activities. Discharge of the river water into the Indian ocean.

3.3.1 Pore water separation

Porewater was separated from the sediment samples within 24 h after samples were collected. Sediment samples were centrifuged at 6000 rpm for 20 min, the pore water was decanted and vacuum filtered using 0.45 μm cellulose acetate filter paper. The pore water collected was stored in 100 mL glass bottles and preserved with 0.01% NaN_3 to minimize bacterial growth prior to batch adsorption experiments.

3.3.2 Separation and characterization of sediment samples

After pore water was removed, the sediment samples were air dried at room temperature in the fume hood for six days, disaggregated manually using a marble mortar and pestle, and sieved using a 425 μm mesh size. Sediment particles that passed through the 425 μm sieve were collected in the receiver and mixed manually to achieve homogeneity and stored in an amber glass bottle under airtight conditions prior to batch adsorption experiments. Soil mineralogical, macro-morphological properties and qualitative elemental analysis were determined using a low angle powder X-Ray diffractometer (XRD) (PANalytica EMPYREAN, Netherland-Holland) using Kα radiation of Cu operated at 40 kV and 40 mA and the spectra were analyzed using Highscore Plus software and quantified using Rietveld, and scanning electron microscopy (SEM) equipped with energy disperse X-ray (EDX). The results are shown in chapter 7. Particle size analysis on each sediment sample was performed by the sieve pipette method. Soil organic matter (SOM) content and cation exchange capacity (CEC) were determined using Walkley Black and barium chloride compulsive exchange methods, respectively, as discussed below.

3.3.2.1 Walkley Black method for soil organic matter determination

Organic carbon (OC), TOC and SOM were determined using wet oxidation/combustion based on a chromic acid digestion method (Walkley and Black, 1934; Tiessen and Moir 1993; Nelson and Sommers 1996; Chan *et al*., 2001; Schumacher 2002). Samples of each soil fraction (1.002 g) were transferred into individual 500 mL Erlenmeyer flasks. Aliquots (10 mL) of 0.167 M of K_2CrO_7 were added in excess to each flask with gentle swirling together with 20 mL of concentrated H_2SO_4. The flask was placed under an insulation pad to minimize rapid heat loss, and allowed to

stand for 40 min. The suspension was further diluted with 100 mL of deionized water to provide a visible suspension at the end. A 10 mL aliquot of 85% H_3PO_4 was added to the suspension to complex the Fe^{3+} originally in the soil (formed during the titration with the ferrous solution) which may, in turn, interfere with the endpoint during titration. The excess dichromate ion was back titrated with 0.5 M ferrous ion solution using barium diphenylamine sulfonate as an indicator (Nelson and Sommers 1996) which gave a colour change from purple to green at the endpoint. The equation for the reaction between chromate with OC in the soil/sediment is:

$$\text{Over all equation: } 2Cr_2O_7^{2-} + 16H^+ + 3C \rightarrow 4Cr^{3+}\ 3CO_2 + 8H_2O$$

Reaction of Fe^{2+} with remaining $Cr_2O_7^{2-}$ is shown in the following equation:

$$\text{Over all equation: } Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

The OC content in each soil fraction was evaluated in triplicate using Eq. (3.1) as proposed by Schumacher (2002):

$$\text{Percentage Carbon (\%C)} = \frac{(B-S)\times M\left(Fe^{2+}\right)\times 12 \times 100 \times f}{\text{mass of soil} \times 4000} \qquad (3.1)$$

where B is the volume of Fe^{2+} solution used to titrate the blank, S is the volume of Fe^{2+} solution used to titrate the sample and M is the concentration of Fe^{2+}. The value of 12/4000 is the milliequivalent weight of carbon in grams, and f = correction factor (1.30). The factor of 1.30 was assumed considering a mean recovery of 76% for OC using the Walkley Black procedure (Walkley and Black, 1934).

The oxidizable organic carbon was converted to total organic carbon (TOC) using Eq. (3.2) as proposed by Sánchez-Monedero *et al*., (1996).

$$\text{Total organic carbon (\% TOC)} = 1.23(OXC) + 0.35 \qquad (3.2)$$

where, OXC is the oxidizable organic carbon (percentage carbon) content and the factors of 1.23 and 0.35 (a and b) were obtained from experiments conducted by Sánchez-Monedero *et al*., 1996. Total organic carbon is converted into SOM using Eq. (3.3):

$$\text{Soil organic matter (\%SOM)} = \frac{\%total\ organic\ carbon}{0.58} \times 1.72 \qquad (3.3)$$

The factor of 1.72 is traditionally used for soils to convert OM to OC, based on the assumption that SOM contains 58% organic carbon (i.e., 1/0.58 = 1.72) (Nelson and Sommers, 1996). TOC and SOM experiments were carried out in triplicate.

The percentage carbon and nitrogen were determined using a TruMac LECO CNS-2000 analyzer (LECO Corporation, USA). Ultrapure oxygen was used as an oxidant set at a pressure of 890 mmHg and combusted at a temperature of 1350°C. The analyses were carried out in triplicate. This test was carried out to determine if OM influenced the partitioning of the hydrophobic PCB pollutants between the aqueous solution and soil particle grain sizes. The loss on ignition (LOI) method was used based on ASTM D 2974 method C. A mass of approximately 10.271 g of each soil particle grain size (<75 µm, 100 µm, 200 µm, 300 µm and 425 µm) was placed in a ceramic crucible, heated in the oven at 105°C until a constant weight was obtained (moisture content determination). The LOI method was thereafter used for determination of OM, which involved the heated destruction of all OM in the soil particle grain sizes. A constant weight of each soil particle grain size was obtained after the moisture content determination. The samples were then placed in a temperature-controled muffle furnace (Labcon, Labdesign Engineering Pty Ltd SN – Li 3246) and heated at 440°C overnight (Nelson and Sommers 1996: ASTM 2000). The samples were then cooled in a desiccator and weighed. The analysis was performed in triplicate. The amount of OM in each soil particle grain size was calculated using Eq. (3.4).

$$\text{SOM}(\%) = \text{LOI}(\%) = \frac{\text{weight}_{105} - \text{weight}_{440}}{\text{weight}_{105}} \times 100 \qquad (3.4)$$

where Weight_{105} is the weight of the soil after oven-drying to 105°C for 24 h and Weight_{440} is the weight of the soil after ignition at 440°C.

Example: In order to determine the sorption capacity of a soil sample (1 g) for the hydrophobic organic pollutant, a wet oxidation (Walkley Black) method was used for the determination of soil organic matter content in the soil sample as described above. The volume of Fe^{2+} solution used to titrate the blank (B) was found to be 31.56 mL, the average volume of Fe^{2+} solution used to titrate the sample was 18.10 mL and the concentration of Fe^{2+} was 0.5.00 M

Calculation: Using equation 3.1 to determine % carbon content.

Percentage Carbon (%C) = $\frac{(B-S)\times M\left(F_e{}^{2+}\right)\times 12\times 100\times f}{\text{mass of soil}\times 4000}$

Percentage Carbon (%C) = $\frac{(31.56-18.10)\times 0.500\times 12\times 100\times 1.4}{1\times 4000}$

Percentage Carbon (%C) = 2.827

For percentage total organic carbon content using equation 3.2

Total organic carbon (% TOC) = $1.23(\text{OXC}) + 0.35$

% TOC = $1.23(2.827) + 0.35$

% TOC = 3.827

Percentage soil organic matter was evaluated as:

Soil organic matter (%SOM) = $\%\ \frac{total\ organic\ carbon}{0.580}\ \times\ 1.72$

% SOM = $\frac{3.827}{0.580}\ \times\ 1.72$

% SOM = 11.348

3.3.2.2 Determination of cation exchange capacity (CEC)

Cation exchange capacity of the different soil and sediment samples were determined using the barium chloride compulsive exchange method as described by Gillman and Sumpter (1986) modified in 2011 and recommended by the Soil Science Society of America. This method was adopted due to its good repeatability, precision, and cost-effectiveness. A 2 g soil sample was weighed into a centrifuge tube with 20 mL of 0.1 mol/L $BaCl_2{\cdot}2H_2O$, which was then capped and agitated for 2 h on the orbital shaker. The solution was centrifuged for 30 min at 10 000 rpm, the supernatants were decanted and filtered using a 0.45 µm filter disc into ICP vials. The

concentrations of Ca, Mg and Al were analyzed using ICP-OES (Perking Elmer Precisely Optima 5300 DV), while the concentration of K was determined with a flame spectrometer (Jenway Ltd. Felsted, Dunmow Essex CMB 3LB, Model PFP7, UK). The CEC of each soil/sediment sample was calculated using equation (3.5) (Hendershot and Duquette 1986).

$$\text{CEC (cmol}_c\text{/kg soil)} = \left(\frac{C_{Ca}}{20} + \frac{C_{Mg}}{12} + \frac{C_K}{39} + \frac{C_{Al}}{9}\right) \text{x } 0.01 \qquad (3.5)$$

where cmol_c/kg is the centimole positive charge per kilogram of soil, C is the concentration of the Ca, Mg, K and Al metals in the soil, respectively. The numbers in the denominator are the equivalent weight of the metals and the number 0.01 is the conversion factor resulting from a 20 mL (0.02 L) of 0.1 M $BaCl_2.2H_2O$ per 2.0 g of soil/sediment samples.

Example: A soil sample was analyzed and found to contain the following concentration of 0.390, 0.228, 1.533 and 0.015 ppm for Ca, Mg, K and Al, respectively. The amount of CEC contained in the soil was calculated in milliequivalent per 100 g of soil as follows:

$$\text{CEC (Meq/100 g)} = \frac{0.390}{20} + \frac{0.228}{12} + \frac{1.533}{39} + \frac{0.015}{9} \div 100$$

$$\text{CEC (Meq/100 g)} = (0.0195 + 0.019 + 0.0393 + 0.00170) \times 100$$

$$\text{CEC (Meq/100 g)} = 7.950$$

3.4 Standards

Stock Solution:

A 100 µg/mL stock solution of the PCB standard mixture was prepared by transferring a weighed mass of each standard (10 mg) to a 100 mL volumetric flask. The solid was dissolved in n-hexane and the solution made up to the mark, and thereafter homogenised. The stock solution was stored in a refridgerator at 4°C prior to use. The lower working standards of the mixed standard solutions were thereafter prepared from the stock solution using appropriate dilutions.

3.4.1 Preparation of stock and working standard solutions

Calculation:

$$\frac{10\ mg}{0.1\ L} = 100\ mg/L$$

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

Then $C_1\ V_1 =\ C_2\ V_2$

For example, a 0.25 µg/mL of PCB was prepared from a 100 µg/mL stock solution of PCB by transferring 25 µL of the stock solutions to a 10 mL volumetric flask and making it up to mark with DCM. The following calculation shows the volume that was required to be transferred:

100 µg/mL xV_1 = 0.25 mg/L x 0.01 L

$$V_1 = \frac{0.25 \times 10^{-3}\ \frac{\mu g}{L} \times 0.01\ L}{100 \times 10^{-3}\ \mu g/L}$$

V_1 = 2.5 x10^{-5} L

V_1 = 25 µL

3.4.2 Preparation of 250 mg/L of humic acid (HA)

A 250 mg/L stock solution of HA was prepared by dissolving 250 mg of commercial HA in 1 L volumetric flask containing 0.1 M NaOH solution with double distilled water, wrapped with aluminium foil and stored in the refridgerator under 4ºC to avoid photodecomposition of HA by light. Lower working standards were prepared from the stock solution.

3.5 GC-MS analysis

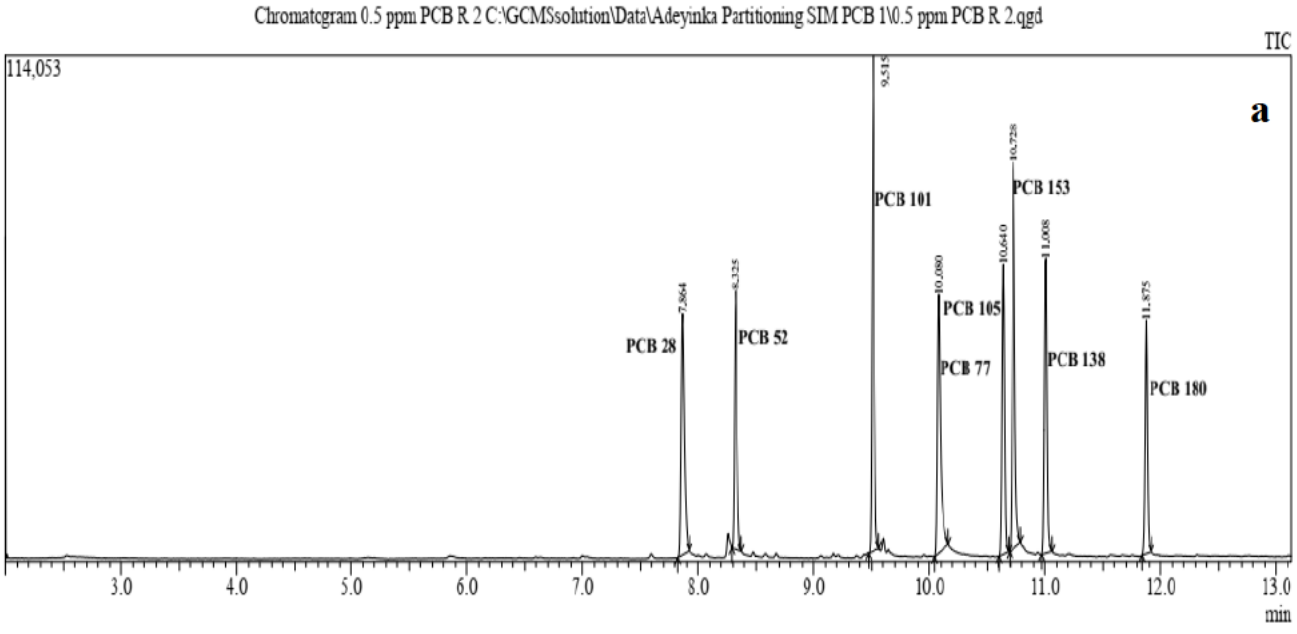
The details of the GC-MS parameters are summarized in **Table** 3.3. Sample extracts were reconstituted in 1 mL of DCM and analyzed using gas chromatography-mass spectrometry (GC-MS) (QP-2010 Ultra Shimadzu, Japan), with a DB-5MS capillary column of length 30 m (0.25 µm internal diameter and 0.25 µm film thickness) in SIM mode and helium was used as the carrier gas.

Table 3.3:

Details of GC-MS parameters

Rate, °C/min	Ramping Temp, °C	Hold time, min	Injection Temp, °C	Detector Temp, °C	flow rate, mL/min	Total flow, mL/s	Linear velocity, cm/s	Purge flow, mL/min	Injection volume, µL
-	150	2	220	320	0.72	31.8	32.2	3.0	1.0
14	295	2							

This method was efficient in achieving the best possible separation and well-resolved peaks for all eight targeted PCB congeners investigated in this study as shown in **Fig**. 3.2 a and b.



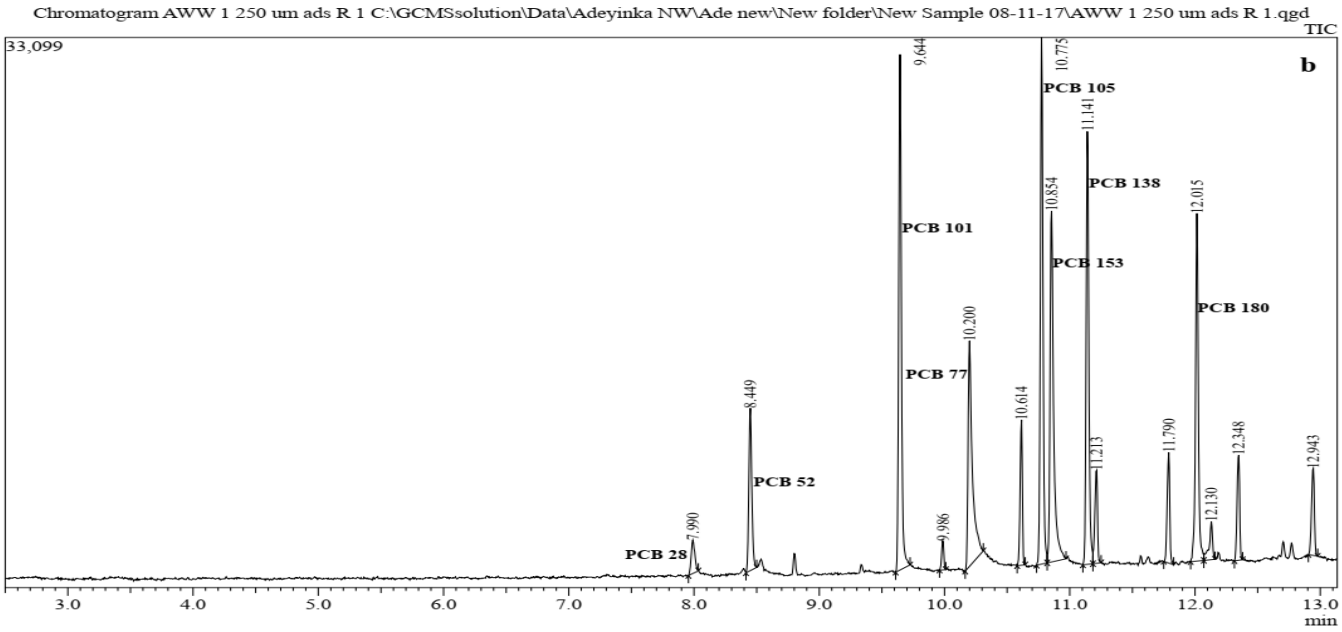


Figure 3.2: a and b: Chromatograms for (a) PCB standards and (b) real water sample spiked with eight selected PCB congeners

3.5.1 Recovery studies

To estimate the efficiency and validate the extraction protocols, a control sample containing an equal concentrations of PCBs in 0.01 mol/L $CaCl_2$ but without soil was subjected to the same procedure as used for the batch adsorption studies described below.

Percentage recovery (%R) = $\frac{x-y}{x} \times 100$ (3.6)

where, x-y is equal to the concentration of PCBs found in aqueous solution after equilibrium was reached (µg/L), and x is the actual concentration of PCBs spiked in the aqueous solution before sorption studies (µg/L).

3.5.1.1 Determination of partition coefficient and extraction efficiency protocols

A 0.01 mol/L $CaCl_2$ solution containing a known mass of soil was spiked with a known concentration of targeted PCB solution and was equilibrated for 24 h. The solution was then extracted with a known volume (5 mL) of organic solvent.

Partition coefficient (K_d) = $\frac{d/vx}{s-d/vw}$ (3.7)

Extraction efficiency = $\frac{d}{s} \times 100$ (3.8)

where, *d* is the amount of PCB extracted (µg/L) from the aqueous phase after equilibrium, *s* is the amount of spiked PCB (µg/L), *vx* (organic phase) is the volume of extracting solvent (mL) and *vw* is the volume of aqueous solution of $CaCl_2$ (mL) (water phase) spiked with the known concentration (0.5 µL) of PCB.

Example calculations for percentage recovery and extraction efficiency:

A 10 mL sample aqueous solution of 0.01 M $CaCl_2$ was spiked with 0.80 µg/L mixture of PCB standards solution (two samples for duplicate analysis) and were subjected to batch adsorption experiments as described in section 3.6. After equilibrium was reached 0.57 µg/L of PCB 28 was found in the aqueous phase after extracting with three times 5 mL volumes of dichloromethane. Therefore, percentage recovery of PCB 28 and others was calculated using equation 3.6. Percentage recovered for other PCB congeners are shown in **Table** 3.2.

%R (PCB 28) = $\frac{0.57}{0.80} \times 100$

%R = 71.50%

A 0.5 µg of PCB mixtures was dissolved in 10 mL aqueous solution containing 0.01 M $CaCl_2$. In order to assess the percentage of PCBs that can be separated from the aqueous solution, a single 15 mL DCM and three consecutive 5 mL portions of DCM were used to extract PCBs from the aqueous solution, respectively. The partition coefficients for all the PCB congeners are shown in **Table** 3.4

Sample calculation for PCB 28 with K_d value of 5.28 (where K_d used for PCBs were literature values)

(a) For a single 15 mL DCM, using equation 3.7:

$5.28 = (d \,/\, 15)/((0.50 - d) \,/\, 10)$

$5.28 = \frac{d}{3} \times \frac{2}{0.50-d}$

2d = 5.28(1.5-3d)

2d = (7.92- 15.84d)

d = $\frac{7.92}{17.84}$, = 0.44 µg

Then, $\frac{0.44}{0.50} \times 100$ gives **88.79% extraction efficiency.**

(b) Three consecutive 5 mL portions:

First extraction:

$5.28 = \frac{d/5}{0.50-d/10}$

$5.28 = \frac{d}{5} \times \frac{10}{0.50-d}$

2d = 2.62 – 5.28d

d = 0.36 µg, so 0.137 µg of PCB remains.

Therefore, %PCB extracted after first extraction was $\frac{0.36}{0.50} \times 100$

= **73%**

Second extraction:

$5.28 = \frac{d/5}{0.137-d/10}$

$5.28 = \frac{d}{5} \times \frac{10}{0.137-d}$

2d = 0.723 – 5.28d

d = 0.099 µg, so 0.037 µg of PCB remains.

Therefore, %PCB extracted after second extraction was $\frac{0.363+0.0993}{0.50} \times 100$

= 92.47%

Third extraction:

$5.28 = \frac{d/5}{0.0373 - d/10}$

$5.28 = \frac{d}{5} \times \frac{10}{0.0373 - d}$

$2d = 0.1991 - 5.28d$

$d = 0.027$ µg, so 0.01 µg of PCB remains.

Therefore, %PCB extracted after third extraction was $\frac{0.36+0.099+0.027}{0.50} \times 100$

= 97.92%

One single extraction with 15 mL of DCM was found to be less effective compared to three-consecutive 5 mL portions for extraction. This process was repeated for all the PCB congeners used in this study with an aqueous solution containing an equal amount of PCB mixture of 0.5 µg/mL. The full results are shown in **Table** 3.4. It was observed that PCB 28 and 105 have the least percentage extraction efficiency for a single extraction. This could be attributed to the fact that PCB 28 has the least number of chlorine atoms attached to its phenyl ring together with its low K_d value compared to other PCBs which could encourage its water solubility. The low single extraction efficiency for PCB 105, which is penta-chloroCB with a higher degree of chlorination could possibly be attributed to its low K_d value however, its percentage recovery was high which may be possibly due to the higher number of chlorine atoms on it. Both PCB 52 and 77 are both tetra-chloroCBs. The slight increase in percentage recovery observed for PCB 77 could be due to its coplanarity, which allows for its free rotation and possibly could enhance its hydrophobicity as compared to PCB 52, which is di-ortho (having chlorine atoms on position 2 and 2'', which could prevent it attaining planarity (non-planar position). All the PCBs with more chlorine atoms such as PCB 101, 138, 153 and 180 were found to have high percentage extraction efficiencies and recoveries with DCM, which is a reflection of their hydrophobicity and higher K_d values which could enhance their affinity for a non-polar organic solvent such as DCM with less water solubility.

Table 3.4:

Percentage extraction efficiency and percentage recoveries for eight PCB congeners

PCB Congener	K_d values*	Three consecutive 5 mL portions of DCM, %			A single 15 mL DCM, %	Percentage recovery, %
		1st 5 mL	2nd 5 Ml	3rd 5 mL		
PCB 28	5.28	73.00	92.47	97.92	88.79	71.50
PCB 52	6.09	75.28	93.89	98.49	90.13	81.14
PCB 77	6.53	76.55	94.50	98.71	90.74	85.81
PCB 101	6.31	75.93	94.21	98.61	90.44	81.67
PCB 105	5.66	73.89	93.18	98.22	89.46	90.20
PCB 138	7.44	78.81	95.51	99.05	91.78	82.40
PCB 153	7.75	79.49	95.79	99.14	92.08	90.72
PCB 180	7.37	78.66	95.44	99.03	91.70	94.78

Note: Percentage obtained for 2nd extraction was the sum of 1st and 2nd 5 mL (10 mL) and the percentage obtained for 3rd extraction was the sum of 1st, 2nd and 3rd extractions of the whole 15 mL. *(ATSDR, 2000)

3.5.2 Determination of limits of detection (LOD) and limits of quantification (LOQ)

According to the International Union of Pure and Applied Chemistry (IUPAC) and American Chemical Society (ACS) LOD is the smallest or lowest amount of analyte that can be analytically detected with the reasonable analytical procedure, (Long and Winefordner, 1983). LOQ is the smallest concentration of an analyte in a sample which can be measured and reliably obtain results using a given analytical method (Shabir *et al*., 2007, Gibbons and Coleman, 2001).

The LOD/LOQ values were evaluated as described by Shrivastava and Gupta (2011) based on the equations of the triplicate calibration graphs.

$$\text{LOD} = 3 * \boldsymbol{Sm}/\boldsymbol{b} \qquad (3.9)$$

$$\text{LOQ} = 10 * \boldsymbol{Sm}/\boldsymbol{b} \qquad (3.10)$$

Where **Sm** is the standard deviation of the response and **b** is the mean of the slopes of the calibration curves.

Peak areas were plotted against six concentrations ranging between 0.125 µg/mL – 5 µg/mL. Each standard was analyzed in triplicate and three individual calibration graphs were plotted. The gradient and y-intercept were determined for each calibration graph (**Fig**. 3.3 a and b). In addition, from the straight-line equations, the standard deviation from the average intercept was determined. This standard deviation was used in **Eqs** 3.9 and 3.10 together with the average slope and intercept to determine the LODs and LOQs for each analyte.

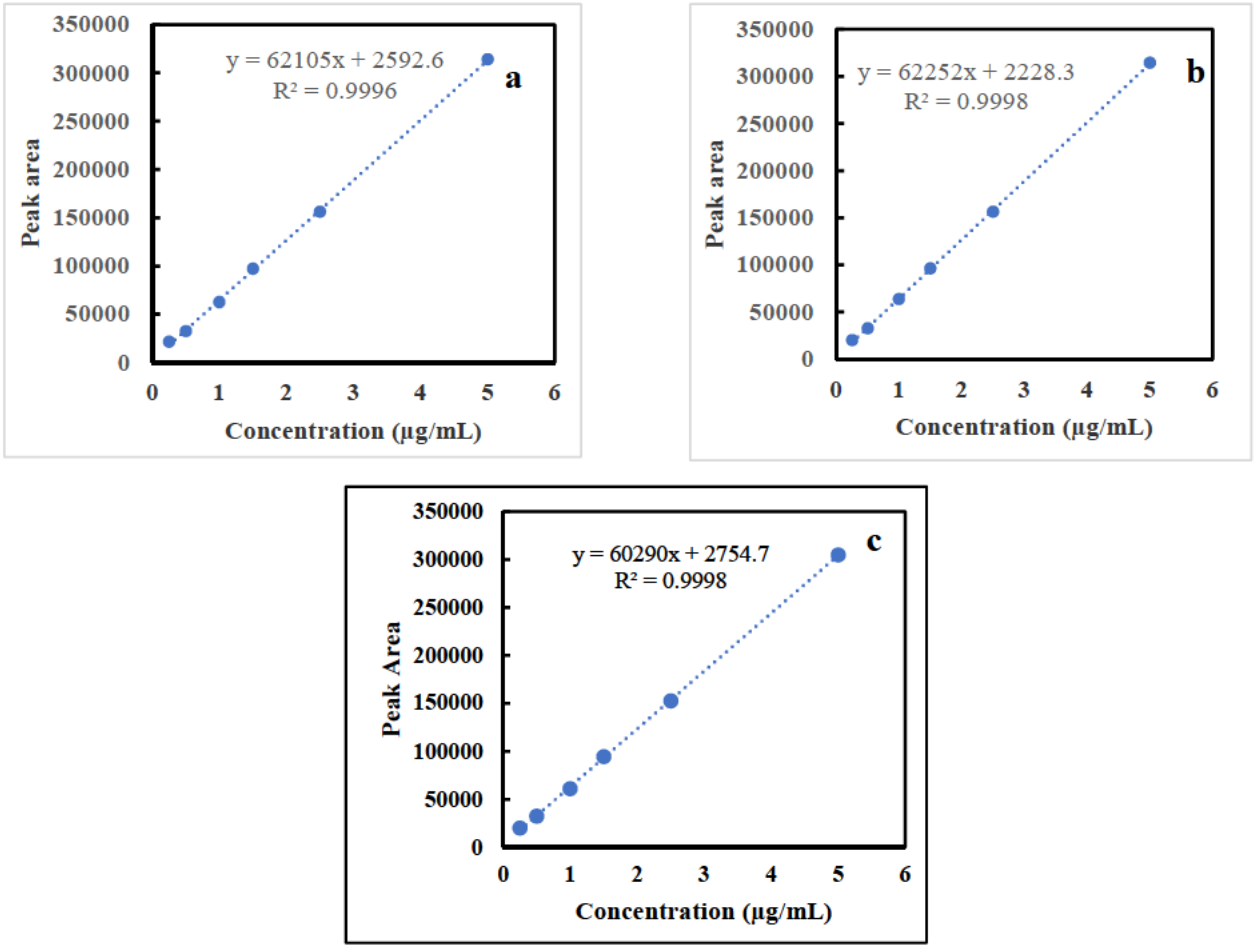


Figure 3.3: a and b Triplicate calibration curves for PCB 77

For example, the values for both standard deviation of the intercept (**Sm**) and mean of the slope (**b**) for the triplicate values were found to be 269.59 and 61549, respectively.

Average intercept = $2592.6 + 2228.3 + 2754.7 \div 3 = 2525.20$

Standard deviation = 269.59

Average slope = $62105 + 62252 + 60290 \div 3 = 61549$

LOD = $\frac{3 \times 269.59}{61549}$ = 0.013 µg/mL

LOQ = $\frac{10 \times 269.59}{61549}$ = 0.044 µg/mL

The average intercept and slope obtained for each analyte was used for the determination of the concentration of that analyte in the samples. However, the amount of water extracted was taken into consideration in order to evaluate the actual method detection and quantification limits of the sample as the value obtained from the calibration represents the instrument detection limit.

3.6 Batch adsorption experiments

The partitioning of the PCBs between the aqueous solution and the soil/sediment samples used in this research was conducted using the batch adsorption method as described in USEPA, 2000 (OECD 106, 107 methods) and Karickhoff *et al*. (1979). Briefly, a soil or sediment solution (porewater/distilled water) ratio of 1:10 containing 10% of 0.01 mol/L of $CaCl_2$ to minimize the CEC and as well as to enhance centrifugation was weighed into stainless-steel centrifuge tubes. The soil or sediment suspension was spiked with a known amount (0.5 µg/mL) mixture of eight selected PCB standards. The suspension was equilibrated on an orbital shaker manufactured by LABCOM at a speed of 350 rpm for a period of 24 h. A period of 24 h was selected based on the preliminary investigations performed on the partitioning of PCBs between aqueous solution and soil particle sizes, which lasted for 48 h. The outcome of the partitioning experiments revealed that a period of 24 h was sufficient for the class of selected PCB congeners to reach equilibrium. After equilibrium was reached, the aqueous solution was separated from the soil system using a centrifuge Rotofix 32 Hettick Zentrifugen, Germany at a speed of 6000 rpm for 30 min. The amount of PCBs remaining in the aqueous solution (supernatant after centrifugation) was extracted using 5 mL DCM, this was done three times, and all three aliquots (extracts) were combined. An

indirect method was used to evaluate the quantity of PCBs sorbed by the soil or sediment by subtracting the amount remaining in the aqueous solution at equilibrium from the amount spiked. To assess the level of external influences on the PCBs adsorption, a blank with the same amount of total volume of deionized water (10 mL) containing 10% of 0.01 mol/L $CaCl_2$ but without PCBs was subjected to the same experimental procedure. This was used to serve as a background check during the analysis and to ascertain that there were no interferences contributing to the results. All the experiments were carried out in duplicate. All the quality control steps such as determination of recovery, LODs and LOQs as well as matrix interferences were followed. The partition coefficient (K_d) and percentage sorption were determined using Eqs. (3.11) and (3.12), respectively. More details of the experimental procedure have been reported in chapter 4.

$$K_{\mathrm{d}} = \left(\frac{C_{\mathrm{o}} - C_{\mathrm{e}}}{C_{\mathrm{e}}}\right)\frac{V_0}{m} \qquad (3.11)$$

$$A_{\mathrm{ti}} = \frac{M_{\mathrm{s}}^{\mathrm{ads}}(t_i)}{M_{\mathrm{o}}} \times 100 \qquad (3.12)$$

where, K_d is the partition coefficient, C_o (mg/L) is the initial concentration, C_e (mg/L) is the aqueous concentration at the equilibrium, V_o (L) is the volume of the solution used and m (g) is the mass of the soil. M_o (mg) is the mass of the test substance in the test tube at the beginning of the experiment and was determined using the following expression: $M_o = V_o \cdot C_o$. M_s^{ads} (mg) is the mass of the test substance adsorbed onto the soil and was determined using the expression $M_{\mathrm{s}}^{\mathrm{ads}} = M_{\mathrm{o}} - C_{\mathrm{aq}}^{\mathrm{ads}} t_{\mathrm{i}} \cdot V_{\mathrm{o}}$, where t_i is time at equilibrium. $C_{\mathrm{aq}}^{\mathrm{ads}}\, at\, t_i$ is the concentration of the adsorbed substances in aqueous phase (mg/L) at time t_i (s) which is further used to determine the percentage adsorption of the PCBs onto the soil samples after the batch adsorption experiments.

3.6.1 Effect of time

Kinetic studies were carried out on the sorption of PCBs on soil for a period of 2 to 48 h of contact time while maintaining a constant initial PCB concentration (2.0 µg/mL), pH 6.5 and the quantity of soil sample (0.5 g). The pH of 6.5 was used for kinetic studies, this was based on the preliminary investigation on the effect of pH which showed that maximum adsorption of the selected PCBs

occurred near neutral pH. The data generated were used for the kinetic studies. Data generated were fitted into three kinetic models; pseudo first-order, pseudo second-order and intraparticle diffusion using equations 3.13, 3.14 and 3.15, respectively (Weber and Morris, 1963; Atkins and Paula, 2006). Details are discussed in chapter 4.

$$\text{Pseudo first-order} = \log(q_e - q_t) = \frac{k_1}{2.303} t \qquad (3.13)$$

A plot of log (q_e-q_t) against t (h) gave a graph (**Fig.** 3.4) which was used to determine the mechanism of PCB 28 sorption onto the soil. Below are examples of the kinetic fittings obtained for PCB 28.

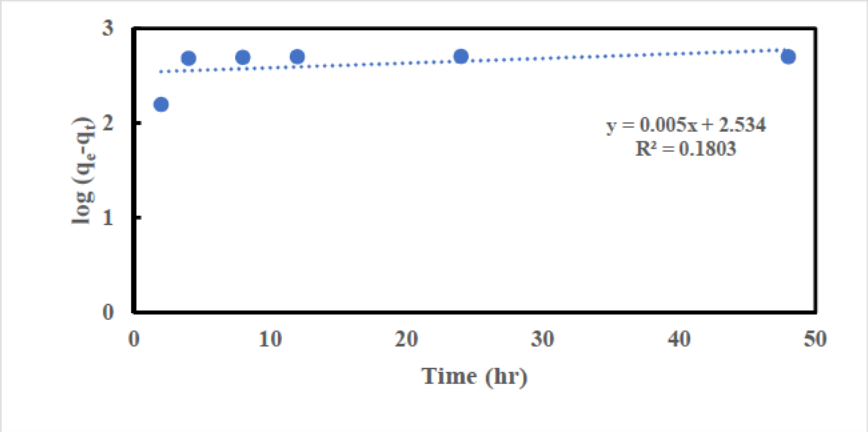


Figure 3.4: Pseudo-first-order fitting for PCB 28

The rate constant of adsorption (k_1) was evaluated by multiplying the slope (0.005) obtained from the plot by 2.303 and q_e^{cal} was obtained from the intercept.

$k_1 = 0.005 \times 2.303 = 0.0115$

$q_e^{cal} = 2.534$, $R^2 = 0.18$

$$\text{Pseudo-second-order} = \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3.14)$$

The plot of t/q_e *versus* time (h) gave a linear graph (**Fig.** 3.5) where q_e^{cal} was obtained from the inverse of the slope and the sorption rate constant k_2 was obtained from the intercept

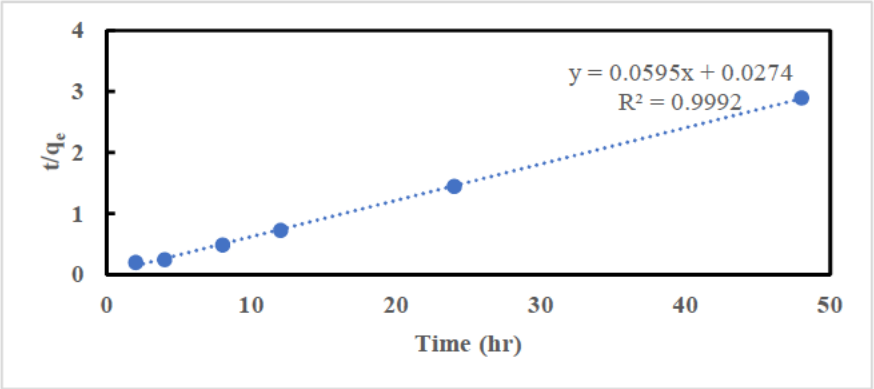


Figure 3.5: Pseudo-second-order fitting for PCB 28

$q_e^{cal} = \frac{1}{0.0595} = 16.801$ mg/g

$k_1 = 0.0274$ and R^2 value is 0.9992

Intraparticle diffusion $q_t = k_{id}\, t^{\frac{1}{2}} + C$ (3.15)

Plotting q_t against $t^{½}$ gave two different straight-line regions, which did not pass through the origin. The rate constants of intraparticle diffusion (k_{id}) and the thickness of the boundary layer C were determined from the slope and intercept of the graph, respectively.

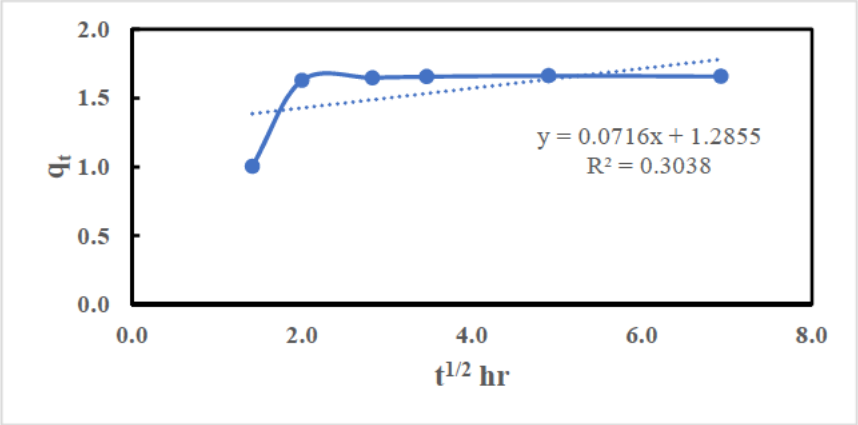


Figure 3.6: Intraparticle diffusion fitting for PCB 28

The rate constants of intraparticle diffusion (k_{id}) = 0.0716

The thickness of the boundary layer C = 1.286, where R^2 = 0.304

3.6.2 Effect of pH

The details of the method are described in chapters 4 and 5. The pH values for 0.01 mol/L of $CaCl_2$ solution were kept at 4.5, 6.5, 7.5, 8.5 and 10. The pH range was selected based on previous results obtained from studies on the uMngeni River (Adeyinka, 2014). Also, a 10 mL aliquot of humic acid (HA) solution (at pH of 12.5) was conditioned with the appropriate amount of 0.1 M HNO_3/NaOH to adjust the pH between 2.5 to 10.5 using a pH meter (HI 9321 Microprocessor pH/*mVi* °C meter pH: 0.00-14.00 Hanna instruments, Portugal). After the desired pH was reached the soil sample was added to the adsorbate solution.

3.6.2 Effect of ionic strength

Briefly, the effect of ionic strength on PCB adsorption was studied using varying concentrations of KCl ranging from 0.0 to 1.0 mol/L prepared in double-distilled water. This was carried out to determine the role of the electrostatic attraction in the adsorption between the non-polar PCBs and soil organic matter in this study. The details are described in chapter 4.

3.6.3 Effect of humic acid concentration

Effect of initial HA concentration on the sorption of PCBs onto the soils was performed by preparing different HA concentrations, ranging from 0 – 50 µg/mL in 0.01 M $CaCl_2$ (background electrolyte) to enhance centrifugation and minimize changes in the ionic strength during the sorption process. A soil solution ratio of 1:10 was used for this experiment. Details are described in chapter 5.

3.6.4 Effect of temperature

The temperature dependence of PCB sorption onto the soils was investigated at five different temperatures of 283, 393, 398, 303 and 313 K using batch adsorption experiments. The temperature ranges were chosen to mimic the environmental conditions such as varying South African weather conditions during winter, spring, summer and autumn. The details are described in chapters 4 and 5. The initial PCB concentration was kept at 2.0 µg/g with the adsorbate solution pH maintained at 6.5. The quantity of soil samples used in this research was kept constant at 0.5 g. The data obtained from this parameter were used for the thermodynamic studies such as Gibbs free energy of the system (ΔG^{o}), enthalpy change (ΔH^{o}), and entropy change (ΔS^{o}) using equations 3.16 and 3.17, respectively.

$$\Delta G^{\circ} = -RT\ln K_{d} \qquad (3.16)$$

$$\ln K_{d} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \qquad (3.17)$$

Partition coefficient (K_d) for the PCB congeners under investigation in this research was evaluated after a sorption equilibration period of 24 h using equation 3.11. A plot of ln K_d *versus* the inverse of temperature (1/T) (**Fig.** 3.7) together with equations 3.16 and 3.17 were used to determine the values of ΔG^{o}, ΔH^{o}, and ΔS^{o}, respectively.

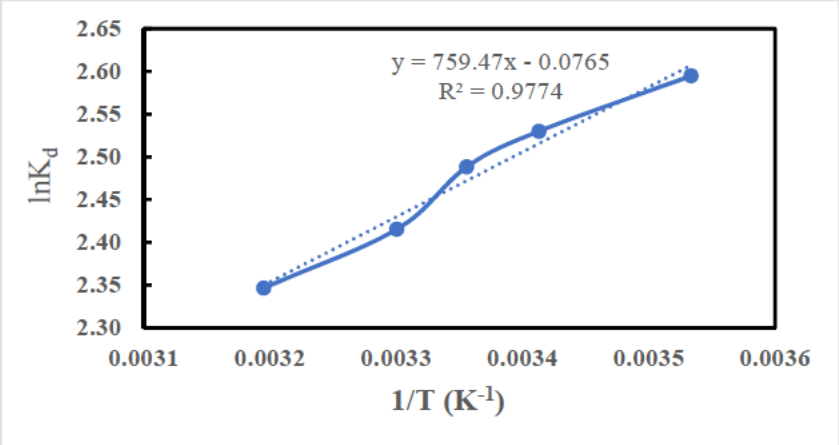


Figure 3.7: Thermodynamic plot of ln K_d *vs* 1/T for PCB 28

Gibbs free energy change of the sorption (ΔG^o) was obtained using equation 3.16 at different solution temperatures where the ideal gas constant (R) is 8.314 (J/(mol·K).

At a temperature of 283 K, the value of ln K_d was 2.59

Then $\Delta G° = -8.314 \times 283 \times 2.595 \div 1000$, gives -6.11 KJ/mol

At 293 K $\Delta G° = -8.314 \times 293 \times 2.530 \div 1000$, gives -6.16 KJ/mol

At 298 K $\Delta G° = -8.314 \times 298 \times 2.488 \div 1000$, gives -6.16 KJ/mol

At 303 K $\Delta G° = -8.314 \times 303 \times 2.415 \div 1000$, gives -5.98 KJ/mol

At 313 $\Delta G° = -8.314 \times 313 \times 2.346 \div 1000$, gives -6.11 KJ/mol

Enthalpy change of the system (ΔH^o) was evaluated as $-slope \times R \div 1000$

Thus, $\Delta H^o = -759.47 \times 8.314 \div 1000$ = -6.31 kJ/mol

Entropy change of the system (ΔS^o) was obtained from $intercept \times R$

Thus, (ΔS^o) = -0.0765×8.314 = -0.64 J/mol.K

The details on the interpretation of the results are discussed in chapter 4.

3.6.5 Effect of initial PCB concentrations

The effect of initial PCB concentrations at 0.5, 1.0, 1.5, 2.0 and 2.5 mg/L were used to investigate the sorption of PCBs between an aqueous solution of HA onto soil with pH of adsorbate solution adjusted to 6.8. Experimental data obtained were used to evaluate the sorption isotherm using equation 3.18 and 3.19, respectively. Details are discussed in chapter 5.

Langmuir $\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b}$ (3.18)

Freundlich $lnq_e = lnK_f + \frac{1}{n} lnC_e$ (3.19)

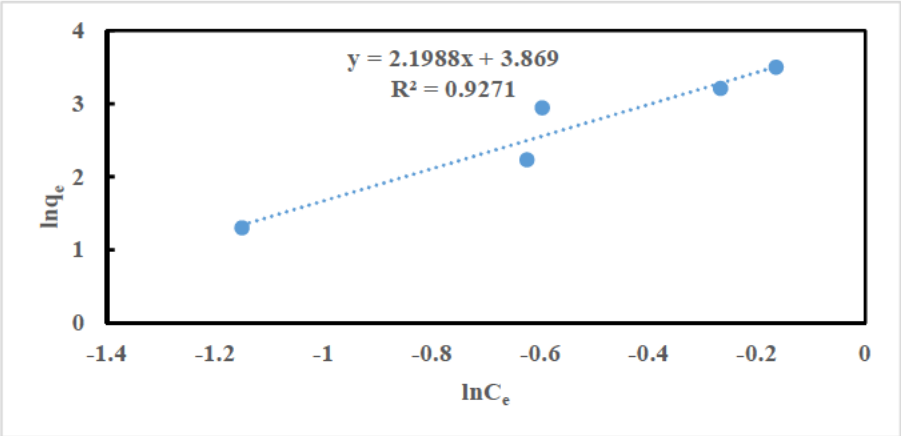


Figure 3.8: Freundlich isotherm plot for PCB 105

REFERENCES

Adeyinka, G. C., (2014). The determination of organochlorinated pesticides and polychlorinated biphenyls in sediment, soil and water of the Msunduzi River, KwaZulu-Natal, South Africa. MSc thesis. University of KwaZulu-Natal, Westville, South Africa.

Atkins, P. W., and De Paula, J., (2006). Physical Chemistry for the life Sciences. W.H. Freeman and Company.

Chan, K.Y., Bowman, A., Oates, A., (2001). Oxidizable organic carbon fractions and soil quality changes in an oxic paleustalf under different pasture leys. *Soil Science.* **166**: 61-67.

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

Gibbons, R. D., and Coleman, D. E., (2001). Statistical methods for detection and quantification of environmental contamination, Canada, John Wiley & Sons. pp 385.

Gillman, G. P., and Sumpter, E. A., (1986). Modification to the compulsive exchange method for measuring exchange characteristics of soils. *Aust. J. Soil Res*. **24**: 61–66.

Hendershot, W.H., and Duguette, M., (1986). A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* 50, 605-608.

Long, G. L., and Winefordner, J. D., (1983). Limit of detection: A closer look at the IUPAC Available from http://nsgl.gso.uri.edu/wiscu/wiscuw85001/wiscuw85001_part5.pdf. *Accessed* 14/04/2018.

Nelson, D.W and Sommers L. E., (1996). Total carbon, organic carbon, and organic matter. In: Methods of Soil Analysis, in Part 2, (A.L. Page et al.). Am. Soc. of Agron. Inc. Madison, Wisconsin. Agronomy. (2nd ed) **9**: 961-1010.

Shabir, G. A., Lough, W. J., Arain, S. A., Bradshaw, T. K., (2007). Evaluation and application of best practice in analytical method validation. *J. Liq. Chromatogr. Relat. Technol*. **30**: 311–333.

Sánchez-Monedero, M. A., Roig, A., Martínez-Pardo, C., Cegarra, J., Paredes, C., (1996). A microanalysis method for determining total organic carbon in extracts of humic substances. Relationships between total organic carbon and oxidable carbon.

Bioresour. Technol. **57**: 291-295.

Schumacher, B. A., (2002). Methods for the determination of total organic carbon (TOC) in soils and sediments. Las Vegas, ERASC.

Shrivastava, A., and Gupta, V. B., (2011). Method for the detection of limit of detection and limit of quantification of the analytical methods. *J. Chronicles of Young Scientists*. **2**, (1): 21-25.

Tiessen, H., and Moir, J. O., (1993). Total and organic carbon. In: Soil Sampling and Methods of Analysis, M.E. Carter, (Ed.) Lewis Publishers, Ann Arbor, Michigan. pp 187-2 11.

US EPA (United State Environmental Protection Agency), (2000). Organization for Economic Corporation and Development (OECD 106) Guideline for the testing of chemicals. Availablehttps://archive.epa.gov/scipoly/sap/meetings/web/pdf/106_adsorption_desorption_using.pdf. *Accessed* 20/07/2016.

Walkley, A., and Black, I. A., (1934). An examination of the Degtjareff method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science*. **63**: 251-263.

Weber, W. J., and Morris, J. C., (1963). Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng*. **89**: 31–60.

You, S-J., Yin, Y., Allen, H. E., (1999). Partitioning of organic matter in soils: effects of pH and water/solution ratio. *Sci. Total Environ*. **227**: 155-160.

RESULTS AND DISCUSSION

CHAPTER 4

MANUSCRIPT 1

Kinetic and thermodynamic studies on partitioning of polychlorinated biphenyls (PCBs) between aqueous solution and modeled individual soil particle grain sizes

Gbadebo Clement Adeyinka[1], Brenda Moodley[1,*]

School of Chemistry and Physics, College of Agriculture, Engineering and Sciences, University of KwaZulu-Natal, Private Bag X54001, Westville, 4000, Durban, South Africa. E-mail: adeyinkagbadebo78.ga@gmail.com

*Corresponding author; e-mail: Moodleyb3@ukzn.ac.za. Tel: +27 31 260 2796; Fax: + 27 31 2603091

ABSTRACT

The significance of soil mineral properties and the environmental secondary conditions such as pH, temperature, ionic strength and time on the partitioning of eight selected polychlorinated biphenyl (PCB) congeners between aqueous solution and different soil particle grain sizes were studied. The mineral properties of a model soil sample were determined and Brunauer-Emmet-Teller (BET) adsorption-desorption isotherm was employed to observe the surface characteristics of the modeled individual soil particle sizes. Batch adsorption experiments were conducted to determine the sorption of PCBs onto soil particle sizes. The results revealed that the sorption of PCB congeners onto the soil was dependent on the amount of soil organic matter, surface area, and pore size distribution of the various individual soil particle sizes. Low pH favoured the sorption of PCBs with maximum sorption occurring between pH 6.5-7.5 with an equilibration period of 8 h. Changes in the concentrations of ionic strength were found to be less significant. Low temperature favoured the sorption of PCBs onto the soil compared to high temperatures. Thermodynamic studies showed that the partition coefficient (K_d) decreased with an increase in temperature and negative and low values of $\Delta H°$ indicated an exothermic and physiosorption process. The data generated is critical and will help to further understand the remediation and cleanup strategy for polluted water.

Keywords: Partitioning, PCBs, Soil particle grain sizes, Kinetics, Thermodynamic studies, pH

4.1 Introduction

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) are one of the dirty dozen chemicals listed under the Stockholm Convention (SC) on POPs, which are of global concern due to their potential for long-range transport and persistence in the environment. They are also able to bio-accumulate and bio-magnify in ecosystems, as well as have significant negative effects on human health and the environment (Muir *et al*., 1996; UNEP, 2013). PCBs have low water solubility ranging between $1.2 \times 10^2 – 4.83 \times 10^6$ ng/L but are freely soluble in non-polar solvents such as oils and biological lipids. Due to the hydrophobic character of PCBs, they tend to partition onto suspended particulate matter (SPM) in the water, soil organic matter (SOM) as well as fatty tissue of animals (Shiu and Mackay, 1986; Buckley-Golder, 1999; Ericson, 20011; ATSDR, 2000; IPCS, 2003). The distribution of organic pollutants (OPs), such as PCBs, in environmental media, is mainly controlled by sorption-desorption processes. The sorption of OPs in the environment depends mainly on factors such as sorbate characteristics; hydrophobicity, polarity, aqueous solubility and nature of functional groups present, as well as the size of the molecule (Belfort, 1984; Rao and Asolekar, 2001). Other important factors that affect partitioning include the amount of organic matter present in the soil itself, the surface area of the soil particle sizes, pore size distribution in the soil, and mineral content. Physicochemical parameters of the solution that also play a key role in the sorption and mobility of the pollutants are solution pH, temperature of the solution, and the ionic strength (Belfort, 1984; Rao and Asolekar, 2001).

Hydrophobic organic contaminants such as PCBs, are commonly associated with the soil organic matter (SOM) and other environmental physicochemical parameters such as pH, temperature and ionic strength (Frankki *et al*., 2006; Hiller *et al*., 2008; Persson *et al*., 2008; Badea *et al*., 2014; Qi *et al*., 2014). Badea *et al*. (2014) noted that the leachability of PCBs positively correlated with an increase in total organic content (TOC) in leachates and was pH dependent, especially low pH. Hiller *et al*. (2008) examined the effect of temperature on the distribution of polycyclic aromatic hydrocarbons (PAHs) on the soil and sediment of eastern Slovakia. Their study found that the sorption of PAHs onto the soil increased with an increase in the SOM content, and positively correlated with low solution temperature. Wang *et al*. (2001) reported the distribution and partitioning of PAHs onto the different soil grain size fractions in sediments from Boston Harbor. The author noted that the highest concentration of PAHs was found in the larger soil fractions

while fine silt and clay fractions were reported to contain relatively low PAH concentrations. Pesticides and testosterone sorption/desorption studies have been investigated on soil particle sizes with the results revealing that contaminants were more associated with smaller soil particle sizes thus leading to higher sorption capacity and lower desorption rate (Wang and Keller, 2008; Qi *et al.,* 2014). Vilanova *et al*. (2001) also reported the role of dissolved particulates on the phase distribution of seven selected PCB congeners in the waters of a high mountain lake in Catalonia, Spain. Lower temperatures and hydrophobicity were reported to favour higher association of PCBs with the particulate phase. Remobilization, volatilization, influence of colloids on sediment-water, partition coefficients and partitioning of PCB congeners in water and in seawater have been investigated but again only on a mixture of soil grain sizes and not on individual grain sizes (Baker *et al*., 1986; Bergen et al., 1993; Achman *et al*., 1993; Gdaniec-Pietryka *et al*., 2013). Studying the effects on individual particle grain sizes is important because the bulk of the soil sample may not provide comprehensive information on the contribution of each soil particle grain size and their significant role in the mobility and sorption of the OPs. Currently, there is no information available on the role of individual soil particle grain sizes and their surface characteristics, on the partitioning of PCBs in environmental media. To the best of our knowledge, there has been no reports of kinetic and thermodynamic studies carried out on natural soil partitioning studies, which this paper presents. Furthermore, this is the first study reported on South African soil taken from a sub-tropical climate, which has a different soil mineralogy and characteristics.

The objectives of this current study were to: (1) characterize soil particle grain sizes in a soil sample collected from the uMngeni River (Latitude 29°48'41" and Longitude 31°02'12"); (2) investigate the effect of soil characteristics such as organic matter content, surface area and pore size distribution of individual soil grain sizes on the partitioning of selected PCBs; (3) determine the effect of physicochemical parameters such as time, pH and ionic strength as well as the temperature of the solution on the partitioning of six selected indicator PCBs and two dioxin-like PCB congeners between aqueous solution and individual soil particle grain sizes. The selected PCB congeners, as shown in **Fig.** 4.1, are among the top priority congeners frequently investigated in environmental media as recommended by the SC on POPs and partitioning studies of these PCBs will provide valuable information on their transportation and remediation strategies in water systems.

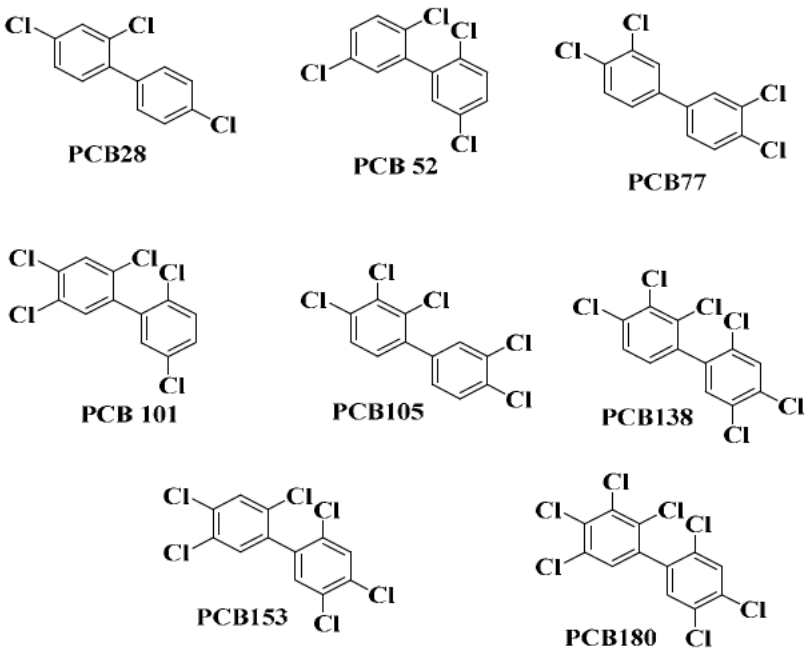


Figure 4.1: Structures of PCB congeners (Created - Used Chem Office 2015 version)

4.2 Materials and methods

4.2.1 Modeled soil

The soil used in this research was obtained from the Blue Lagoon site, which is the mouth of the uMngeni River, a major river in the province of KwaZulu-Natal, South Africa. This soil was chosen to serve as a model soil sample based on composition and physicochemical properties and to mimic the environmental effect of sample matrices such as TOC, SOM and cation exchange capacity (CEC) along the uMngeni River of KwaZulu-Natal of South Africa. The effect of physicochemical properties such as temperature, pH and ionic strength were investigated on the modeled soil sample. The soil was first separated into five particle grain sizes of 75, 100, 200, 300 and 425 µm using a mechanical sieve method. The soil grain sizes of 75, 100, 200, 300 and 425 µm were chosen in this study to represent different soil particle sizes such as clay, silt, fine sand, medium sand and coarse sand, respectively (USEPA, 2008). Each fraction of soil particle size was extracted in triplicate using both *n*-hexane and dichloromethane as well as methanol to remove the targeted OPs of interest (PCBs), leaving behind a soil sample free of PCBs that was used as a

model soil sample. To ascertain that the soil samples used for the batch adsorption experiments were free of PCBs, the extracted soils were re-extracted and the extract analysed using GC-MS in SIM mode (Shimadzu, Japan). The chromatograms were found to contain no traces of PCB peaks as compared to the standards.

4.2.2 Soil characterization

The specific surface areas, pore volumes and pore size distributions of each soil fraction were measured using the Brunauer-Emmet-Teller (BET) method with initial degassing temperature set at 90°C for 2 h and raised to 200°C and held at that temperature for a further 6 h under vacuum. The results were obtained through N_2 adsorption-desorption at 77.35 K using TriStar II 3020, Autosorb Automated gas sorption system analyzer (2012 surface area and porosity Micrometritics, USA).

The functional groups of each fraction of soil particle grain size were determined using fourier transform infrared spectroscopy (FTIR) (Precisely spectrum 100 Perkin Elmer, USA).
The experimental procedure for the determination of the soil organic matter using the Walkley Black Method and the cation exchange capacity are described in chapter 3 (**Section** 3.3.2.1 and 3.3.2.2).

4.2.3 Reagents and chemicals

All reagents and chemicals were of HPLC/analytical-grade and the eight-selected PCB standards were purchased from Sigma Aldrich^R (South Africa). The mixtures of PCB standard stock solutions of 50 µg/mL were prepared using *n*-hexane and stored in the refrigerator at 4°C. The lower working concentrations for the PCB standards were prepared by appropriate dilution in *n*-hexane. All the solvents were purchased from Capital Labs, South Africa. Potassium chloride was purchased from Merck South Africa, both calcium chloride 4-8 mesh and magnesium chloride were purchased from B/M Scientific South Africa. Aluminium chloride hexahydrate was obtained from Saarchem Ltd. South Africa. Barium chloride was purchased from Associated Chemicals and diammonium iron (II) sulfate 6-hydrate was purchased from BDH laboratory England. Ammonium ferrous sulfate hexahydrate CP was supplied by research-lab Fine Chem. Industries (Mumbai, India) and

barium diphenylamine sulfonate was purchased from General Chemical and Pharmaceutical Ltd., Sudbury. Reagent grade sulfuric acid (specific gravity 1.84, Promark Chemicals) was used for acidification. All the glassware was baked in the oven at approximately 130°C prior to use.

4.2.4 Batch adsorption experiments

The batch sorption method was used to evaluate the partitioning of the PCBs between aqueous solution and the soil fractions in this research as described by USEPA, 2000 (OECD 106, 107 methods) and Karickhoff *et al*. (1979). A 1 g sample of each model soil fraction was weighed into a stainless steel centrifuge tube together with a 10 mL aliquot of 0.01 mol/L $CaCl_2$, added to minimize the CEC and to improve centrifugation. The soil solution was spiked with 0.5 µg/mL of the PCB mixture and equilibrated for 24 h using an orbital shaker LABCOM at 350 rpm to allow for partitioning of the PCBs to the soil particles. An equilibration period of 24 h was chosen in this study after preliminary studies using mixtures of soil particle sizes lasting up to 48 h showed that such a period was adequate to achieve sorption equilibrium of PCBs between aqueous solution and soil. The soil suspension was separated by centrifugation at 6000 rpm for 30 min (Rotofix 32A Hettick Zentrifugen, Germany). The indirect method was used to determine the amount of PCBs that remained in the aqueous phase by extraction of the decanted aqueous solution. This was done three times using 5 mL DCM aliquots each time. The amount of PCBs sorbed (partitioned) onto the soil particles were evaluated as the difference between the amount of PCB spiked (initial concentration) in the solution and the amount remaining in the aqueous phase after centrifuging. To evaluate the stability and recovery as well as possible adsorption of the PCBs on the surface of the test vessel, a control sample with the same concentration of PCBs in 0.01 mol/L $CaCl_2$ but without soil was subjected to the exact same steps as described above. In addition, a blank run per soil fraction with the same amount of soil and total volume of 10 mL of 0.01 mol/L $CaCl_2$ solution but without PCBs was subjected to the same experimental procedure. This was used to serve as a background check during the analysis and to ascertain that there were no interferences or soil contamination affecting the results. All the experiments were carried out in duplicate. The partition coefficient (K_d) and percentage sorption were determined using Eqs. (4.1) and (4.2), respectively.

$$K_d = \left(\frac{C_o - C_e}{C_e}\right)\frac{V_0}{m} \qquad (4.1)$$

$$A_{\mathrm{ti}} = \frac{M_{\mathrm{s}}^{\mathrm{ads}}(t_i)}{M_{\mathrm{o}}} \times 100 \quad (4.2)$$

where, K_{d} is the partition coefficient, C_{o} (mg/L) is the initial concentration, C_{e} (mg/L) is the aqueous concentration at equilibrium, V_{o} (L) is the volume of the solution used and m (g) is the mass of the soil. M_{o} (mg) is the mass of the test substance in the test tube at the beginning of the experiment and was determined using the following expression: $M_o = V_o \cdot C_o$. $M_{\mathrm{s}}^{\mathrm{ads}}$ (mg) is the mass of the test substance adsorbed onto the soil and was determined using the expression $M_{\mathrm{s}}^{\mathrm{ads}} = M_{\mathrm{o}} - C_{\mathrm{aq}}^{\mathrm{ads}} t_{\mathrm{i}} \cdot V_{\mathrm{o}}$, where t_i is time at equilibrium and $C_{\mathrm{aq}}^{\mathrm{ads}} = C_e \cdot t_i$. A_{ti} (%) is the percentage adsorption.

4.2.5 Effect of ionic strength

The effect of ionic strength on the partitioning of PCBs between the aqueous solution and soil particle grain size was investigated, with KCl used as the electrolyte. The effect was investigated at varying concentrations of KCl ranging from 0.0 to 1.0 mol/L prepared in double distilled water. Approximately 1 g model soil sample of each soil fraction was weighed into the centrifuge tube together with 10 mL aqueous electrolyte solution of different concentrations. The mixture was spiked with the 0.5 µg/mL mixture of PCB standards. The suspensions were equilibrated for 48 h using a shaker at 350 rpm, and centrifuged at 6000 rpm for 30 min. The supernatant was decanted and extracted three times with 5 mL aliquots of DCM each time. The extracts were evaporated to dryness and reconstituted to 1 mL prior to GC-MS analysis. The percentage sorption of PCBs was evaluated using Eq. (4.2).

4.2.6 Effect of pH

The pH value of 0.01 mol/L of $CaCl_2$ solution was adjusted to 4.5, 6.5, 7.5, 8.5 and 10 based on previous research on water environmental conditions (Adeyinka, 2014) by adding 0.1 mol/L NaOH or 0.1 mol/L HNO_3 (You *et al*., 1999; Burton *et al*., 2004). The effect of pH on the sorption capacity of PCBs between water and soil particle sizes was studied using a pH meter (HI 9321 Microprocessor pH/*mVi* °C meter pH: 0.00-14.00 Hanna instruments, Portugal). Batch experiments were carried out as described above to determine the PCB concentrations sorbed onto the soil particle grain sizes.

4.2.7 Effect of temperature

The effect of temperature on the sorption experiments were carried out using the batch method according to the following procedure. A sample of soil (1 g): 0.01 mol/L $CaCl_2$ solution (10 mL) (1:10) was spiked with 500 µL mixture of PCB standards resulting in a final concentration of 0.5 µg/mL. $CaCl_2$ served as the background electrolyte. Batch samples were equilibrated on the temperature controlled rotating shaker (Model number 204 Protea, South Africa) between 10 and 40°C. After equilibration, the suspension was separated by centrifugation at 6000 rpm for 30 min. The supernatant was decanted and extracted three times using liquid-liquid extraction with 5 mL aliquots of DCM each time. The extracts were combined and evaporated to dryness and reconstituted to 1 mL prior to GC-MS analysis.

The thermodynamic parameters were evaluated using **Eqs**. (4.3) and (4.4):

$$\Delta G^\circ = -RT\ln K_\mathrm{d} \qquad (4.3)$$

$$\ln K_\mathrm{d} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (4.4)$$

where, ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° (kJ/(mol.K))are Gibbs free energy change, enthalpy change, and entropy change in the sorption process, respectively; T (K) is the temperature and R (J/(mol·K)) is the ideal gas constant.

A plot of 1/T (K^{-1}) *versus* ln K_d was used to obtain the Gibbs free energy of the system while Van't Hoff (equation 4.4) was used to determine the magnitude of the observed enthalpy change (ΔH°) and entropy (ΔS°) of the adsorption from the slope and y-intercept of the graph, respectively.

4.2.8 GC-MS analysis

Sample extracts were reconstituted and analyzed using gas chromatography-mass spectrometry (GC-MS) (QP-2010 Ultra Shimadzu, Japan), with a DB-5MS capillary column of length 30 m (0.25 µm internal diameter and 0.25 µm film thickness) in SIM mode. Helium was the carrier gas with a flow rate of 0.72 mL/min and a total flow of 31.8 mL/sec, a linear velocity of 32.2 cm/s at

purge flow of 3.0 mL/min. The injection port and detector temperatures were set at 220 and 320°C, respectively. The oven temperature was set at 150°C and held for 2 min, ramped to 295°C at 14°C/min and held for a further 2 min. A 1 µL injection volume using splitless injection mode was used. All the quality control steps were followed. Percentage recovery as well as background interference checking were carried out as discussed in the batch adsorption experiments. Standards were running intermittently between samples to monitor changes in the instrument's sensitivity. An external calibration method was used for the quantification of 8 PCB congeners based on the peak areas of the targeted compounds. Analytes were identified by comparing their retention times with those of the PCB standards. The efficiency of the batch adsorption method was checked for any possible PCB adsorption on the surface of the test vessel and the percentage recoveries were found to be 81.14% – 94.78%.

4.3 Results and discussion

4.3.1 Soil characterization

4.3.1.1 FTIR characteristics of the soil particle grain sizes

Fig. 4.2 shows the FTIR spectra of the different soil particle grain sizes. The spectra shows a broad peak at 3363-3650 cm^{-1}, which is attributed to the free hydroxyl groups of the alcohol/phenolic group or probably a substituted amino group. The broad peak was clearly visible in the soil particle size of 75 µm but gradually disappeared in the soil particle sizes of 100 µm and greater. The reduction in this characteristic peak with increasing grain size is possibly due to the higher C/N ratio observed in the larger soil particle grain sizes, which has resulted from the gradual loss in the nitrogen-rich proteinaceous organic matter content as the grain size increased. Other notable peaks were absorption bands of 1637 and 1419 cm^{-1} in the soil particle size of 75 µm but much smaller in the 100 µm soil grain size. The peak at 1637 cm^{-1} could be indicative of aliphatic nitro compounds (N-H stretching) or carboxylates (C=O stretching). The absorption band at 1419 cm^{-1} could be attributed to aliphatic C-H deformation or O-H bending vibration of carboxylic groups or C-O stretching of phenolic OH as noted by Guo *et al*. (2012). There is a prominent peak at 999-1031 cm^{-1} common to all the soil particle grain sizes, which is due to Si-O vibrations of clay impurities or possibly C-O stretching of polysaccharides from the humic substances in the soil samples (Rivero *et al*., 1998; Shin *et al*., 1999; Li *et al*., 2005; Liying *et al*., 2009).

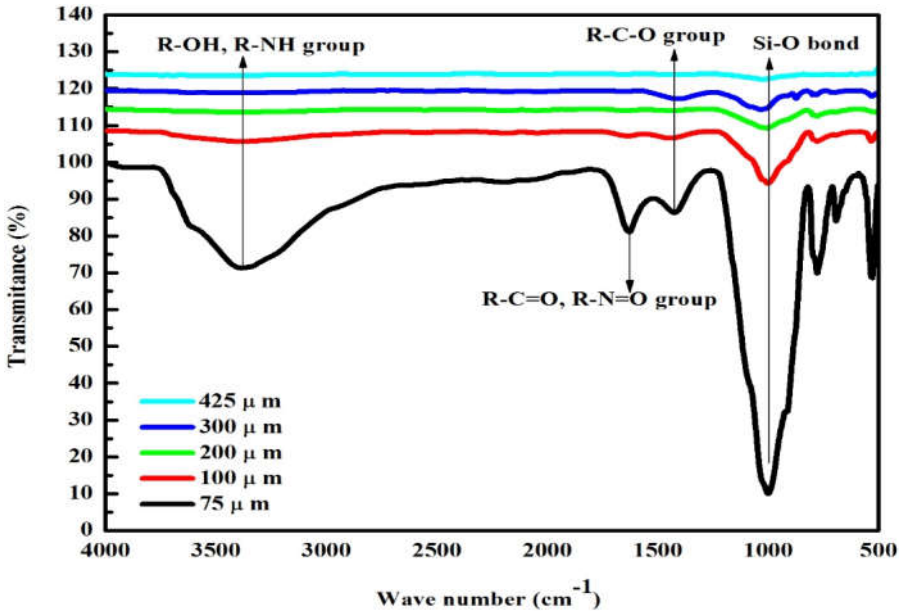


Figure 4.2: FTIR spectra of different soil particle grain sizes

Table 4.1:

Soil physicochemical parameters and N_2 adsorption-desorption isotherms

Soil grain size, µm	TOC, mg/g		SOM, mg/g	C/N ratio		CEC, Meq/100 g	S-BET, m^2/g	Pore size, nm	Pore volume, cm^3/g
	A	B		A	B				
75	4.02±0.23	0.92±0.02	11.92±0.69	14.43±1.13	17.62±1.32	7.90±0.02	13.36	10.64	0.035
100	2.14±0.08	0.87±0.17	6.35±0.24	19.94±0.36	21.30±0.88	5.02±0.00	3.89	11.73	0.010
200	1.64±0.23	0.84±0.04	4.86±0.69	23.75±1.24	25.30±1.46	3.46±0.01	1.51	19.65	0.005
300	1.70±0.11	0.84±0.15	5.07±0.34	24.99±1.47	27.06±1.22	1.71±0.01	1.20	9.79	0.004
425	1.42±0.01	0.74±0.01	4.22±0.28	27.49±1.53	26.52±1.34	1.34±0.00	0.88	12.83	0.003

All analyses were carried out in triplicate except for C/N analyses, which was carried out in duplicate.

A: sample before organic carbon was removed. B: sample after the removal of the organic carbon content at 440°C.

TOC: total organic carbon, SOM: soil organic matter, CEC: cation exchange capacity.

The physicochemical parameters and N_2 adsorption-desorption isotherms are shown in **Table** 4.1. TOC and SOM content were found to be highest for soil particle size 75 µm with a mean triplicate

analyses of (4.02±0.23) mg/g and (11.92±0.69) mg/g, respectively as determined by the wet oxidation method. Coarser soil particle sizes were found to have the least values for both TOC and SOM in the range of 1.42 - 1.70 mg/g and 4.22 - 5.07 mg/g, respectively. The ratio of carbon to nitrogen (C/N) ratio revealed that larger particle sizes had a higher carbon *versus* nitrogen content compared to the smaller soil grain size of 75 µm. In addition, the corresponding C/N ratio after the OC was removed was found to be again higher in the larger particle size fractions compared to the smaller soil particle sizes.

The cation exchange capacities of the different soil particle sizes were in the range of (1.34±0.00) to (7.90±0.02) Meq/100 g. The CEC of a soil depends largely on the available SOM in the soil, which is responsible for the charge of the soil (CUCE, 2007). Thus, the higher CEC for the smaller particle grain sizes confirmed the higher OM present in the smaller particle sizes. Soil made up of pure silica and oxygen (quartz) will result in a soil material with no charge thereby leading to low or no CEC in the soil (CUCE, 2007). Pore size distributions of the various soil particle sizes in this work were 9.79-19.65 nm indicating the mesoporous nature of the soil grain sizes (2-50 nm for mesoporous material) and a type IV isotherm with the higher surface area was found for the smaller soil grain size.

4.3.2 Sorption capacity

The higher sorption capacity of the smaller soil particle sizes, 75 and 100 µm, in this study for the PCB congeners (**Fig.** 4.3 a and b) could be attributed to the higher surface area, TOC, SOM and higher CEC as well as pore size distribution (**Error! Reference source not found.**). There was also a sharp decrease in the sorption capacity of approximately 70% to 28% between soil particle size 200 to 300 µm and a subsequent small increase in adsorption with soil grain size of 425 µm. This effect could be because of the higher pore size observed in 200 and 425 µm as compared to 300 µm (**Table** 4.1) rather than the effect of SOMs. This could be attributed to the fact that large soil porosity allows for more pollutant to enter its pore space (i.e., the portion of the soil's volume that is not occupied by solid materials). There is a significant difference in the pore size between soil particle size of 200 µm > 425 µm > 300 µm. Rao and Asolekar (2001) noted that pore size is one of the sorbent characteristics that determines the sorption of the organic pollutant. Larger pores

were said to be associated not only with larger soil particles but also with smaller particles in some cases (Nimmo, 2004). Meanwhile, larger surface area and SOM observed in soil particle grain sizes of 75 and 100 µm could rather be an overriding factor responsible for the sorption of higher amounts of PCB congeners.

To evaluate the significance of TOC/SOM content in the sorption of hydrophobic PCBs between aqueous solution and soil, the soil particle sizes were subjected to a high temperature of 450°C to remove the soil organic carbon content. The sorption capacity of the soil grain sizes presented in **Fig.** 4.3a shows a higher sorption capacity for soil before removal of the soil organics and an approximately 48% decrease when the soil organic matter was removed (**Fig**. 4.3b). This suggests that the presence of the SOM plays a significant role in the adsorption of the pollutants. The C/N ratio further confirmed the increase in the carbon content from smaller soil particle size to larger soil particle sizes as shown in **Table** 4.2 (75 µm < 100 µm < 200 µm < 300 < 425 µm). This implies that as the C/N ratio increases there could also be a decrease of the nitrogen-rich, proteinaceous matter. After the SOM has been removed, a further increase in C/N is observed from low to high soil particle size. This suggests that more nitrogen than carbon content is removed when the SOM is removed leading to the higher C/N ratios. This follows a similar trend as reported by Meyers, (1994). Furthermore, the microbial content in soil is generally a source of the nitrogen rich matter (Meyers, 1994). Any reduction of the microbial content in the soil will result in less nitrogen being present and lead to higher C/N ratios thus affecting the partitioning of the PCBs.

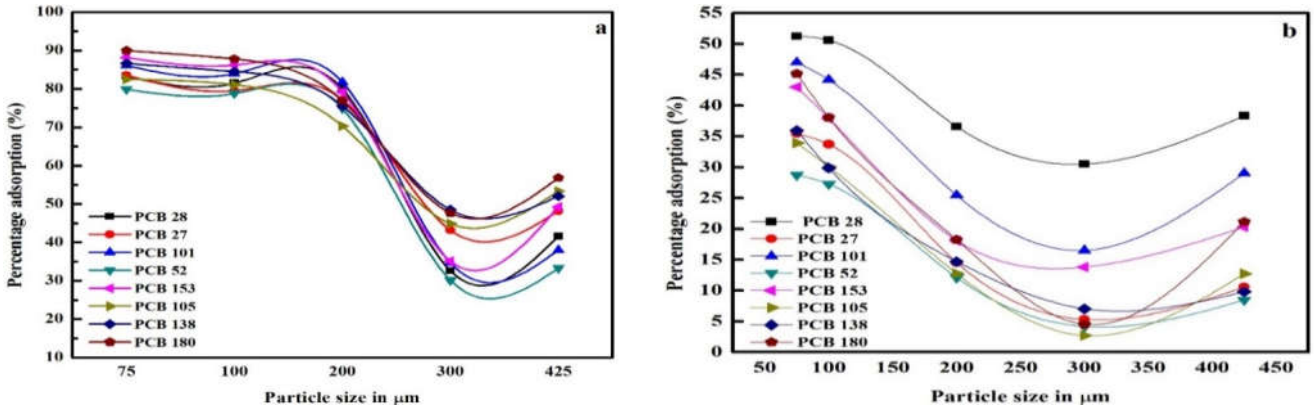


Figure 4.3: Percentage sorption capacity of PCB congeners onto different soil particle sizes (a) before and (b) after removal of soil organic matters at 440°C

Table 4.2:

Physical and chemical properties of the PCB congeners

PCB congeners	Molecular weight, g/mol	Molecular formula	Melting point, ℃)	Boiling point, ℃ (at 20 mmHg)	Solubility	Partition coefficients		Vapour pressure, mm Hg (at 25°C)	Henry's law constant, atm-m^3/mol (at 25°C)
					Water, mg/L	log K_{ow}	log K_{oc}		
PCB 28	257.54	$C_{12}H_7Cl_3$	57-58	206-207	0.0085	5.67	5.28	2.8×10^{-7}	32.20
PCB 52	291.98	$C_{12}H_6Cl_4$	87-89	268	0.046	5.84	5.91	7.3×10^{-7}	31.41
PCB 77	291.98	$C_{12}H_6Cl_4$	173	360	0.00055	6.36	4.41-5.75	4.4×10^{-8}	0.43×10^{-4}
PCB 101	326.43	$C_{12}H_5Cl_5$	77	380	0.00012	6.38	**	2.9×10^{-8}	35.50
PCB 105	326.43	$C_{12}H_5Cl_5$	**	**	0.0034	6.66	**	8.6×10^{-9}	8.24×10^{-4}
PCB 138	360.88	$C_{12}H_4Cl_6$	78.5-80	400	0.016	6.83	5.21-7.3	4.0×10^{-9}	1.07×10^{-4}
PCB 153	360.88	$C_{12}H_4Cl_6$	103-104	**	0.00091	6.92	4.75-7.68	1.9×10^{-9}	2.78×10^{4}
PCB 180	395.32	$C_{12}H_3Cl_7$	109-110	240-280	0.00031-0.0066	7.37	5.78-6.9	1.3×10^{-9}	1.07×10^{-4}

ATSDR, 2000; Mills *et al*. 2007; Dunnivant *et al*. 1992.
**Data not available

Fig. 4.3 shows the sorption of the PCB congeners by soil particle grain sizes are also possibly dependent on the characteristics of the individual PCBs, their degree of chlorination, water solubility and soil–water partitioning coefficients (log K_{oc} and log K_{ow}) (**Table** 4.2) as well as the orientation of the congeners **(Fig.** 4.1**)**. Among the PCBs studied in this research, the partitioning to organic matter was in the order of PCB 180 > PCB 153 > PCB 138 > PCB 28 > PCB 101 > PCB 105 > PCB 77 > PCB 52. Thus, the more chlorinated the PCBs the more hydrophobic they are, leading to more partitioning onto the non-polar organic matter of the soil (Shiu and Mackay, 1986; ATSDR, 2000; IPCS, 2003). PCB solubility also affects partitioning. Low solubility corresponded to high log K_{ow} values for PCB 180, PCB 153 and PCB 138 as compared to the relatively high solubility values (relatively lower log K_{ow} values) observed for PCB 77 and PCB 52 in **Table** 4.2. PCB 28 was also found to show higher partitioning onto the soil as compared to some of the *tetra*

and *penta*-chlorinated PCBs despite being a *tri*-chloro biphenyl (lower degree of chlorination). This may possibly be due to its moderate water solubility and low log K_{ow} value as well as the stereochemistry of the PCB. All the selected PCB congeners, except for PCB 77 and PCB 28, were all clustered together and have their chlorine atoms on positions 2 and 2' which do not allow them to have a planar configuration compared to PCB 77 and PCB 28, which may allow for partial rotation due to their non-ortho and mono-ortho configuration of the chlorine atom (Lung *et al*., 2000; Badea *et al*., 2014).

4.3.3 Effect of time

The effect of time on the equilibrium sorption of PCBs between the aqueous solution of $CaCl_2$ and soil was investigated for 2 to 48 h of contact time, while keeping the initial PCB concentration (2.0 µg/g), pH 6.5 and the quantity of soil sample (0.5 g) constant (**Fig** 4.4). It was found that the percentage of PCBs sorbed onto the soil increased significantly in the first 4-6 h. Sorption slowly continued reaching an equilibrium after 8 h, with 80% – 92% of PCBs sorbed. After equilibrium was reached, minimal changes in adsorption were observed. Badea *et al*. (2014) conducted batch experiments on the leacheability and desorption of PCBs from soil, and found that 48 h was sufficient to equilibrate the PCBs between the solution and the soil. Also, Taha and Mobasser (2015) reported that percentage adsorption of PCBs by multi walled carbon nanotubes, nano-clay and nano-alumina increased with time and gradually attained equilibrium after 20 h.

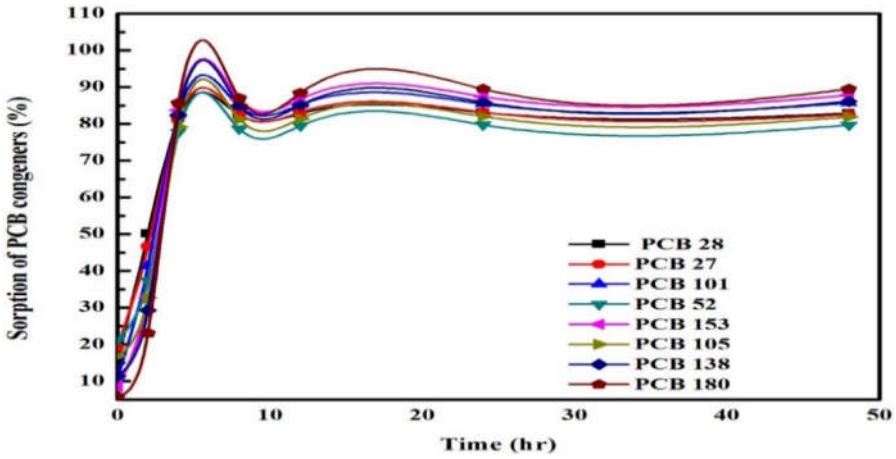


Figure 4.4: Effect of time on the equilibrium sorption of PCB congeners between aqueous solution of 0.01 mol/L $CaCl_2$ and soil

4.3.3.1 Pseudo-first order, pseudo-second order and intra-particle diffusion models

The partitioning of eight PCB congeners between water and soil particle sizes within the experimental period was best fitted into the kinetic model of pseudo-second order. Three kinetic models- pseudo-first order, pseudo-second order and intra-particle difussion were evaluated using **Eqs**. (4.5), (4.6) and (4.7), respectively (Weber and Morris, 1963; Atkins and Paula, 2006).

$$\log(q_{e-}q_t) = \frac{k_1}{2.303}t \qquad (4.5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2 k_2} + \frac{t}{q_e} \qquad (4.6)$$

$$q_t = k_{id}\, t^{1/2} + C \qquad (4.7)$$

where, t (hr), q_e (mg/g), q_t (mg/g) and k_1 (g/mg), k_2 (g/(mg·min)), and k_{id} (g/(mg·min$^{1/2}$)) are time, amounts of PCB adsorbed at equilibrium, amounts of PCB adsorbed at time t, rate constants of adsorption (k_1 and k_2), and intra-particle diffusion rate constant, respectively. $t^{1/2}$ is the square root of the time and C (mg/g) is the intercept referring to the thickness of the boundary layer.

Table 4.3 shows the values obtained for the pseudo-first order, pseudo-second order and intra-particle diffusion kinetic. The results best fitted the pseudo-second order (**Appendix A 3**), which suggests that the sorption process of the selected PCBs occurred in more than one-step between aqueous solution and soil active components in soil. The q_e^{cal} was evaluated from the inverse of the slope and the partitioning rate constant k_2 was obtained from the intercept of t/q_e *versus* t. There was close agreement between the calculated q_e, and experimental q_e, which further confirmed the adsorption kinetics followed the pseudo-second order. The pseudo-second order model assumes that the rate-limiting step for PCB sorption onto the soil may be due to interaction through exchange of electrons between the π-π bonds of the phenyl rings of the PCBs and the polymeric group of the SOM components in the soil. This indicated that the sorption rate of PCBs onto the soil was determined by a bimolecular interaction between the PCBs and the active sites on the soil. To further understand the sorption mechanism involved and the possibility of intra-particle diffusion contribution as well as prediction of rate controlling step in the sorption process between PCB and soil, the kinetic data were modelled using Weber and Morris (1963) (**Eq**. (4.7)), by

plotting q_t against $t^{½}$. The model predicts the mechanism of sorption, thus, if the plot gives a straight line, the sorption process is controlled by intra-particle only, and if the plot exhibits multi-linear then, there are two or more steps involved in the sorption process (Tan *et al*., 2009; Alhooshani, 2015).

Table 4.3:

Kinetic parameters of the interaction of PCBs between water and soil particle sizes

Isotherm parameter	Pseudo-first order			Pseudo-second order			Intra-particle diffusion			q_e^{exp}, mg/g
PCBs	R^2	k_1, min^{-1}	q_e^{cal}, mg/g	R^2	q_e^{cal}, mg/g	k_2, g/mg. min	R^2	k_{id}, mg/g. $min^{1/2}$	C	
PCB 28	0.180	0.0115	2.534	0.9992	16.807	0.0274	0.304	0.0716	1.286	16.580
PCB 52	0.143	0.0115	2.517	0.9980	16.313	0.0496	0.251	0.0713	1.269	15.936
PCB 77	0.180	0.0173	2.408	0.9983	16.341	0.0157	0.317	0.0982	1.198	16.097
PCB 101	0.183	0.0168	2.486	0.9980	17.513	0.0454	0.306	0.0926	1.110	17.138
PCB 105	0.186	0.0226	2.424	0.9958	16.892	0.0635	0.321	0.122	1.113	16.377
PCB 138	0.181	0.0200	2.396	0.9931	17.921	0.0793	0.301	0.138	10.920	17.221
PCB 153	0.183	0.0246	2.374	0.9951	18.182	0.0683	0.315	0.126	1.0620	17.561
PCB 180	0.180	0.0309	2.324	0.9838	18.975	0.110	0.313	0.138	1.0215	17.895

The plot did not pass through the origin, and gave two different straight lines. The non-linearity of the plot indicated that the rate limiting process was not only due to the intra-particle diffusion, but other rate determining mechanisms may also be involved. Therefore, sorption of PCBs from aqueous solution onto the pores of the soil may proceed *via* two steps. The rate constants of intra-particle diffusion (k_{id}) and the thickness of the boundary layer C were determined from the slope and intercept of the graph, respectively. The small values of intra-particle rate constants (k_{id})

obtained in this study indicated that PCB sorption from aqueous solution onto soil was dependent on more than intra-particle diffusion of soil alone.

4.3.4 Effect of pH

The partitioning of the PCBs onto different soil particle grain sizes with varying pH was investigated and the results are shown in **Fig.** 4.5 and **Appendix C 2**. The results revealed that the sorption capacity of the PCB congeners onto the soil was pH dependent. A low pH results in protonation of the carboxylic acid group on the soil organic matter, resulting in a hydrophobic material. Hence, the PCB analytes, which are also neutral to hydrophobic, were attracted to the hydrophobic material resulting in increased adsorption. In basic pH, the OH^- abstracts the hydrogen from the carboxylic acid group of the soil organic matter resulting in a negatively charged material. The water molecules from the water column form hydrogen bonds with the negatively charged material resulting in the formation of a hydrophilic material (Gondar *et al*., 2013). Thus, the hydrophobic PCB is not attracted to the hydrophilic material resulting in decreased adsorption at high pH. In addition, PCBs are neutral molecules and thus prefer to partition at neutral pH values. Furthermore, at low pH, most humic acid precipitates out leaving behind only fulvic acid, so adsorption is due to the presence of protonated fulvic acid. As the pH increases to neutral pH, humic acid becomes more soluble and adsorption is due to the organic matter in the soil made up of both fulvic acid and humic acid. At high pH, the concentration of fulvic acid decreases (You *et al*., 1999) and this together with the deprotonation of the humic acid leads to decreased adsorption. Thus, maximum adsorption is observed at neutral pH and decreases as the pH increases. For all these reasons, the maximum adsorption occurs at pH values of 6.8 - 7.5 as observed in **Fig.** 4.5, which was also observed in previous studies by Ertli *et al*. (2004) and Flores *et al*. (2009). PCB 180 shows a slightly different trend with a maximum adsorption at low pH. Of all the PCBs studied, PCB 180 has the highest number of chlorine atoms which makes it most hydrophobic. Therefore, **Fig.** 4.5b and 5c show the highest adsorption of PCB 180 at low pH values.

In addition, changes in pH play a significant role in the larger soil particle grain sizes as they contain lower SOM and CEC and their surface areas are also lower compared to the smaller particle

grain sizes. As the soil particle grain size increases, the lower soil organic matter present means there is less humic substance present. Humic substance has a polymeric aromatic chemical structure, which means there will now be less π-π interactions between the soil organic matter and the aromatic structure of the PCBs. The PCBs therefore lose their affinity for soil in larger soil particle grain sizes and are released into the aqueous solution resulting in a reduction in the adsorption capacity.

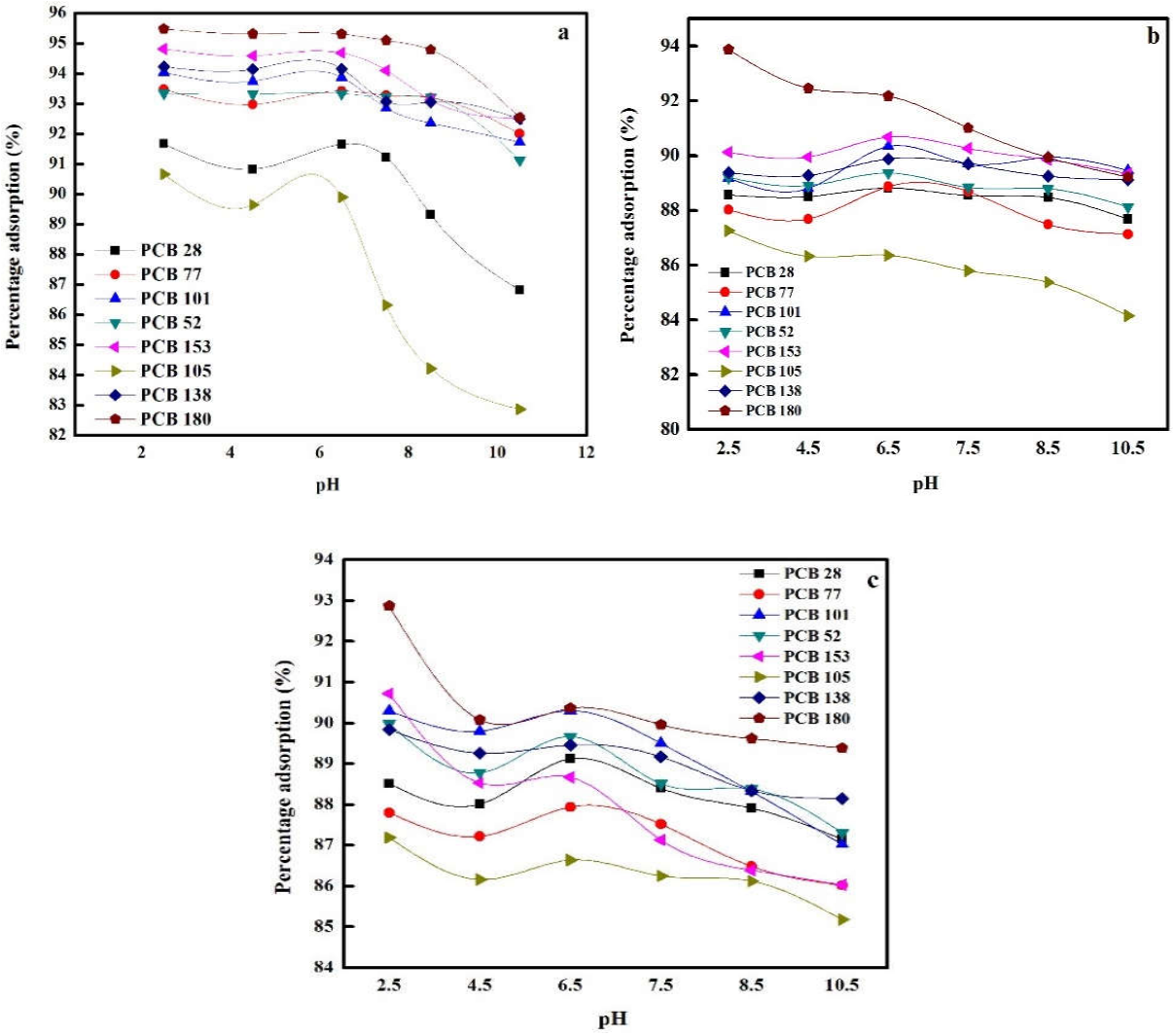


Figure 4.5: Effect of pH on the sorption of PCBs between aqueous solutions of $CaCl_2$ on different soil particle grain sizes. (a) 75 µm soil; (b) 100 µm soil; (c) 200 µm soil

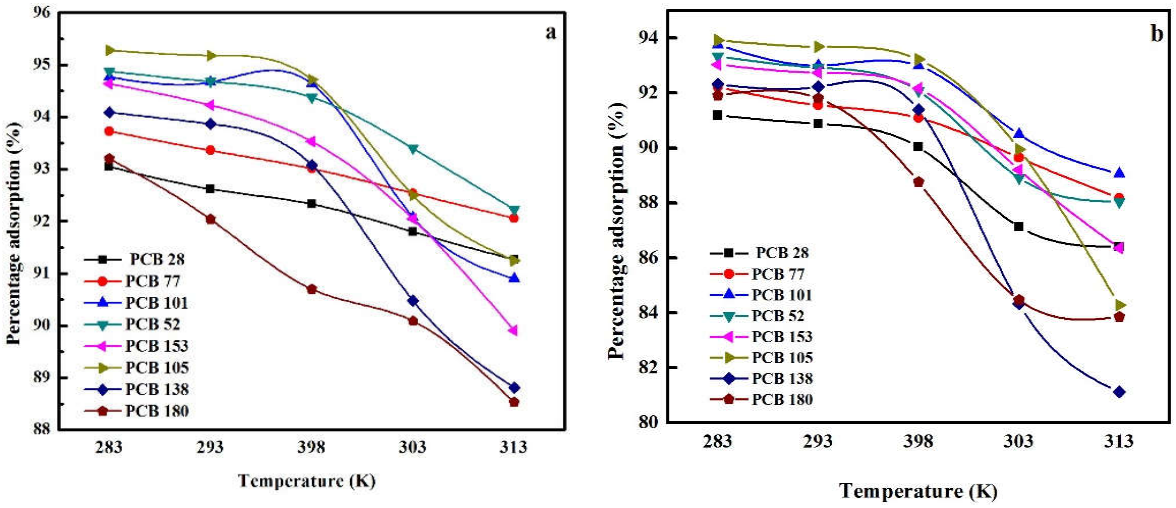
4.3.5 Effect of ionic strength

The effect of ionic strength on the sorption capacity of PCBs and soil particle sizes (75, 100, 200, 300 and 425 µm) was investigated. The effect was found to be less significant at varying concentrations of KCl electrolyte (0.0-1.0 mol/L) as shown in the supplementary data **(Appendix C 1)**. The fact that the sorption capacity was not affected with the change in the electrolyte concentration is evidence that electrostatic attraction was not as important as hydrophobic interaction between the non-polar PCBs and soil organic matter in this study. A similar sorption behavior was reported by Duan and Naidu (2013), and Gondar *et al*. (2013) for phenanthrene, and non-ionic pesticides metalaxyl and penconazole, respectively.

4.3.6 Effect of temperature

The effect of temperature on the partitioning of the PCBs between water and soil particle grain sizes was studied at temperatures of 283, 393, 398, 303 and 313 K. The results **(Fig.** 4.6 and **Appendix C 4)** revealed that the PCBs generally partitioned more onto the soil at lower temperatures.

For the temperature studies, a neutral pH was used as it was the pH where maximum adsorption of all the PCBs occurred. However, PCB 180 actually had a maximum adsorption at low pH. Thus, at the neutral pH used for the temperature studies, PCB 180 was at a pH that was not suitable for its maximum adsorption and therefore is observed as the lowest adsorbed PCB. **Fig.** 4.6 shows that PCB 180 is the lowest adsorbed PCB at all temperatures studies, which suggests that for PCB 180, pH plays a more significant role in its adsorption rather than temperature.



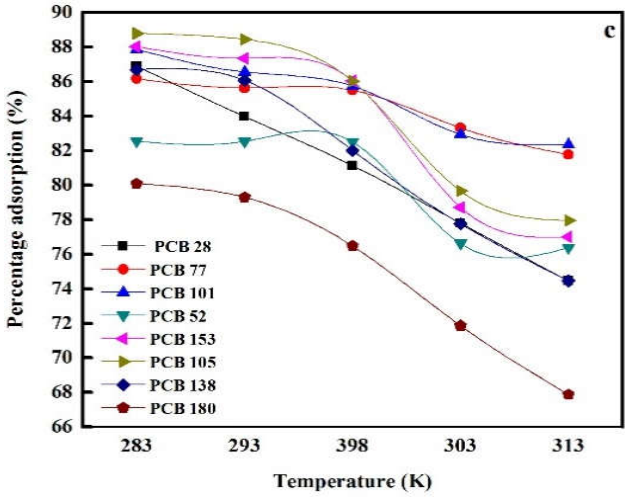


Figure 4.6: Effect of temperature on the partitioning of the PCBs between aqueous solution and various soil particle sizes. (a) 75 µm soil; (b) 100 µm soil; (c) 425 µm soil

The thermodynamic parameters of PCBs were investigated under the five temperature values selected. In general, the results of **Table** 4.4 and **Appendix D 1**, show that the partition coefficient (K_d) decreases with an increase in temperature. This could be due to an increase in the solubility of PCBs at higher temperature (Kipling, 1965; Delle Site, 2001). Also, all the standard free energy change (ΔG^o) of PCB sorption was found to be negative at the temperatures under investigation, indicating the spontaneity of the process. The negative values of the enthalpy change ($\Delta H°$) suggested that the soil to PCB interaction was exothermic which corresponds to the increase in partitioning at low temperature. Similar results were reported on the sorption and desorption of testosterone by Qi *et al*. (2015), and Borriruwisitsak *et al*. (2012) on the octanol-water partition coefficient of bisphenol A. In addition, the negative values of $\Delta H°$, obtained as the slope of a plot of $1/T$ *versus* ln K_d, suggests that an increase in solution temperature does not favour PCB partitioning onto the soil (Vaghese *et al*., 2004; Zheng *et al*., 2004; Salam and Burk, 2010). The lower values of enthalpy change ($\Delta H°$) of PCB interactions with soil obtained in this study are consistent with weak hydrophobic interactions of non polar organic molecules sorbed onto soil organic matter with no additional contribution from electrostatic interaction (Karickoff, 1984; Qi *et al*., 2014). Therefore the lower values of $\Delta H°$ obtained in this study suggest a physiosorption process (Qi *et al*., 2014, 2015). Increases in temperature also lead to an increase in partitioning of

the PCBs to the aqueous phase and increases its disorderliness in the aqueous phase. Hence, there is a reduction in partitioning of the PCBs in the soil with an increase in temperature. This is further confirmed by the negative values of $\Delta S°$ obtained in this study shown in **Table** 4.4 (Salam and Burk, 2010; Qi *et al*., 2015). Comparing the K_d values between the different soil particle grain sizes, the smallest soil particles have the highest partitioning compared to the larger soil particle sizes at all temperatures studied.

Table 4.4:

Thermodynamic studies of the interaction of PCBs with water and soil particle sizes

Parameter	75 µm		100 µm		200 µm		300 µm		425 µm	
Temperature, K	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol
283	13.39	-6.11	12.35	-5.91	7.85	-4.85	5.60	-4.06	6.64	-4.45
293	12.55	-6.16	11.92	-6.04	7.60	-4.94	5.31	-4.07	5.24	-4.04
298	12.04	-6.16	10.05	-5.72	7.54	-5.01	5.27	-4.12	4.30	-3.62
303	11.19	-5.98	5.55	-4.32	7.28	-5.00	4.87	-3.99	3.50	-3.16
313	10.45	-6.11	4.71	-4.03	7.06	-5.09	4.66	-4.01	2.92	-2.78
$\Delta H°$, kJ/mol	-6.32		-26.70		-2.65		-4.69		-21.14	
$\Delta S°$, kJ/(mol·K)	-0.64		-72.15		-7.82		-2.15		-58.84	

4.4 Conclusions

Batch experiments showed that different soil particle sizes have different sorption capacities for PCB congeners. The sorption capacity of soil particle grain sizes positively correlated with SOM content, surface area as well as pore size distribution among the soil particle grain sizes. Smaller soil particle grain size had the highest sorption capacity of PCB congeners compared to the larger soil particle grain sizes. Other factors that were significant in the sorption capacity of PCBs between aqueous solution and soil particle grain sizes were CEC and C/N ratio. The amount of PCBs sorbed by soil increased with increase in contact time reaching an equilibrium within 8 h. The results of kinetic studies on the sorption of PCBs on the mixture of soil particles fitted into the pseudo-second order kinetic model. Low solution pH values favoured the sorption of PCB congeners due to the hydrophobic interactions between the PCB congeners and the organics in the

individual soil particle grain sizes. Ionic strength w as found to be less significant in the sorption of PCBs between aqueous solution and soil particle grain sizes.

The results also indicated that the sorption of PCBs was temperature driven; low temperatures resulted in higher partitioning of the PCBs onto the soil. The negative values of $\Delta G°$ showed that PCB interaction with soil particle sizes was a spontaneous process. The negative and low values of $\Delta H°$ showed that the partitioning process was exothermic and occured through a physiosorption process. Therefore, this study has provided insights into understanding the role of soil physicochemical properties as well as the influence of environmental conditions such as pH, temperature and ionic strength, on PCBs partitioning/sorption in the environment.

Acknowledgments

The authors sincerely acknowledge the University of KwaZulu-Natal and School of Chemistry and Physics at UKZN for laboratory facilities.

REFERENCES

Achman, D. R., Hornbuckle, K. C., Eisenreich, S. J., (1993). Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. *Environ. Sci. Technol*. **27**: 75-87.

Adeyinka, G. C., (2014). The determination of organochlorinated pesticides and polychlorinated biphenyls in sediment, soil and water of the Msunduzi River, KwaZulu-Natal, South Africa. MSc thesis. University of KwaZulu-Natal, Westville, South Africa.

Alhooshani, K. R., (2015). Adsorption of chlorinated organic compounds from water with cerium oxide activated carbon composite. *Arab. J. Chem*. http://dx.dio.org/10.1016/j.arabjc.2015.04.013.

ASTM, (2000). Standard test methods for moisture, ash, and organic matter of peat and other organic soils. Method D 2974-00. American Society for Testing and Materials. West Conshohocken, PA.

Atkins, P. W., and De Paula, J., (2006). Physical Chemistry for the life Sciences. W.H. Freeman and Company. Oxford, UK : Oxford University Press ; New York. pp 699.

ATSDR (Agency for Toxic Substances and Disease Registry), (2000). Toxicological Profile for Polychlorinated Biphenyls (PCBs). Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Atlanta, Georgia. Available http://www.atsdr.cdc.gov/ToxProfiles/ tp17.pdf. *Accessed* 21/04/2016.

Badea, S-L., Mustafa, M., Lundstedt, S., Tysklind, M., (2014). Leachability and desorption of PCBs from soil and their dependency on pH and dissolved organic matter. *Sci. Total Environ*. **499**: 220-227.

Baker, J. E., Capel, P. D., Eisenreich, S. J., (1986). Influence of colloids on sedimentwater partition coefficients of polychloro biphenyls congeners in natural waters. *Environ. Sci. Technol*. **20**: 1136-1143.

Belfort, G., Altshuler, G. L., Thallam, K. K., Feerick, Jr. C. P., Woodfield, K. L., (1984). Selective adsorption of organic homologues onto activated carbon from dilute aqueous solutions: Solvophobic interaction approach IV. Effect of simple structural modifications with aliphatics. *AIChE J.* **30**: 197–207.

Bergen, B. J, Nelson, W. G., Pruell, R. J., (1993). Partitioning of polychlorinated biphenyl congeners in the seawater of New Bedford Harbor, Massachussets. *Environ. Sci. Technol*. **27**: 938-942.

Borriruwisitsak, S., Keenan, H. E., Gauchott-Lindsay, C., (2012). Effect of salinity, pH and temperature on the Octanol-Water partitioning coefficient of bisphenol A. *IJESD*. **3**: 460-464.

Buckley-Golder, D., (1999). Compilation of EU dioxins exposure and health data. Summary report for European Commission DG Environment and the UK Department of the Environmental Transport and the Regions. Available http: greenpeace.se/files/file.72.pdf. *Accessed* 22/09/2016.

Burton, E. D., Phillips, I. R., Hawker, D. W., (2004). Sorption and desorption behavior of tributyltin with natural sediments. *Environ. Sci. Technol*. **38**: 6694-6700.

CUCE, Cornell University Cooperative Extension (2007). Cation Exchange Capacity (CEC). Agronomy Fact Sheet Series # 22. Department of Crop and Soil Sciences, College of Agriculture and Life Sciences, Cornell University. Available http://nmsp.cals.cornell.edu/publications/factsheets/factsheet22.pdf. *Accessed* 24/08/2016.

Delle Site, A., (2001). Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. *J. Phys. Chem. Ref. Data*. **30**: 187–439.

Duan, L., and Naidu, R., (2013). Effect of ionic strength and index cation on the sorption of Phenanthrene. *Water Air Soil Pollut.* **224**: 1700-1718.

Erickson, M. D., and Kaley, R. G., 2nd (2011). Applications of polychlorinated biphenyls. *Environ. Sci. Pollut. Res. Int*. **8**: 135-151. doi 10.1007/s11356-010-0392-1

Ertli, T., Marton, A., Földényi, R., (2004). Effect of pH and the role of organic matter in the adsorption of isoproturon on soils. *Chemosphere*. **57**: 771-779.

Flores, C., Morgante, V., González, M., Navia, R., Seeger, M., (2009). Adsorption studies of the herbicide simazine in agricultural soils of the Aconcagua valley, central Chile. *Chemosphere*.**74**: 1544-1549.

Frankkis, S., Persson, Y., Tysklind, M., Skyllberg, U., (2006). Partitioning of CPs, PCDEs, and PCDD/Fs between particulate and experimentally enhanced dissolved natural organic matter in a contaminated soil. *Environ. Sci. Technol*. **40**: 68-73.

Gdaniec-Pietryka, M., Mechlinska, A., Wolska, L., Galuszka, A., Namiesnik, J., (2013). Remobilization of polychlorinated biphenyls from sediment and its consequences for their transport in river waters. *Environ. Monit. Assess*. **185**: 4449-4459.

Gondar, D., López, R., Antelo, J., Fiol, S., Arce, F., (2013). Effect of organic matter and pH on the adsorption of metalaxyl and penconazole by soils. *J. Hazard. Mater*. **260**: 627–633.

Guo, X. J., He, X. H., Zang, H., Deng, Y., Cheng, L., Jiang, A.Y., (2012). Characterization of the effect of organic matter extracted from the fermentation effluent of swine manure slurry using spectroscopic techniques and parallel factor analysis (PARAFAC). *Microchem. J*. **102**: 115-122.

Hiller, E., Jurkovic, L., Bartal, M., (2008). Effect of temperature on the distribution of polycyclic aromatic hydrocarbons in soil and sediment. *Soil and Water Res*. **3**: 231-240.

IPCS, Concise International Chemical Assessment Document 55 (2003). Polychlorinated Biphenyls: Human Health Aspects. Geneva, Switzerland: World Health Organization; pp. 1–60. Available http://whqlibdoc.who.int/publications/2003/9241530553.pdf. Accessed 14/07/2016.

Karickhoff, S. W., Brown, D. S., Scott, T. A., (1979). Sorption of hydrophobic pollutants on natural sediments. *Water Res*. **13**: 241–248.

Kipling, J. J., (1965). Adsorption from Solution of Non-electrolytes. Academic Press. London, New York. pp 328.

Li, L. B., Yan, S., Han., C. B., Shan, G. B., (2005). Comprehensive characterization of oil refinery effluent-derived humic substances using various spectroscopic approaches. *Chemosphere.* **60**: 467-476.

Liying, S., Weiling, S., Jinren, N. I., (2009). Partitioning of water soluble organic carbon in three sediment size fractions: Effect of the humic acid substances. *J. Environ. Sci*. **21**: 113-119.

Lung, S-C., Yanagisawa, Y., Ford, T. E., Spengler, J. D., (2000). Characterization of sorption losses of polychlorinated biphenyl congeners onto glass surfaces. *Chemosphere*. **41**: 1857-1867.

Meyer, P. A., (1994). Preservation of elemental and isotopic sources identification of sedimentary organic matter. *Chem. Geol*. **114**: 289-302.

Mills, S. A 3rd, Thal, D. I., Barney, J., (2007). A summary of the 209 PCB congener nomenclature. *Chemosphere*. **68**: 1603–1612. doi:10.1016/j.chemosphere.2007.03.052 PMID:17499337.

Muir, D. C. G., Ford, C. A., Rosenberg, B., Norstrom R. J., Simon, M., Béland, P. (1996). Persistent organochlorines in beluga whales (*Delphinapterus leucas*) from the St Lawrence River estuary-I. Concentrations and patterns of specific PCBs, chlorinated pesticides and polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Environ. Pollut*. **93**, (2): 219-234.

Nimmo, J. R.., (2004). Porosity and pore size distribution, in Hillel, D., ed. Encyclopedia of Soils in the Environment: London, Elsevier, v. 3, p. 295-303.

Persson, Y., Hemstrom, K., Oberg, L., Tysklind, M., Enell, A., (2008). Use of a column leaching test to study the mobility of chlorinated HOCs from a contaminated soil and the distribution of compounds between soluble and colloid phase. *Chemosphere*. **71**: 35-42.

Qi, Y., and Zhang, T. C., (2015). Sorption and desorption of testosterone at environmentally relevant levels: Effects of aquatic conditions and soil particle size fractions. *J. Environ. Eng*. **142**: 1-9.

Qi, Y., Zhang, T., Ren, Y. Z., (2014). Testosterone sorption and desorption: Effects of soil particle size. *J. Hazard. Mater.* **279**: 493–501.

Rao, B. H., and Asolekar, S. R., (2001). QSAR models to predict effect of ionic strength on sorption of chlorinated benzenes and phenols at sediment-water interface. *Water Res*. *35*: 3391-3401.

Rivero, C., Senesi, N., Paolini, J., D'Orazio, V. D., (1998). Characteristics of humic acids of some Venezuelan soils. *Geoderm.* **81**. 227-239.

Salam, M. A., and Burk, R. C., (2010). Thermodynamics and kinetics studies of pentachlorophenol adsorption by multi-walled carbon nanotubes. *Water Air Soil Pollut*. **210**: 101-111.

Shin, H. S., Monsallier, J. M., Chopping, G. R., (1999). Spectroscopic and chemical characterization of molecular size fractionated humic acid. *Talanta*. **50**: 641-647.

Shiu, W. Y., and Mackay, D., (1986). A critical review of aqueous solubilities, vapor pressures, Henry's Law constants, and octanol–water partition coefficients of the polychlorinated biphenyls. *J. Phys. Chem. Ref. Data*. **15**: 911– 29.

Taha, M.R., and Mobasser, S., (2015). Adsorption of DDT and PCB by nanomaterials from residual soil. *PLoS ONE*. **10**, (12): 1-16

Tan, I., Ahmad, A., Hameed, B., (2009). Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *J. Hazard. Mater*. **164:** 473–482.

UNEP, United Nations Environment Programme (2013). Results of the global survey on the

concentrations in human milk of persistent organic pollutants by the United Nations Environment Programme and the World Health Organization. Available http://wedocs.unep.org/bitstream/handle/20.500.11822/19392/UNEPPOPSCOP6INF33English_%281%29.pdf?sequence=1&isAllowed=y UNEP/POPs/COP.6/INF/33. *Accessed* 26/09/2016.

USEPA, Environmental Protection Agency (2008). Fate, Transport and Transformation Test Guidelines OPPTS 835.1230 Adsorption/Desorption (Batch Equilibrium). Environmental Fate and Effects Division, Office of Pesticide Programs, USEPA. Washington DC. Available http://www.epa.gov/oppefed1/ecorisk_ders/soils_foreign.htm. Accessed 30/09/2016.

USEPA, United State Environmental Protection Agency (2000). Organization for Economic Corporation and Development (OECD 106) Guideline for the testing of chemicals. Available https://archive.epa.gov/scipoly/sap/meetings/web/pdf/106_adsorption_desorption_using.pdf . *Accessed* 20/07/2016.

Verghese, S., Vinod, V. P., Anirudhan, T. S., (2004). Kinetic and equilibrium characterization of phenols adsorption onto a novel activated carbon in water treatment. *Indian J. Chem. Technol*. **11**: 825-833.

Vilanova, R. M., Fernandez, P., Grimalt, J. O., (2001). Polychlorinated biphenyl partitioning in the waters of a remote mountain lake. *Sci. Total Environ*. **279**: 51-62.

Wang, P., and Keller, A. A., (2008). Particle-size dependent sorption and desorption of pesticides within a water-soil-nonionic surfactant system. *Environ. Sci. Tech*. **42**: 3381-3387.

Wang, X-C., Zhang, Y-X., Chen, R. F., (2001). Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. *Marine Pollut. Bullet*. **42**, (11): 1139-1149.

Weber, W.J., and Morris, J.C., (1963). Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng*. **89**: 31–60.

You, S-J., Yin, Y., Allen, H. E., (1999). Partitioning of organic matter in soils: effects of pH and water/solution ratio. *Sci. Total Environ*. **227**: 155-160.

Zheng, S., Yang, Z., Jo, D. H., Park, Y. H., (2004). Removal of chlorophenols from ground water by chitosan sorption. *Water Res*. **38**: 2315-1322.

CHAPTER 5

MANUSCRIPT 2

Effect of aqueous concentration of humic acid on the sorption of polychlorinated biphenyls onto soil particle grain sizes

Gbadebo Clement Adeyinka and Brenda Moodley*

School of Chemistry and Physics, College of Agriculture, Engineering and Sciences, University of KwaZulu-Natal, Private Bag X54001, Westville, 4000, Durban, South Africa. E-mail: adeyinkagbadebo78.ga@gmail.com
*Corresponding author; e-mail: Moodleyb3@ukzn.ac.za. Tel: +27 31 260 2796; Fax: + 27 31 2603091

ABSTRACT

The role of aqueous humic acid (HA) concentrations, as well as secondary environmental conditions on the sorption of six indicator PCB congeners PCB 28, 52, 101, 138, 153 180 and two dioxin-like PCBs, PCB 77 and 105 onto soil particle grain sizes, were investigated in this study. Scanning electron microscopy (SEM) equipped with energy disperse X-ray (EDX) and fourier transform infrared spectroscopy (FTIR) were used for the internal morphology and qualitative elemental analysis, as well as identification of possible functional groups found in commercial HA. Batch adsorption experiments were used for sorption studies. The results showed that the sorption of PCBs onto soil decreased with an increase in the aqueous HA concentrations. The adsorption of the selected PCBs onto the soils were found to decrease with an increase in the solution pH of humic acid. Thermodynamic studies showed that the partition coefficient (K_d) values increased with an increase in solution temperature. All the standard free energy ($\Delta G°$) were negative indicating the spontaneity and feasibility of the sorption process. Both the enthalpy ($\Delta H°$) and entropy ($\Delta S°$) values of the system were found to be positive and high. The high values of $\Delta H°$ and $\Delta S°$ indicated that the sorption of PCBs was an endothermic and entropy driven process. The sorption was best fitted with the Freundlich isotherm with the intensity parameter 1/n found to be greater than 1. This indicated a possible multi-layer and nonlinearity of sorption of hydrophobic organic contaminants (HOCs) in the soil particle grain sizes used in this study.

Key words: Sorption, soil particle sizes, isotherms, thermodynamic studies, *humic acid, PCBs*

5.1 Introduction

Soil contamination by persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) is an environmental problem, which has drawn scientific attention, due to their toxic effects (Colborn *et al*., 1996). The 2004 Stockholm Convention on POPs consisting 179-member states including South Africa, signed a treaty which prohibits the production of PCBs, although PCBs can be used in equipment until 2025 (UNEP, 2004). Although PCBs have been banned for several decades worldwide, there are still a few current sources of PCBs into the environment. One such source is the improper handling of old equipment wastes (e-waste) (Leung *et al*., 2006; UNEP, 2009; Hu and Hornbuckle, 2010) and the disassembling of ships has also been identified as a significant source of occupational exposure (Basel Convention, 2003). Similarly, due to their persistence, bioaccumulation, and long-range of transportation, they are still present in trace amounts in the environment, most especially in soils and sediments around the world (Buckley-Golder, 1999; UNEP, 2001; UNEP, 2011). Generally, there are various environmental pathways through which these contaminants can enter soils and sediments. These include volatilization, diffusion, plant uptake, and adsorption and desorption as well as degradation (Hu and Hornbuckle, 2010). Soils and sediments particularly are reserviours for recalcitrant and hydrophobic pollutants, such as PCBs, and thus have increased adsorption as a result of the organic carbon contained in soils, which encourages their partitioning to the soil (Buckley-Golder, 1999).

Sorption is a phase distribution process whereby organic compounds can be associated with soil organic matter in the soil or sediment (Huang *et al*., 2003). Sorption is a significant factor that affects the fate and behaviour of organic pollutants due to the amount of soil organic matter (SOM) (Chefetz and Xing, 2009). The roles of sorption in determining the fate and distribution of hydrophobic organic contaminants (HOCs) are complex and largely dependent on factors such as, the physicochemical properties of the soil/sediment, the molecular structure of the HOCs as well as environmental conditions such as temperature, pH and ionic strength (Hiller *et al*., 2008; Chefetz and Xing, 2009). Generally, sorption limits the aqueous biodegradation of HOCs such as polycyclic aromatic hydrocarbon (PAHs) and pesticides by decreasing their aqueous solubility, which then inhibits their accessibility to microbial degradation in water (Ogram *et al*., 1985; Rao *et at*., 1993; Scow, 1993: Guthrie-Nichols *et al*., 2003; Chefetz and Xing, 2009). However, studies have revealed that sorption can act as a major pathway for HOCs biodegradation process. For

instance, Park *et al*. (2003) reported that sorption encourages the dissolution of atrazine while Schnurer *et al*. (2006) noted that microbes can degrade sorbed glyphosate and Van Loosdrecht *et al*. (1990) found that sorption could increase biodegradation of the pollutant by reducing the toxic environment of the substrate to the microorganisms involved in its degradation. Hence, sorption is considered important in regulating HOCs, such as PAH mobility and transport in the environment (Chefetz and Xing, 2009). Similarly, the partitioning of HOCs onto dissolved organic matter has been reported to enhance the mobility of pollutants in the environment due to colloid facilitated transport (Van Loosdrecht, 1990). Therefore, SOM is the primary material responsible for adsorption of HOCs in soils and sediments if the total organic carbon is > 0.1% (Schwarzenbach, and Westall, 1981). However, the physicochemical parameters of SOM also play an important role in the sorption of organic compounds onto soils and sediments (Gauthier *et al*., 1987; Rutherford *et al*., 1992; Luthy *et al*., 1997; Chin *et al*., 1997; Chiou *et al*., 2000). Due to the high affinity of HOCs to SOM, the removal of the pollutant can be described by an organic carbon normalized sorption coefficient (K_{oc}) rather than based on a total sorbent mass sorption partition coefficient (K_d). K_{oc} reduces the variability of K_d (Gerstel, 1990).

Soil organic matter may often contain a range of heterogeneous organic materials such as biopolymer like polysaccharides, lipids, protein, and geopolymers. These substances are referred to as humic substances (HSs) (Kordel *et al*., 1997). HSs are natural substances consisting of both humic acid (HA) (**Fig**. 5.1) which is soluble at high pH but precipitates under acidic conditions (low pH), and fulvic acid (FA) which is soluble at all pH values (Claret *et al.,* 2003). HSs occur in water as colloids and constitute a large part of the dissolved organic carbon (Riffaldi *et al*., 1998; Warren *et al*., 2003). The speciation of HOCs in natural water is primarily affected by the presence of humic substances. The degree of water solubility and acidic strength of HSs decreases as the molecular weights of the HS constituents increase (Ding *et al*., 2001). The presence of natural organic matter (NOM) such as HA in ground water is known to decrease the adsorption rate as well as the adsorption of organic pollutants such as PAHs and trichloroethylene on activated carbon (Pirbazari *et al*., 1989; Weber and Smith, 1989; Wilmanski and Breemen, 1990). Although many researchers have reported the role of humic substances on HOCs, such as PAHs, in developed countries (Maie *et al*., 2004; Shirshova *et al*., 2006; Liying *et al*., 2009), there is no scientific information available on the role of initial aqueous concentrations of HA on the sorption of PCBs onto soil particle grain sizes. This study was therefore undertaken in order to fill this gap and fully

understand the sorption interaction and mechanisms of PCBs onto soils based on HA concentrations. Also, there is paucity of data available on the role of HA between the aqueous solution and soil systems on the partitioning of hydrophobic organic contaminant, and the few that are available are outdated. Therefore, there is need for further studies to be carried out on this important area in order to further understand the partitioning process of hydrophobic HOCs within the environmental media based on the change in the environmental situations as well as climatic diversity, which necessitated this current study. This is the first report on the role of initial concentrations of humic acid on PCB adsorption onto different soil particle grain sizes. The aim of this study was to investigate the role of the initial concentration of HA and secondary environmental conditions such as pH, temperature, and effect of initial PCB concentrations on the sorption of PCBs onto the selected modeled sub-tropical soil particle grain sizes found in KwaZulu-Natal, South Africa. The results of this study provide information that contributes to the understanding of partitioning of organic pollutants to soil and sediment, which is important for the remediation of water systems, particularly in water stressed regions.

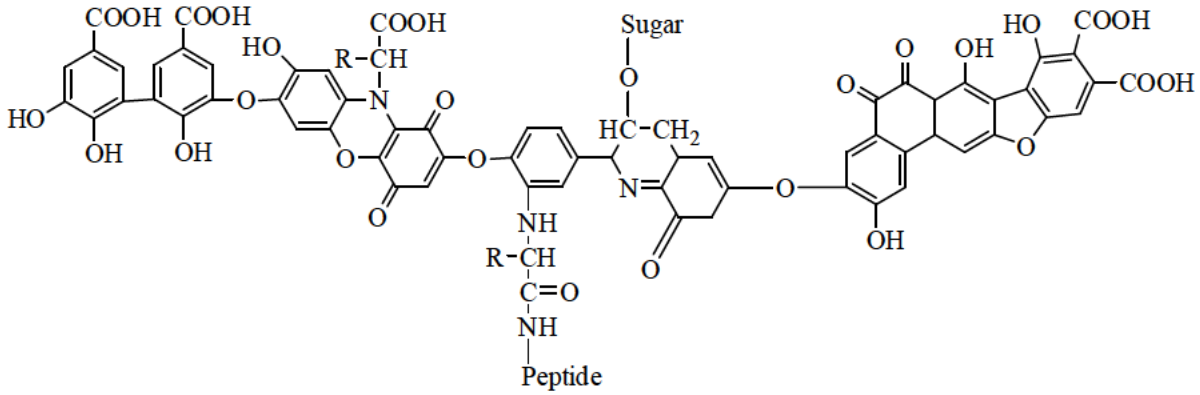


Figure 5.1: Structure of humic acid (Created - Used Chem Office 2015 version) (Stevenson, 1982)

5.2 Materials and methods

5.2.1 Chemicals and materials

Humic acid (CAS number 68131-04-4) and eight-selected PCB standards were purchased from Sigma Aldrich^{R} (South Africa). All reagents and chemicals were of HPLC/analytical-grade and used without further purification. A stock solution of 250 mg/L of HA was prepared by dissolving

250 mg of HA in 0.1 M NaOH solution and stored in the dark at 4°C. Lower working concentrations were prepared from the stock solution for further use. All glassware were baked in the oven at approximately 130°C prior to use.

5.2.2 Characterization

The soil sample used for this study was obtained from the Blue Lagoon site of the uMngeni River, of KwaZulu-Natal, South Africa. The details of the soil sample collection, sample preparation and the characterization used in this research have been discussed in chapters 3 and 4. In addition to the characterisations discussed in Chapter 4, elemental analysis was carried out using a Bruker energy dispersed X-ray (EDX) detector with Espirit 1.8.5 software for elemental mapping. The elemental composition is presented in **Table** 5.1.

A commercial HA obtained from Sigma Aldrich South Africa was used to simulate the effect of HSs in the river water. The surface morphology and elemental analysis that identified the weight percentage of both major and minor elements present were determined by scanning electron microscope (SEM) equipped with an EDX system for qualitative and elemental mapping. The microphotograph was recorded using Concise FEGSEM 6100 Zeiss Ultra Plus Germany at an accelerated voltage of 20.0 kV with secondary electrons in low vacuum mode.

5.2.3 Sorption processes

5.2.3.1 Effect of pH

The effect of pH on the sorption of PCBs onto the soil particle grain sizes in the presence of HA solution was investigated. A 10 mL aliquot of HA solution (natural pH of 12.5) was conditioned with the appropriate amount of 0.1 M HNO_3/NaOH to adjust the pH between 2.5 to 10.5. A sample of soil (approximately 1 g) was added to the solution/suspension (depending on the pH) together with a 500 µL aliquot of the mixture of PCB standards resulting in a final concentration of 0.5 µg/mL of PCBs. The mixture was placed on the orbital shaker preset at 25ºC and agitated for 24 h. Preliminary investigations on the sorption of PCBs onto different soil particle grain sizes (Adeyinka and Moodley, 2018) revealed that a 24 h equilibration period was sufficient for the

PCBs to sorb onto the soil containing soil organic matter (SOM) up to 11.92 % having cation exchange capacity of 7.90 Meq/100 g at different pH.

5.2.3.2 Effect of HA

Sorption experiments were carried out using a modified batch adsorption method as described by Sharma *et al*. (2008, 2009). Effect of initial HA concentration on the sorption of PCBs onto the soils was performed by preparing different HA concentrations, ranging from 0 – 50 µg/mL in 0.01 M $CaCl_2$ (background electrolyte) to enhance centrifugation and minimize changes in the ionic strength during equilibration. A soil solution/suspension ratio of 1:10 was added into 50 mL stainless steel centrifuge tubes, and 250 µL of the PCB mixture was added to the soil solution/suspension, already adjusted to a pH 6.5. An aliquot of 0.02 % NaN_3 (200 µL) was added to the solution to minimize bacterial growth. The tubes were capped and the outside lined with aluminium foil to minimize spills and volatilization and agitated on a reciprocal shaker in the dark for 24 h at 25°C. Solution/suspension mixtures were then centrifuged at 5 000 rpm for 10 min using Rotofix 32A centrifuge, (Hettich Zentrifugen, Germany). The supernatants were decanted and extracted thrice stepwise using 5 mL dichloromethane (DCM) each time, all three extracts were combined. The extracts were evaporated almost to dryness and stored in the refrigerator to avoid bacterial growth prior to GC-MS analysis. To assess the effectiveness and possible loss of PCBs to the walls of the centrifuge tubes and glass surfaces, an aqueous solution/suspension of HA spiked with the mixture of eight PCB congeners without soil samples was subjected to the same analytical procedure as carried out on the original samples. A blank extraction was also carried out simultaneously along with the sample of soil and HA to ensure there were no interferences from other sources during sample preparation. All the experiments were performed in duplicate. Parallel control tests to check the efficiency of the batch adsorption method showed that the percentage recoveries were in the range of 92 – 99%. The partition coefficient (K_d), organic carbon normalized adsorption coefficient (K_{oc}) and percentage sorption were determined using equations 5.1 - 5.3, respectively. K_{oc} describes the partitioning of non-polar organic pollutants between the organic carbon in the soil or sediment and water.

$$K_d = \left(\frac{C_o - C_e}{C_e}\right)\frac{V_0}{m} \qquad (5.1)$$

$$K_{oc} = \frac{K_d}{\%OC} \times 100 \qquad (5.2)$$

$$\%\ sorption\ (Ati) = \frac{M_s^{ads}(ti)}{M_o}\ x\ 100 \qquad (5.3)$$

Where K_d is the partition coefficient (L/g), C_o is the initial concentration (mg/L), C_e is the aqueous concentration at equilibrium (mg/L), V_o is the volume of the solution used (L) and m is the mass of the soil (g). K_{oc} is the organic carbon normalized adsorption coefficient (L/g) %OC is the percentage organic carbon fraction in the soil. M_o was determined using the following expression: $M_o = V_o x C_o$ and $M_s^{ads} = M_o - C_{aq}^{ads} t_i x V_o$. *Ati* is the % adsorption, M_o (mg) is the mass of the test substance in the test tube in solution at the beginning of the experiment and M_s^{ads} (mg) is the mass of the test substance adsorbed onto the soil. $C_{aq}^{ads}\ at\ t_i$ is the concentration of the adsorbed substances in aqueous phase (mg/L) at time t_i (s) which is further used to determine the percentage adsorption of the PCBs onto the soil samples after the batch adsorption experiments.

.

5.2.3.3 Sorption isotherm

The enthalpy of PCB adsorption on soil particle grain sizes in the presence of HA was determined using batch adsorption experiments as described above. The sorption experiments were performed at five different temperatures of 283 K, 288 K, 298 K, 303 K and 313 K. Batch samples were equilibrated on the temperature controlled rotating shaker (Protea Model). The PCB concentrations used for the study were 0.5, 1.0, 1.5, 2.0 and 2.5 mg/L. The sorption data for the soil mixture were fitted into the sorption isotherms using equations 5.4 and 5.5.

Freundlich $lnq_e = lnK_f + \frac{1}{n} lnC_e \qquad (5.4)$

Langmuir $\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \qquad (5.5)$

where q_e is the concentration of PCBs adsorbed on the soil phase (mg/g), C_e is the aqueous phase concentration after sorption equilibrium (ng/mL); K_f is the Freundlich sorption constant (L/mg), and 1/n is the Freundlich intensity parameter, (an indicator of sorption linearity); q_m is the maximum sorption capacity (mg/g) and b is the sorption equilibrium constant (L/mg).

5.2.3.4 Thermodynamics

The thermodynamic parameters were evaluated using equations 5.6 and 5.7:

$$\Delta G° = -RTlnK_d \qquad (5.6)$$

$$lnK_d = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (5.7)$$

where $\Delta G°$ (kJ/mol), $\Delta H°$ (kJ/mol), and $\Delta S°$ (kJ/(mol.K) are Gibbs free energy change, enthalpy change, and entropy change in the sorption process, respectively, T is the temperature (K) and R is the ideal gas constant (J/(mol.K)).

A plot of 1/T (K^{-1}) *versus* ln K_d was used to obtain the Gibbs free energy of the system while Van't Hoff equation (5.7) was adopted to evaluate the magnitude of the enthalpy change ($\Delta H°$) and entropy ($\Delta S°$) of the sorption from the slope and y-intercept of the graph, respectively.

5.2.4. GC-MS analysis

The details of GC-MS were presented in chapters 3 and 4.

5.3 Results and discussion

5.3.1 Characterization of humic acid and soil particle sizes

The surface morphology of HA and soil particle grain sizes, analyzed by scanning electron microscopy (SEM), shown in **Fig**.5.2 and **Appendix B** 1 (a-e) shows a uniform structure with particles close to each other formed by aggregation of the HA particles. The energy dispersive X-ray (EDX) elemental analysis of both HA and soil particle sizes (**Table** 5.1) showed high carbon content, oxygen, silicon and aluminium and the characteristic aluminosilicate minerals (Si, O Al, Na K and Ca). Elements such as Ti, Fe Cr, Cu, and Au were also present in smaller percentages in

soil samples. The characteristic elements, most especially, Si, Al, and Fe form oxides, which are responsible for the sorption of non-ionic pollutants onto the soil (Shen, 2000). The ratio of Si to the sum of Al and Fe present in the soil samples help to predict the soil's affinity to sorb HOCs (Shen, 2000). Other factors such as SOM, surface area of the soils, percentage soil minerals such as montmorillonite, kaolinite, and illite have been reported to play a key role in the sorption of HOCs (Grathwohl, 1990: Ray *et al*., 1995; Clark *et al*., 2010: He *et al*., 2011).

The results of SOM content determined by wet oxidation and N_2 adsorption-desorption BET-surface area isotherms on the soil particle sizes have been reported previously in chapter 4. The results of SOM for the smaller and larger particle grain sizes were 11.92±0.69 mg/g and 4.02±0.23 mg/g, respectively and surface area for the smaller and larger soil particle sizes were 13.36 m^2/g and 0.88 m^2/g, respectively. This indicated that the smaller soil particle size had more SOM content and surface area compared to higher soil particle grain sizes. This is because the higher surface area of the smaller particle sizes has more binding sites for the SOM. Soil particle grain size with high SOM content as well as the high surface area were found to enhance the sorption capacity of the soil for PCBs (Chapter 4).

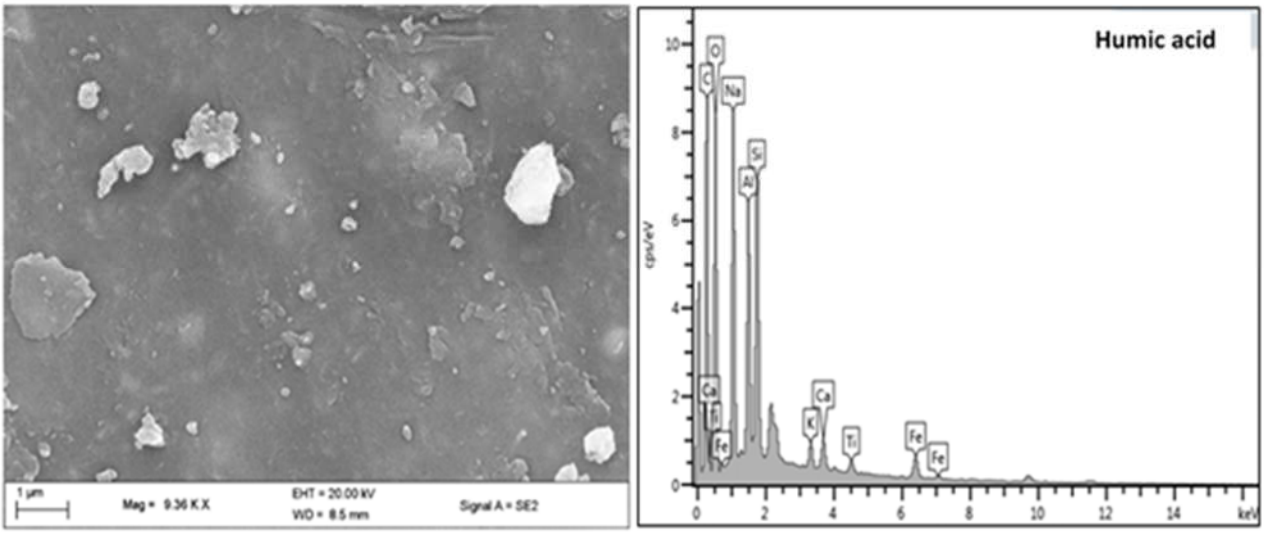


Figure 5.2: SEM image and EDX elemental composition of commercial humic acid

Table 5.1:

Weight and atomic percentage compositions of soil particle size and HA obtained by SEM/EDX analysis

Soil particle sizes	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**		**Humic Acid**	
Elemental composition	Weight, %	Atomic, %	Weight, %	Atomic, %	Weight, %	Atomic, %	Weight, %	Atomic, %	Weight, %	Atomic, %	Weight, %	Atomic, %
Carbon (C)	7.35	13.51	15.39	26.01	13.32	23.28	42.36	58.66	26.81	42.36	2.08	44.07
Oxygen (O)	37.39	51.56	38.65	49.03	38.04	49.91	27.72	28.82	28.36	33.63	1.33	33.65
Aluminium (Al)	9.87	8.07	6.40	4.83	2.83	2.21	1.05	0.64	8.15	5.73	0.19	4.56
Silicon (Si)	13.52	10.62	7.31	10.11	10.08	7.53	1.34	0.74	12.98	8.77	0.21	4.97
Potassium (K)	1.78	1.01	0.64	0.33	0.12	0.06	-	-	1.99	0.97	0.05	0.69
Sodium (Na)	5.81	5.58	0.57	0.50	4.37	3.99	0.86	0.62	1.91	1.58	0.37	9.13
Calcium (Ca)	0.31	0.17	8.74	0.11	12.40	6.50	18.09	7.51	0.55	0.26	0.66	0.82
Iron (Fe)	6.75	2.67	8.38	3.05	2.15	0.81	1.57	0.47	4.00	1.36	0.11	1.64
Titanium (Ti)	0.82	0.38	0.08	0.18	1.65	0.72	-	-	0.13	0.05	0.06	0.47
Chromium (Cr)	0.32	0.13	0.19	0.88	0.49	0.20	0.13	0.04	0.53	0.19	-	-
Gold (Au)	1.30	0.15	1.05	0.11	1.37	0.15	0.52	0.04	1.27	0.12	-	-
Copper (Cu)	11.80	4.10	11.80	4.10	12.34	4.08	4.02	1.05	10.52	3.14	-	-

The FTIR spectrum of HA (**Fig**.5.3) showed an intense prominent broad peak at 3442 cm^{-1} which corresponds to O-H/N-H stretching vibrations indicating the presence of phenols/alcohols, amine/amide and possibly carboxylic acid groups in the polymeric HA. The intensity of the two shoulder peaks at 2923 cm^{-1} and 2855 cm^{-1} could possibly correspond to the presence of asymmetrical C-H aliphatic alkane bands and symmetrical aliphatic carbon (CH_2), respectively (Tatzber *et al*., 2007; Rodrigues *et al*., 2008). The sharp peak at 1559 cm^{-1} can be assigned to the C=O stretching vibration in the carboxylate functional group or probably to the C=C stretching vibration in the aromatic ring or alkene groups. The peak at 1375 cm^{-1} could be assigned to the stretching and deformation of phenolic O-H or stretching vibrations of the C-O bond in alcohol or phenol and possibly bending vibrations of methyl groups. The absorbance at 1085 cm^{-1} is a characteristic band of C-OH stretching of aliphatics. While the peak at 1030 cm^{-1} represents the presence of C-O stretching of polysaccharide related substances or Si-O bending vibrations and the peak at 913 cm^{-1} could be characteristic fingerprint bands of aromatics (Tatzber *et al*., 2007). The data obtained in this present study was compared to the previous work done on commercial HA by other researchers and showed good agreement with previous data reported (Rodrigues *et al*., 2008; Liying *et al*., 2009; Jia *et al*., 2010).

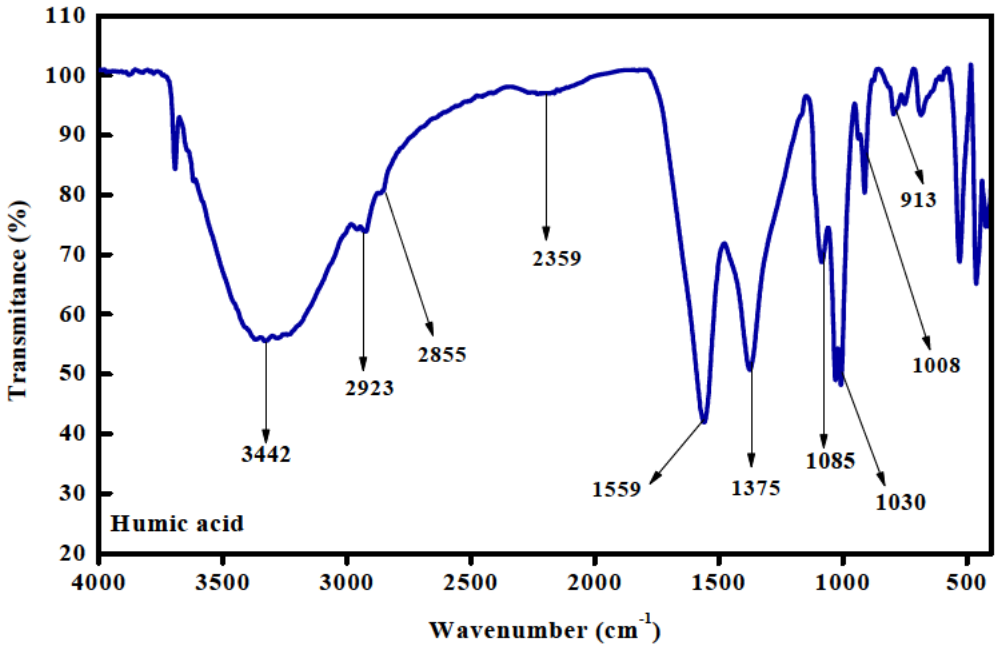


Figure 5.3: FTIR spectrum of HA

5.3.2 Effect of aqueous HA concentration

The effect of HA concentration on the sorption of PCBs onto soil was studied at a solution pH of 6.5 and the results shown in **Fig**. 5.4. The results revealed that an increase in the initial concentration of HA caused a reduction in the sorption of PCBs onto the soil, even though it was a very slight decrease. This could be attributed to the presence of hydrophobic HA in water that encourages aqueous solubility of PCBs due to the hydrophobic nature of the PCB congeners. Thus, more PCBs partition to the aqueous phase and less are partitioned to the soil. HA has been reported to serve as a water solubility enhancer for hydrophobic organic pollutants (Carter and Suffet, 1982; Chiou *et al*., 1986; Kile and Chiou, 1989; Peiyu *et al*., 2016). HA has a high molecular weight, the high carbon content is aromatic in nature and has a large non-polar volume with hydrophilic functional groups. PCBs have similar characteristics as HA but it is not soluble in water due to the non-existence of polar groups in PCBs. However, once PCBs are in water that contains HA, they become soluble due to the PCBs interaction with the HA which is already soluble in water. At the studied pH of 6.5, HA is sparingly soluble in water. Generally, aqueous solubility of HA increases as the solution pH increases and HA tends to precipitate at low solution pH values below 2.5. At a pH of 6.5, HA is partially soluble in water and forms hydrophobic aggregates, thus the

solubility of hydrophobic PCBs in water is primarily due to its partitioning into the hydrophobic portion of the HA aggregates. This result followed the same outcome of Chiou et al. (1983) who investigated the sorption of nonionic organic pollutants between soil organic matter and water and found that the partitioning process of nonionic pesticides is purely through hydrophobic interactions. One possible mechanism of interaction between hydrophobic PCBs and HA could best be explained to occur through π–π interactions. The benzene rings in PCB molecules act as π–acceptors, which enables free interactions with the electron-rich aromatic moieties of humic acid via π–π electron donor-acceptor interaction. Furthermore, research has shown that the pores (35 Å in size) of activated carbon becomes blocked when there are high concentrations of HA molecules in aqueous solution (Zhao and Vance 1998; Sharma et al. 2009). In the same way, soil particle pores may also become blocked when there is a high concentration of HA molecules in aqueous solution, thus explaining why there is a decrease in sorption of PCBs onto soil when HA concentration increases.

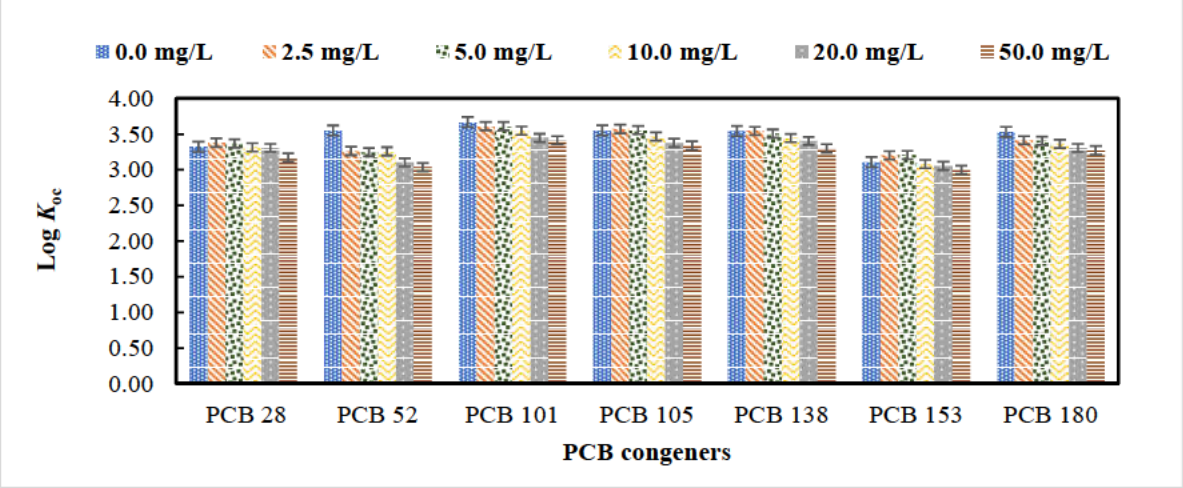


Figure 5.4: Effect of HA concentrations on the sorption of PCBs onto the soil mixture (pH 6.5, temperature = 25°C, mass of soil = 1 g, volume of HA solution = 10 mL)

5.3.3 Effect of pH

The amount of PCBs sorbed onto the individual studied soil particle sizes was investigated at different pH values ranging from 2.5 to 10.5. **Fig**. 5.5 and **Appendix C 2** shows the sorption of PCBs as a function of pH in aqueous solution of HA. The values of log K_{oc} (**Fig**. 5.5 and **Appendix**

C 2) were correlated with changes in the solution pH of HA. The results revealed that log K_{oc} values increased as the pH of HA solution decreased with the maximum adsorption occuring at pH 6-7. An increase in the log K_{oc} value at low pH of the soil solution indicated that there is more sorption of PCBs onto the soil SOM and HA mixture. This is because at a low pH value soil SOM combines with the larger HA aggregates thereby enhancing the sorption of PCBs to the soil (Pan *et al*., 2007). A change in the solution pH can affect the configuration of the organic content of the soil and consequently the partitioning of the PCB to the soil. An increase in the solution pH will lead to more solubility of HA in the aqueous phase, as well as a reduction in the hydrophobic sites in the soil SOM. This leads to more partitioning of PCBs to the aqueous phase and a decrease in PCB affinity for soil (Sebald, 2012).

The results of **Fig**. 5.5 (a-b) and **C 2** (a-b) in the **Appendix** showed that the sorption capacity of low chlorinated PCBs onto soil was higher than that of highly chlorinated PCBs. This could be due to the molecular size of PCBs playing a key role in its sorption onto the soil minerals (Peiyu *et al*., 2016). Tao *et al*. (2013) noted that the more chlorine atoms found on a PCB molecule, the larger is its molecular volume resulting in a change in the molecules surface area. This then leads to increased hydrophobicity thereby increasing its sorption to soil. It has been reported that large molecules that initially possess low aqueous solubility become more soluble in water containing HA. This is because the highly chlorinated PCBs tend to bind more strongly to the humic substrate present in aqueous solution. Humic acid has hydrophobic moieties which when partially dissolved in water may lead to water becoming more hydrophobic which originally is hydrophilic in nature, thereby encouraging more solubility of hydrophobic PCBs (low K_{oc} values) (Laundrum *et al*., 1984; Chiou *et al*., 1987; Chin and Weber, 1989). At low pH, the charges on HA tends to decrease which reduces its hydrophilic character with a corresponding increase in the hydrophobic tendency. HA tends to precipitate out but the highly chlorinated PCBs bind to the HA due to the hydrophobic character of the PCBs and the HA, resulting in low sorption to soil. This leads to low log K_{oc} values for highly chlorinated PCBs at low pH (PCBs 105, 138, 153 and 180). When pH increases, HA becomes more soluble in water and the hydrophobic PCBs that have interacted with the hydrophobic HA also becomes more soluble in the aqueous phase. This leads to even lower log K_{oc} values for the highly chlorinated PCBs.

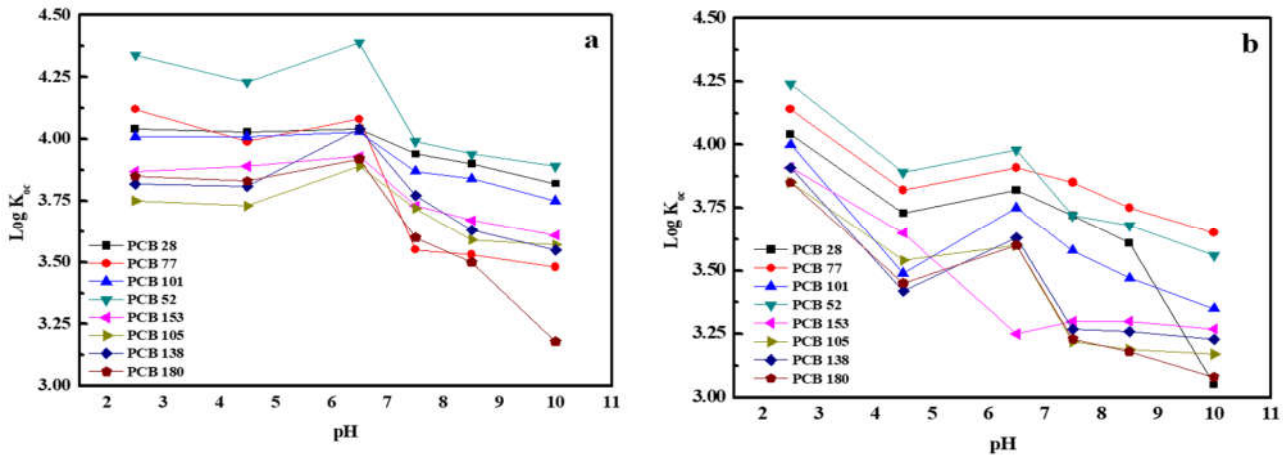


Figure 5.5: Effect of pH on the sorption of PCBs between an aqueous solution of HA (with a concentration of 20 mg/L at room temperature) and soil particle sizes. (a) 75 µm soil; (b) 100 µm soil.

5.3.4 Effect of temperature

In order to determine the effect of temperature on the sorption of PCBs between aqueous solutions of HA and soil particle sizes, batch adsorption experiments were carried out at different temperatures of 283, 288, 298, 303 and 313 K at pH 6.5. A 20 mg/L of HA solution was used in this study for the effect of pH, temperature, and concentrations of PCB.

The results are shown in **Fig**.5.6 a-b and **Appendix C 5** (a-c) revealed that low temperature encourages solubility of PCBs in the aqueous solution of HA thereby reducing the amount of PCBs sorbed onto the soil particle sizes. Carter and Suffet, (1982) reported that at low temperature between 282 to 298 K, the water solubility of hydrophobic OPs such as DDT increased. The sorption of PCBs onto different soil particle sizes was found to increase significantly as the temperature of HA solution was raised to 303 and 313 K. This could be as result of a decrease in the binding affinity of PCBs onto dissolved HA in water at high temperature. This then leads to an increased penetration of PCBs into the micropores of soils at higher temperatures, resulting in high percentage adsorption (**Fig**.5.6 a-b and **Appendix C 5** (a-c)).

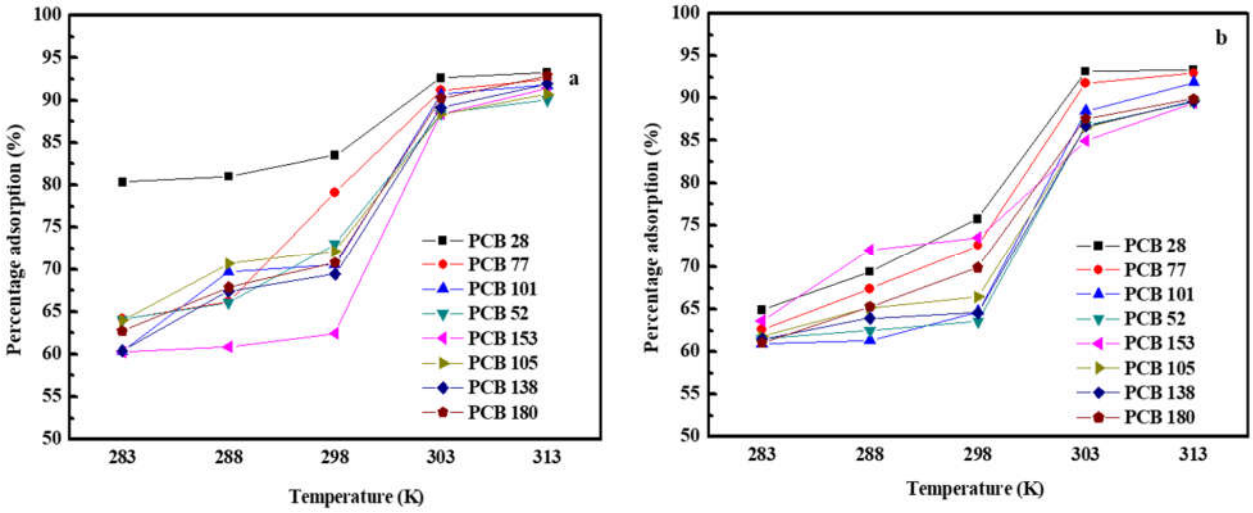


Figure 5.6: Effect of temperature on the sorption PCBs between aqueous HA and soil particle sizes. (a) 75 µm soil; (b) 100 µm soil

The sorption of PCBs onto different soil particles in the presence of HA was studied at 283, 293, 298, 303 and 313 K and the results are shown in **Table** 5.2 and **D 2 (**a-g**)** in the **Appendix**. $\Delta G°$ was calculated from equation 5.6 while $\Delta H°$ and $\Delta S°$ of the sorption were evaluated using equation 5.7. The results showed that the partition coefficient (K_d) increased with an increase in the solution temperature indicating that sorption of PCBs onto the soil was favoured by an increase in temperature. The $\Delta G°$ values at all temperatures were negative indicating that the sorption of PCBs to soil particle sizes was a spontaneous process and feasible. The sorption enthalpy ($\Delta H°$) of PCBs onto soil particle sizes from the aqueous solution of HA ranged from 39.23 to 73.74 kJ/mol and indicated that the sorption process was an endothermic process. Haung and Weber Jr., (1997) noted that sorption to soil/ sediment for nonionic chemicals are in most cases a negative enthalpy ($\Delta H°$) value while the sorption process is inversely dependent on the temperature. Hence, the positive and high enthalpy values observed in this current study could probably influence the aqueous solubility of PCBs enhanced by HA at low temperature. Hence, there is a reduction in aqueous solubility of PCBs at elevated temperature.

The positive and high values of $\Delta S°$ obtained in this study (**Table** 5.2) showed a high disorderliness in the solution. This indicates that the solution is in a state of "chaos" with random constant motion of the water molecules in the solution containing water and humic acid. However, the soil is more

stable and thus the PCBs find it easier to move towards the more stable soil than bond with the "chaotic" water phase. Hence, there is a weak interaction between PCBs and the liquid phase at high solution temperature during the sorption process and hydrophobic bonding between the PCBs and the soil. Thus, the sorption process is entropy driven and indicates that hydrophobic bonding was the main process involved in the sorption of PCBs from the solution. Large values of ΔS^{o} resulting from high temperature led to PCBs moving towards the soil leading to hydrophobic interactions but there could also be some London dispersion forces (i.e instantaneous dipole-induced dipole interactions) playing a role in the adsorption of PCBs onto the soil.

Table 5.2:

Thermodynamic studies of the interaction of PCB 28 with aqueous solution HA and soil particle sizes

Parameters	75 µm		100 µm		200 µm		300 µm		425 µm	
Temperature, K	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol
283	3.43	-8.07	2.14	-5.035	2.37	-5.575	2.08	-4.889	2.58	-6.061
293	3.49	-8.35	2.54	-6.088	3.16	-7.560	3.06	-7.318	2.71	-6.480
298	3.70	-9.18	3.06	-7.570	3.55	-8.786	3.51	-8.686	3.59	-8.902
303	4.76	-11.98	4.84	-12.192	4.53	-11.407	4.52	-11.378	4.58	-11.525
313	4.86	-12.64	4.87	-12.666	4.85	-12.623	4.58	-11.929	4.77	-12.405
$\Delta H°$, kJ/mol	39.229		73.737		60.448		61.464		60.586	
$\Delta S°$, kJ/(mol.K)	165.881		277.588		234.446		236.691		234.521	

5.3.5 Sorption isotherms

The effect of PCB adsorption onto soil in the presence of HA was investigated using batch adsorption experiments with initial PCB concentrations between 0.5 to 2.5 µg/mL at pH 6.5. The results of the sorption isotherms are shown in **Table** 5.3. Sorption of PCBs fitted best with the Freundlich model based on the R^2 values, which implied that the sorption of PCBs occurred

through a heterogeneous surface in soil particle grain sizes. The 1/n value of the Freundlich equation indicates the degree of nonlinearity and favourability between PCB solution concentration and adsorption. The following assumptions were used for the types of processes involved in the adsorption. The value of 1/n = 1 means the adsorption is linear; if 1/n < 1, then adsorption is a chemical process (strong bond) and if 1/n > 1, then a physical process (weak bond) is predominant in the adsorption (Desta, 2013; Qi *et al*., 2016). All the values of 1/n were found to be greater than 1 in this study and indicate that the adsorption is dominated by a physical process and the adsorption isotherm for the PCBs onto the soil that includes organic matter and hydrophobic aqueous HA interaction was nonlinear. The relatively high value of 1/n observed in this study could be due to the competition of PCB molecule interaction between HA in aqueous solution and soil for adsorption sites due to the presence of the hydrophobic character possessed by HA which encourages more solubility of PCBs in the aqueous phase.

Table 5.3:

Sorption isotherms of PCB congeners

PCB congeners	Freundlich				Langmuir			Log K_{oc}
	K_f, L/mg	1/n	N	R^2	q_m, mg/g	b, mL/µg	R^2	
PCB 28	1.795	5.988	0.167	0.8572	0.0175	0.0372	0.424	3.09
PCB 52	1.899	5.791	0.173	0.8923	0.0279	0.014	0.2287	3.40
PCB 77	1.299	4.135	0.242	0.8997	0.0226	0.043	0.5257	3.01
PCB 101	2.080	4.679	0.214	0.6654	0.0617	0.0788	0.4191	2.82
PCB 105	2.199	3.869	0.258	0.9271	0.1104	0.107	0.7536	2.76
PCB 138	3.059	4.209	0.238	0.8891	0.1940	0.2283	0.7989	2.69
PCB 153	3.183	4.439	0.225	0.8291	0.1575	0.1967	0.7172	2.70
PCB 180	5.072	3.980	0.251	0.8613	0.9517	1.095	0.7118	2.60

5.4 Conclusion

The role of the concentration of HA, pH and temperature on the sorption of PCBs onto soil particles were presented. It is evident that the solubility of hydrophobic PCBs in water was positively correlated with HA in the water phase. Aqueous HA solution with a low pH favoured the sorption of PCBs onto the soils.

Partition coefficient (K_d) values for the PCB congeners increased with an increase in solution temperature. Thermodynamic studies revealed a negative value for $\Delta G°$ demonstrating that the PCB interactions between HA solution and soil particle sizes were a spontaneous process. The high values of $\Delta H°$ and $\Delta S°$ in this study indicated that the sorption of PCBs was an endothermic and entropy driven process.

The isotherm results showed that the sorption was best fitted for the Freundlich model with the intensity parameters 1/n greater than 1 indicating that sorption of PCBs is heterogenous nonlinear and a physical process.

The results of this study suggest the following:

The presence of water-soluble organic particulate matters such as humic substances in the aquatic environment may enhance the dissolution of more organic pollutants in water thereby resulting in more pollution of water bodies.

Interaction of hydrophobic contaminants with soil particle mineral components may facilitate the contaminants mobility onto the soil minerals, with consequent reduction in pollutants concentrations in the water body.

Secondary pollution of river water may possibly be altered depending on variations in environmental conditions such as pH and temperature. However, the presence of organic pollutants in alkaline soils having less organic matter content could increase the chances of leaching of organic pollutants causing ground water contamination.

Soil rich in HA concentration will tend to pose less of a risk of HOCs such as PCBs to the aquatic environment.

Acknowledgments

The authors sincerely acknowledge the University of KwaZulu-Natal and School of Chemistry and Physics at UKZN for laboratory facilities.

REFERENCES

Basel Convention 2003. Technical guideline for the environmentally sound management of the full and partial dismantling of ships. United Nations Environment Program. Available from:http://www.basel.int/Portals/4/Basel%20Convention/docs/meetings/sbc/workdoc /techgships-e.pdf. *Accessed* 03/06/2017.

Buckley-Golder, D., (1999). Compilation of EU dioxins exposure and health data. Summary report for European Commission DG Environment and the UK Department of the Environmental Transport and the Regions. Available from: http://www.greenpeace.se/ files/file_72.pdf. *Accessed* 29/05/ 2017.

Carter, C. W., and Suffet I. H., (1982). Binding of DDT to dissolved humic materials. *Environ. Sci. Technol.* **16**, (11): 735-740.

Chefetz, B., and Xing, B., (2009). Relative role of aliphatic and aromatic moieties as sorption domains for organic compounds: A review. *Environ. Sci. Technol.* **43**: 1680–1688.

Chin, Y. P., and Webber, W. J. Jr, (1989). Estimating the effects of dispersed organic polymers on the sorption of contaminants by natural solids.1.A Predictive thermodynamic humic substance-organic solute interaction model. *Environ. Sci. Technol.* **23**: 978-984.

Chiou, C. T., Malcolm, R. L., Brinton, T. I., Kile, D. E., (1986). Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environ. Sci. Technol*. **20**: 502-508

Chiou, C. T., Kile, D. E., Rutherford, D. W., Sheng, G., Boyd, S. A., (2000). Sorption of selected organic compounds from water to a peat soil and its humic-acid and humin fractions: Potential sources of the sorption nonlinearity. *Environ. Sci. Technol.* **34**, (7): 1254–1258.

Chiou, C. T., Kile, D. E, Brinton, T. I., Malcolm, R. L., Leenheer, J. A., MacCarthy, P., (1987). A comparison of water solubility enhancements of organic solutes by aquatic humic materials and commercial humic acids. *Environ. Sci. Technol*. **21**: 1231-1234.

Chiou, C. T., Porter, P. E., Schmeddling, D. W., (1983) Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environ. Sci. Technol*. **17**: 227—231.

Claret, F., Schafer, T., Bauer, A., Buckau, G., (2003). Generation of humic and fulvic acid from Callovo-Oxfordian clay under high alkaline conditions. *Sci. Total Environ*. **317**: 189–200.

Clark Ehlers, G. A., Forrester, S. T., Scherr, K. E., Loibner, A. P., Janik, L. J., (2010). Influence of the nature of soil organic matter on the sorption behaviour of pentadecane as determined by PLS analysis of mid-infrared DRIFT and solid-state 13C NMR spectra. *Environ. Pollut.* **158**: 285–291.

Colborn, T., Dumanoski, D., Myers, J. P., (1996). Our Stolen Future Ed. 1996; New York, USA: Dutton. pp 306.

Desta, M. B., (2013). Batch sorption experiment: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto Teff Straw (Eragrostis tef) agricultural waste. *J. Thermodyn*. **6**: 1-6.

Ding, G., Mao, J., Herbert, S., Amarasiriwardena, D., Xing, B., (2001). Spectroscopic evaluation of humin changes in response to soil managements. In: Ghabbour, E.A., Davies, G. (Eds.), Humic Substances. Structures, Models and Functions. The Royal Society of Chemistry, Cambridge, UK, pp. 271.

Gauthier, T.D., Seitz, W.R., Grant, C.L., (1987). Effects of structural and compositional variations of dissolved humic materials on pyrene Koc values. *Environ. Sci. Technol.* **21**, (3): 243– 248.

Gerstel, Z., (1990). Estimation of organic chemical sorption by soils. *J. Contam. Hydrol.* **6**: 357–375.

Grathwohl, P., (1990). Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on Koc correlations. *Environ. Sci. Technol.* **24**: 1687−1693.

Guthrie-Nichols, E., Grasham, A., Kazunga, C., Sangaiah, R., Gold, A., Bortiatynski, J., Salloum, M., Hatcher, P., (2003). The effect of aging on pyrene transformation in sediments. *Environ. Toxicol. Chem*. **22**, (1): 40–49.

He, Y., Liu, Z., Zhang, J., Wang, H., Shi, J., Xu, J., (2011). Can assessing for potential contribution of soil organic and inorganic components for butachlor sorption be improved? *J. Environ. Qual.* **40**: 1705−1713.

Hiller, E., Jurkovic, L., Bartal, M., (2008). Effect of temperature on the distribution of polycyclic aromatic hydrocarbons in soil and sediment. *Soil and Water Res.* **3**: 231 240.

Hu, D., and Hornbuckle, K. C. (2010). Inadvertent polychlorinated biphenyls in commercial paint pigments. *Environ. Sci. Technol.* **44**, (8): 2822–2827

Huang, W., Peng, P., Yu, Z., Fu, J., (2003). Effect of organic matter heterogeneity on the sorption and desorption of organic contaminants by soils and sediments. *Applied Geochem.* **18**: 955-972.

Jia, C., You, C., Pan, G., (2010). Effect of temperature on the sorption and desorption of perfluoroactane sulfonate on humic acid. *J. Environ. Sci.* **22**, (3): 355-361.

Kile, D. E., and Chiou, C. T. (1989). Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration. *Environ. Sci. Technol.* 23: 832-838.

Kordel, W., Dassenakis, M., Lintelmann, J., Padberg, S. (1997). The importance of natural organic material for environmental processes in waters and soils. *Pure and Appl. Chem.* **69**: 1571-1600.

Landrum, P. F., Nihart, S. R., Eardie, B. J., Gardner, W. S., (1984). Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural water. *Environ. Sci. Technol.* **18**: 187-192.

Liying, S., Weiling, S., Jinren, N. I. (2009). Partitioning of water soluble organic carbon in three sediment size fractions: Effect of the humic substances. *J. Environ. Sci.* **21**: 113-119.

Leung, A., Cai, Z. W., Wong, M. H. (2006). Environmental contamination from electronic waste recycling at Guiyu, southeast China. *J. Mat. Cycles and Waste Manag.* **8**, (1): 21–33.

Luthy, R. G., Aiken, G. R., Brusseau, M. L. Cunningham, S. D., Gschwend, P.M., Pignatello, J. J, Reinhard, M., Traina, S. J., Weber, W. J., Westall, J. C., (1997). Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* **31**, (12): 3341–3347.

Maie, N., Watanabe, A., Kimura, A., (2004). Chemical characteristics and potential source of fulvic acids leached from the plow layer of paddy soil. *Geoderma*, **120**, (3-4): 309-323.

Ogram, A.V., Jessup, R. E., Ou, L.T., Rao, P.S., (1985). Effects of sorption on biological degradation rates of (2, 4-dichlorophenoxy) acetic acid in soils. *Appl. Environ. Microbiol.* **49**, (3): 582–587.

Pan, B. O., Ghosh, S., Xing, B., (2007). Nonideal binding between dissolved humic acids and polyaromatic hydrocarbons. *Environ. Sci. Technol*. **41**, (18): 6472-6478.

Park, J. H., Feng, Y., Ji, P., Voice, T. C., Boyd, S. A., (2003). Assessment of bioavailability of soil- sorbed atrazine. *Appl. Environ. Microbiol*. **69**, (6): 3288–3298.

Peiyua, L., Luping, X., Hui, X., Wen, X., (2016). Research of adsorption on PCBs: Isotherm modeling and influencing factors. MATEC Web of Conferences, 67: 06030

Pirbazari, M., Ravindran, V., Wong, S. P., Stevens, M. R., (1989). Adsorption of micropollutants on activated carbon. In Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, eds. I. H., Suffet, P., MacCathy. American Chemical Society Series, New York. pp 549-578.

Rao, P. S. Bellin, C. A., Brusseau, M. L., (1993). Coupling biodegradation of organic chemicals to sorption and transport in soils and aquifers: Paradigms and paradoxes. In sorption and degradation of pesticides and organic chemicals in soil; Linn D. M., Carski T. H.,

Brusseau M. L., Chang A. C., Eds., SSSA and ASA: Madison, WI, 1993; Vol. SSSA Spec. Publ. 32, pp 1- 26.

Ray, A. B., Ma, J., Borst, M., (1995). Adsorption of surfactant on clays. *Hazard. Waste Hazard. Mater*. **12**: 257-364.

Riffaldi, R., Levi-Minzi, R., Saviozzi, A., Benetti, A., (1998). Adsorption on soil of dissolved organic carbon from farmyard manure. *Agric. Ecosyst. Environ.* **69**: 113–119.

Rodrigues, A., Brito, A., Janknecht, P., Proenca, M.F., Nogueira, R., (2008). Quantification of humic acids in surface water: effects of divalent cations, pH, and filtration. *J. Environ. Monit.* **11**: 377-382.

Rutherford, D. W., Chiou, C. T., Kile, D. E., (1992). Influence of soil organic matter composition on the partition of organic compounds. *Environ. Sci. Technol.* **26**, (2): 336–340.

Schnurer, Y., Persson, P., Nilsson, M., Nordgren, A., Giesler, R., (2006). Effects of surface sorption on microbial degradation of glyphosate. *Environ. Sci. Technol.* **40**, (13): 4145–4150.

Scow, K. M., (1993). Effect of sorption-desorption and diffusion processes on the kinetics of biodegradation of organic chemicals in soil. In Sorption and Degradation of Pesticides and Organic Chemicals in Soil; Linn, D. M., Carski, T. H., Brusseau, M. L., Chang, F. H., Eds.; SSSA and ASA: Madison, WI, Vol. SSSA Spec. Publ. 32. pp 73-114.

Sebald, W., (2012). Yellow River Tou Dao Guai section of the PCBs distribution characteristics and adsorption mechanism. Inner Mongolia, Inner Mongolia Agricultural University. 15-48.

Sharma, B., Gardner, K.H., Melton, J., Hawkins, A., Tracey, G., (2009). Effect of humic hcid on adsorption of polychlorinated biphenyls onto organoclay. *Environ. Eng. Sci.* **26**, (8): 1279-1287.

Shen, Y. H., (2000). Sorption of non-ionic surfactants to soil: the role of soil mineral composition. *Chemosphere*. **41**: 711-716.

Shirshova, L.T., Ghabbour, E. A., Avis, G., (2006). Spectroscopic characterization of humic acid fractions isolated from soil using different extraction procedures. *Geoderma*, **133**, (3-4): 204-216.

Tao, C., Chengxun, S., Weiwe, C., (2013). Effects of surfactants on the absorption of PCBs on soil. *Environ. Pollut. Control*. **35**: 59-64.

Tatzber, M., Stemmer, M., Spiegel, H., Katzlberger, C., Haberhauer, G., Axel Mentler, A., Gerzabek, M. H., (2007). FTIR-spectroscopic characterization of humic acids and humin fractions obtained by advanced NaOH, $Na_4P_2O_7$, and Na_2CO_3 extraction procedures. *J. Plant Nutr. Soil Sci*. **170**: 522–529.

UNEP, United Nation Environmental Programme (2001). Text of the Stockholm Convention on Persistent Organic Pollutants and implementation activities; amended 2009. United Nations Environment Programme Available from: http://chm.pops.int/ The Convention/Overview/Text of the Convention/ tabid/2232. *Accessed* 24/06/2017.

UNEP, United Nation Environmental Programme (2004). Guidance for a Global Monitoring programme for persistence organic pollutants, 1st edition, June 2004. United Nations Environment Programme, Chemicals, Geneva, Switzerland. For download: http//www.chem.unep/gmm/Guidance GPM.pdf old version. *Accessed* 24/06/2017.

UNEP, United Nation Environmental Programme (2009). Sustainable Innovation and Technology Transfer Industrial Sector Studies: Recycling – From E-waste to Resources. United Nations Environment Programme. Available from: http://www.unep.org/pdf/Recycling_From_e-waste_to_resources.pdf. *Accessed* 24/06/2017.

UNEP, United Nation Environmental Programme (2011). The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal. United Nations Environment Programme. Available from: http://www.basel.int/Portals/4/Basel%20Convention/docs/text/ BaselConventionText-e.pdf. *Accessed* 24/06/2017.

Van Loosdrecht, M.C., Lyklema, J., Norde, W., Zehnder, A. J., (1990). Influence of interfaces on microbial activity. *Microbiol. Mol. Biol. Rev*. **54**, (1): 75–87.

Warren, N., Allan, I. J., Carter, J. E., House, W. A., Parker, A., (2003). Pesticides and other micro-organic contaminants in freshwater sedimentary environments—a review. *Appl. Geochem.* **18**: 159–194.

Weber, W. J Jr, Smith, E. H., (1989). Effects of humic background on granular activated carbon treatment efficiency. In Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, eds. I. H, Suffet P, MacCathy. American Chemical Society Series, New York. pp 501-532.

Wilmanski, K., Breemen, A. N. V., (1990). Competitive adsorption of trichloroethylene and humic substances from groundwater on activated carbon. *Water Res.* **24**: 773-779.

Zhao, H., Vance, G. F., (1998). Sorption of trichloroethylene by organoclays in the presence of humic substances. *Water Res.* **32**: 3710-3716.

CHAPTER 6

MANUSCRIPT 3

Effect of sorbate stereochemistry on the sorption/desorption of polychlorinated biphenyls between natural soil and an aqueous solution

Gbadebo Clement Adeyinka and Brenda Moodley*

School of Chemistry and Physics, College of Agriculture, Engineering and Sciences, University of KwaZulu-Natal, Private Bag X54001, Westville, 4000, Durban, South Africa. E-mail: adeyinkagbadebo78.ga@gmail.com

*Corresponding author; e-mail: Moodleyb3@ukzn.ac.za. Tel: +27 31 260 2796; Fax: + 27 31 2603091

ABSTRACT

Sorbate characteristics may play an important role in the transportation, distribution, fate, and bioavailability as well as remediation of hydrophobic organic pollutants in the environment. The role of chemical characteristics (stereochemistry) on the sorption of polychlorinated biphenyls (PCBs) onto the natural soil collected from uMngeni River of KwaZulu-Natal province of South Africa was investigated in this study. Non-ortho and ortho-substituted PCBs were selected for this study. Soil physicochemical properties were characterized using Walkley Black, cation exchange capacity, BET adsorption-desorption, and FTIR methods. Batch adsorption experiments were used for the sorption studies. The results indicated that non-ortho compounds were found to sorb more to the soil compared to the di-ortho substituted congener of the same homolog. The effect of initial concentrations of both non-ortho and ortho-substituted PCBs revealed that low initial PCB concentrations were mostly favoured for the sorption while sorption was generally low for ortho-substituted PCBs at high concentration. This could be because of soil interlayer pore blockage which is influenced by the position of the chlorines. The sorption/desorption of PCBs was found to be dependent on the PCB chemical properties, such as stereochemistry and their hydrophobicity character. Ortho-substituted congeners are more likely to be susceptible to aqueous solubility and re-suspended back to surface water or leach to the groundwater when sorbed by soil and may possibly pose more risk to the aquatic ecosystem relative to its non-ortho substituted congener of the same homolog.

Keywords: *Stereochemistry, polychlorinated biphenyls, ortho-substituted and non-ortho-substituted soil, sorption studies, uMngeni River*.

6.1 Introduction

The polychlorinated biphenyl (PCB) is a class of hydrophobic contaminants consisting of 209 different congeners, however out of these, less than half have been detected in reasonable amounts in the environment (Metcalfe, 1994). In the past, analysis of PCBs had been based purely on the commercial mixture such as Aroclor, Kaneclor (Duinker *et al*., 1991). However, the need to treat and analyze PCBs as individual congeners rather than commercial mixtures was widely accepted by the late 1980s because processes such as bioaccumulation, metabolism, and toxicity could vary significantly based on individual congener composition (Duinker *et al*., 1989). All PCB congeners can be classified into two major sub-groups based on the position of chlorination and their toxicity. The first group contains 12 PCB congeners, which are referred to as dioxin like-PCBs (DL-PCBs) or planar PCBs (non-ortho-substituted). The name was assigned due to their relatively fewer or no chlorine atoms at the ortho-position (position 2 and 2') (**Fig.** 6.1**)** of the phenyl rings which allows them to rotate freely and assume planar positions, and also to their toxicity resemblance to dioxins such as polychlorinated dibenzodioxins/dibenzofurans (PCDD/Fs) in animals and humans. These congeners have been assigned toxicity equivalency factors (TEF) like that of dioxins, for example, both PCB 77 and PCB 105 have a TEF of 1×10^{-5} assigned by WHO in 1998 but PCB 105 was revised in 2005 to 3×10^{-5} (Van den Berg *et al*., 2006). PCBs are also considered more toxic due to their action with an aryl hydrocarbon (the binding and ligand-activated molecule that controls and mediates the activity of a gene) which could result in immune system suppression and carcinogenic effects in animals and possibly in humans (Safe, 2001; Okey, 2007). The second group is referred to as non-dioxin-like PCBs (NDL-PCBs) which comprises the remaining 197 congeners (Loran *et al*., 2010). This group has chlorine atoms at both position two (ortho-positions) and sometimes even at the para positions. This makes it more difficult for congeners in this group to assume a planar position and rotate freely. The NDL-PCBs also have their own toxicological profile but are less toxic than DL-PCBs. PCBs were previously widely used in industrial applications such as, hydraulic and heat transfer equipment, as insulating fluids in transformers and capacitors, electrical, plasticizers in paints, elastic polymers, surface coating materials and carbonless copy paper (ATSDR, 2000; Erickson, 2001; Erickson & Kaley, 2011). The production and use of PCBs has stopped in most countries, which has led to the regional decrease in the concentration of PCBs. However, a world-wide reduction in PCB concentrations may be mostly impossible especially in developing countries due to continual inputs into the

environment. These inputs include possible leakages from landfill sites and emissions from incinerators of old equipment containing PCBs, unauthorised disposal of PCB wastes, and undetected seepage from electrical transformers (Tanabe, 1988; UNEP, 2001; UNEP, 2009; Hu and Hornbuckle, 2010; UNEP, 2011). In addition, PCBs are widely detected in all environmental matrices (Ghosh *et al*., 2003; King *et al*., 2004; Wurl and Obbard, 2005) and have been detected even in distant locations, such as the Arctic and Antarctic (Ballschmiter *et al*., 1997; Stegeman *et al*., 2001). PCBs are resistant to degradation, and humans exposure is through ingestion of contaminated food and sometimes through inhalation and dermal absorption (ATSDR, 2000; IOM, 2003). PCBs are highly hydrophobic in nature, have extremely low water solubilities, which range between 1 x 10^{-5} to 1.21 mg/L, and are thus soluble in many organic solvents (Hutzinger *et al*., 1974b; ATSDR, 2000).

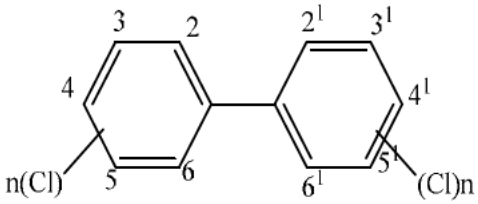


Figure 6.1: General basic structure of PCBs (Created - Used Chem Office 2015 version)

Hydrophobic organic contaminants (HOCs) tend to partition to soil/sediment organic carbon when they reach aquatic systems. Therefore, the distribution of HOCs such as PCBs in the environment is controlled by many factors, one of them being soil/sediment properties such as amount and types of colloids (organic matter content) present, pore volume and particle size distribution, water content, and mineral surfaces present (Weber and Weed, 1974). The major site available for sorption in soil/sediment is the internal pores that have a fixed, flat arrangement, and the heterogeneous, aromatic, carbon containing geosorbents referred to as soil/sediment organic matter (SOM) (Cornelissen *et al*., 2005; Jonker and Koelmans, 2002). Solution physicochemical parameters such as pH, temperature, and ionic strength are important as well. The pollutant characteristics such as polarity, ionizability, volatility, molecular size, aqueous solubility and hydrophobicity as well as stereochemistry or branching of attached groups are highly important for the determination of a pollutant's fate (sorption, bioavailability, transformation) in the

environment (Belfort, 1979; Rao and Asolekar, 2001). Partitioning to black carbon (BC) has been reported for planar (non-ortho) compounds, such as PAHs (Jonker and Koelmans, 2002) and planar (non-ortho) PCBs (Bucheli, and Gustafsson 2003; You *et al*., 2007). The non-ortho compounds were found to enter the internal pores of the soil particles where they interact with aromatic pore walls by π–π interactions, and similar interactions were involved for the sorption of non-ortho compounds to the geosorbent surface. In addition, previous studies by Bucheli, and Gustafsson (2003) on planar (non-ortho) and nonplanar (mono or di-ortho substituted) PCBs revealed that sorption to pure diesel soot is approximately 10 times stronger for non-ortho PCBs than for ortho-substituted ones of the same hydrophobicity. Even though there have been many studies conducted on the presence of HOCs such as PAHs, PCBs and diuron in sediment mixed with activated carbon, limited studies have been carried out on interactions of HOCs with natural sediment (Zimmerman *et al*., 2004; Millward *et al*., 2005; Sun and Ghosh, 2007: Kathleen *et al*., 2008). The adsorption of HOCs with differing chemical properties, onto OC and BC, and the influence of natural BC in sediment on the bioavailability to aquatic species has also been investigated (Gustafsson *et al*., 1997; Jonker and Smedes, 2000; Cornelissen *et al*., 2004, 2005). The result indicated that the presence of BC that affects the bioavailability of HOCs depends not only on the type and on concentration of BC present, but also the stereochemistry of the HOCs. Thus, the partitioning and interactions of differently orientated PCBs (non-ortho and ortho-substituted) between the aqueous solution and natural soil also requires further research. The objectives of this current study were to: (i) selectively study the sorption of a non-ortho PCB such as PCB 77, and ortho-substituted PCB of the same homolog (PCB 52), (ii) assess the steric effect of other PCB congeners on the sorption of the selected non-ortho and ortho-substituted congener onto the natural soil, (iii) determine the effect of aqueous concentration of non-ortho and ortho-substituted PCB congeners on its partitioning and (iv) investigate the hydrophobicity effect of eight PCB congeners for the sorption/desorption process.

Eight indicator PCB congeners (PCB 28, PCB 52, PCB 77, PCB 101, PCB 105, PCB 138, PCB 153, and PCB 180) (**Fig.** 6.2), were chosen because they are recommended by the Stockholm Convention on persistent organic pollutants (POPs) and the International Council for the Exploration of the Sea (ICES) to characterize and systematically monitor in the environment (WHO, 2010). It was expected that the outcome of this study will contribute significantly to the knowledge on how orientation (stereochemistry) of PCB congeners influence the distribution

between aqueous solution and interlayer surface of natural soil components which will aid in pollutant remediation studies.

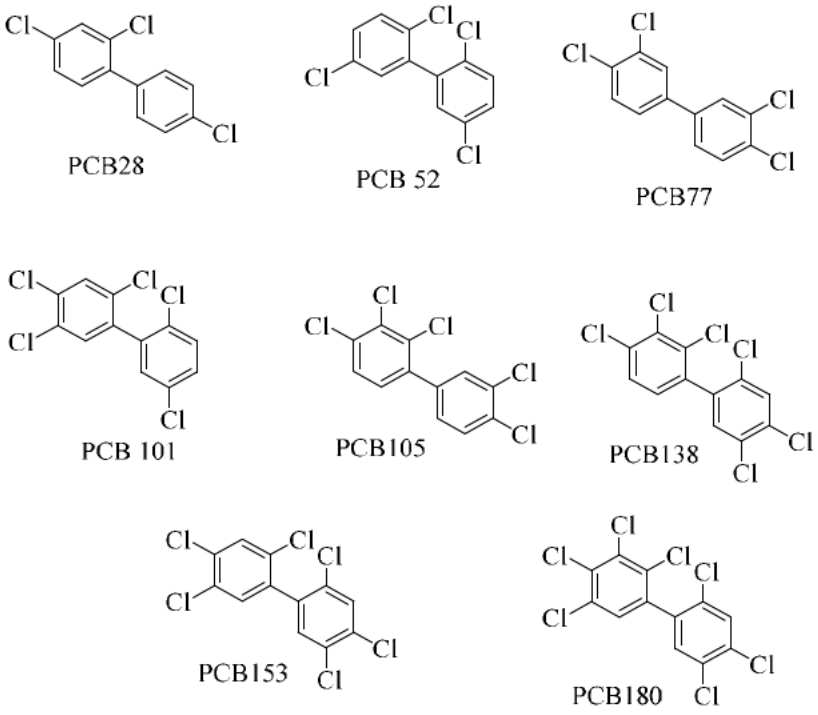


Figure 6.2: Structures of PCB congeners (Created - Used Chem Office 2015 version)

6.2 Materials and methods

6.2.1 Soil sample

A natural soil sample was obtained from uMngeni River of KwaZulu-Natal province of South Africa. Detailed characterization of soil used for this study has been discussed in chapter 4. Briefly, the soil physicochemical parameters such as SOM, cation exchange capacity (CEC), carbon-nitrogen ratio, and surface areas were determined using the Walkley Black method (wet oxidation), the barium chloride compulsive exchange method, TruMac LECO CNS-2000 analyzer (LECO Corporation, USA), and the Brunauer-Emmet-Teller (BET) method, respectively. The surface morphology and elemental analysis that identified the weight percentage of all elements present in the soil sample were determined by scanning electron microscopy (SEM) equipped with an elemental diffraction X-ray (EDX) system for qualitative and elemental mapping. The

microphotograph was recorded using Concise FEGSEM 6100 Zeiss Ultra Plus Germany at an accelerated voltage of 20.0 kV with secondary electrons in low vacuum mode. The soil functional groups were determined using fourier transform infrared spectroscopy (FTIR) (Precisely spectrum 100 Perkin Elmer, USA).

6.2.2. Reagents and chemicals

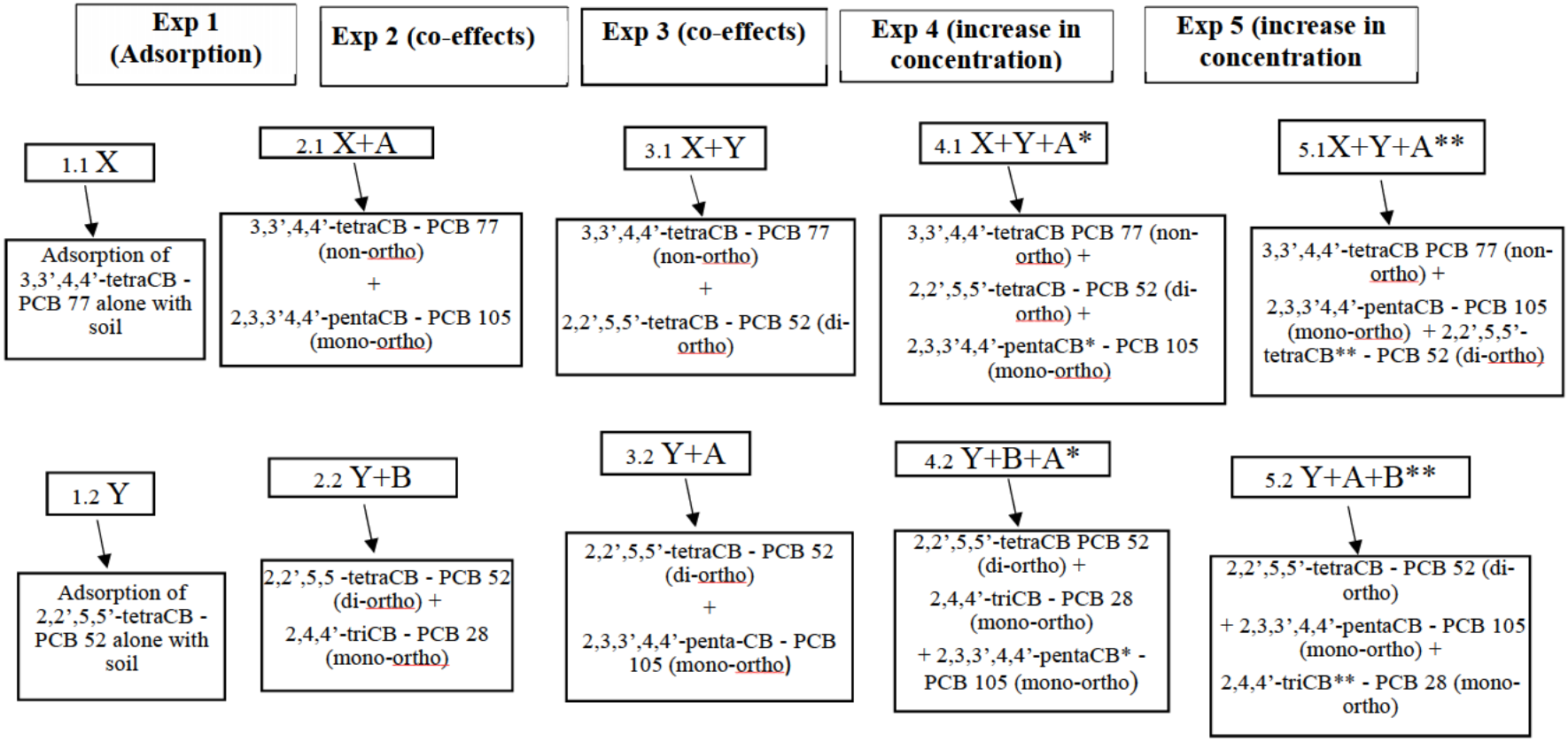
The details for the reagents and chemicals used in this work have been provided in chapters 3 and 4.

6.2.3 Batch sorption experiments

The standard batch sorption equilibration method as described by USEPA, 2000 (OECD 106, 107 methods) and Karickhoff *et al*. (1979) was used to determine the sorption characteristic of selected non-ortho and ortho-substituted PCBs between the aqueous solution and the natural soil sample. The effect of planar (non-ortho) and nonplanar (ortho) PCBs, as well as the influence of molecular structure on the sorption of PCB congeners, were investigated. A set of six stainless centrifuge tubes containing approximately 1 g of soil sample, each together with 10 mL aliquots of 0.01 mol/L $CaCl_2$, added to minimize the CEC and to improve centrifugation, was used to conduct the sorption experiments. The soil solutions were spiked with 1.0 µg/mL of the 3,3',4,4'-tetraCB (non-ortho substituted – PCB 77) in the first tube and a similar procedure was performed for 2,2',5,5'-tetraCB (di-ortho substituted – PCB 52). The details of the experimental setup of non-ortho and ortho-substituted congeners, as well as co-effects on the sorption of non-ortho-substituted and ortho-substituted congeners is presented in **Fig.** 6.3. Another set of experiments were conducted to determine if there was any possible competition among PCBs. This involved spiking soil solutions with 1.0 µg/mL mixtures of all the selected eight PCB congeners investigated in this study. Sorption isotherm equilibrium studies were investigated in the concentration range of 0.5–5 µg/mL. The experiments were conducted at room temperature (24ºC) and the solution pH of 6.5 was maintained due to preliminary investigations, which found a pH value near neutral was most suitable for the sorption of selected PCB congeners (details in Chapter 4). The samples were placed on an orbital shaker LABCOM for 24 h at a speed of 350 rpm to allow for partitioning of the PCBs

to the soil particles. Our preliminary kinetic experiments showed that an equilibrium period of 24 hr was sufficient to achieve an equilibrium for PCBs to partition between aqueous solution and soil and has been discussed in chapter 4. The soil slurry was thereafter separated by centrifugation at 6000 rpm for 30 min (Rotofix 32A Hettick Zentrifugen, Germany). The supernatant was extracted three times using 5 mL dichloromethane (DCM) aliquots each time.

Another experiment was conducted immediately after batch adsorption to evaluate the degree of desorption of PCB congeners from the soil to the water system. This was carried out using a decant-refilled method by thoroughly decanting the incubated solution and replacing it with a fresh background solution containing the same concentration of $CaCl_2$ and NaN_3 but no PCBs. To establish the amount of soil remaining in the tube, before conducting desorption experiments, the tube together with the soil was weighed and recorded. The mass of the empty tube, which was weighed at the start of the adsorption experiments, was then subtracted from this mass. Desorption experiments were conducted for PCBs within 12 h. This was repeated and showed no significant amount of PCB was measured in the aqueous solution after the second cycle. The amount of PCBs remaining in the soil sample at each desorption stage was determined as the difference between the initially sorbed amount and the final desorbed amount. All the experiments were carried out in duplicate. Recovery studies and all the quality control measures were carried out as enumerated in chapters 3 and 4 and the percentage recoveries were in the range of 95 – 102%.



X = 3,3',4,4'-tetraCB (non-ortho); Y = 2,2',5,5'-tetraCB (ortho); A = 2,3,3'4,4'-pentaCB (ortho); B = 2,4,4'-triCB (ortho)

* = Increased the concentration of penta-CB in X and Y while keeping the concentrations of other two congeners constant, ** = Increased the concentration of di-ortho-substituted in X and mono-ortho-substituted in Y while keeping the two congeners concentrations constant. (A) 3,3',4,4'-tetraCB, (B) 2,4,4'-triCB

Figure 6.3: Experimental procedure followed to determine the co-effects of PCBs on the sorption of non-ortho and di-ortho-substituted congeners

6.2.4 Data treatment

The amount of PCBs removed from solution was calculated from the initial (C_o) and final (C_e) concentrations in solution after the equilibration period using Eq. (6.1). The partition coefficient (K_d) and percentage sorption were determined using Eqs. (6.2) and (6.3), respectively.

$$q_e = \left(\frac{C_o - C_e}{m}\right) V_o \qquad (6.1)$$

$$K_d = \left(\frac{C_o - C_e}{C_e}\right) \frac{V_o}{m} \qquad (6.2)$$

$$A_{ti} = \frac{M_s^{ads}(t_i)}{M_o} \times 100 \qquad (6.3)$$

where, q_e is the amount of PCBs sorbed (mg/kg), C_o (mg/L) is the initial concentration, C_e (mg/L) is the aqueous concentration at the equilibrium, V_o (L) is the volume of the solution used, m (g) is the mass of the soil and K_d is the partition coefficient. M_o (mg) is the mass of the test substance in the test tube at the beginning of the experiment and was determined using the following expression: $M_o = V_o \cdot C_o$. M_s^{ads} (mg) is the mass of the test substance adsorbed onto the soil and was determined using the expression $M_s^{ads} = M_o - C_{aq}^{ads} t_i \cdot V_o$, where t_i is time at equilibrium and C_{aq}^{ads} at t_i. is the concentration of the adsorbed substances in aqueous phase (mg/L) at time t_i (s) which is further used to determine the percentage adsorption of the PCBs onto the soil samples after the batch adsorption experiments.

6.2.5. GC-MS analysis

The details regarding GC-MS analysis were provided in chapters 3 and 4.

6.3 Results and discussion

6.3.1 Effect of stereochemistry

The effect of stereochemistry on the sorption of non-ortho and ortho PCBs between natural soil and the aqueous solution was investigated using batch sorption experiments. The results, as shown in **Fig.** 6.4, revealed that non-ortho congener (3,3',4,4'-tetraCB – PCB 77) was found to have a slightly higher sorption onto the soil compared to the corresponding ortho-substituted (2,2',5,5'-

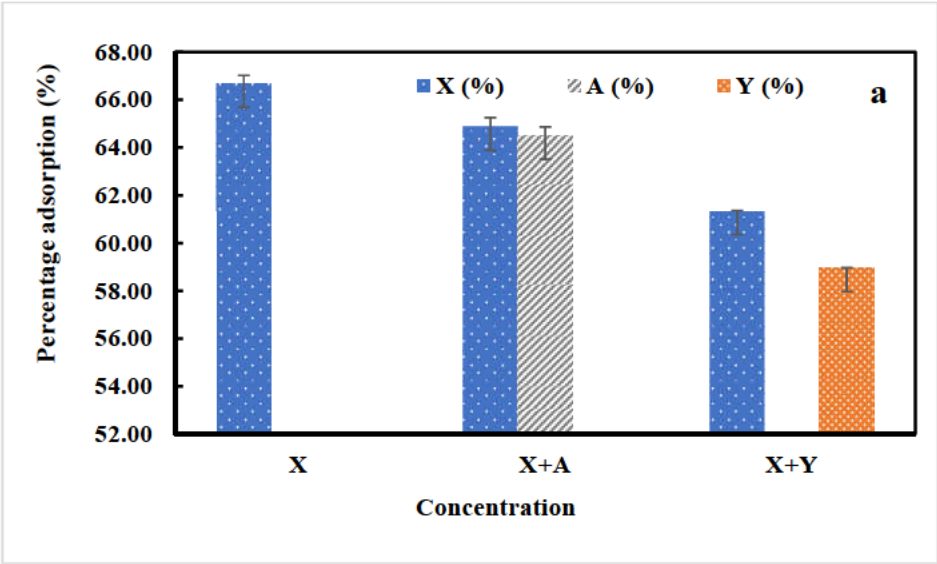
tetraCB – PCB 52) congener of the same homolog. The lower sorption of ortho-substituted (2,2',5,5'-tetraCB – PCB 52) could be attributed to the stereochemistry of PCB 52 that prevents it from assuming a coplanar conformation. This is due to the steric hindrances of chlorine atoms in the ortho position which may restrict free rotation around the 1, 1' carbon bond. Jonker and Koelmans, (2002), and Cornelissen *et al*. (2004) investigated the sorption capacity of various forms of soot and soot-like materials, and BC for non-ortho and ortho-substituted HOCs. The results revealed that HOCs of similar hydrophobicity but different stereochemistry were found to sorb to BC differently. It was noted that adsorption of ortho-substituted HOCs was lower than that of non-ortho compounds of similar hydrophobicity (having the same number of chlorine atoms around the phenyl rings) on various forms of BC soot and soot-like materials. Cortes *et al*. (2009) also investigated the sorption of three selected non-ortho, three mono-substituted and five di-ortho-substituted PCB congeners on the soil samples collected from Dystric Gleysols in a forested area near Lake Maggiore, Italy. The outcome of their investigation revealed that sorption of non-ortho-substituted PCBs was found to be higher than that of both mono-ortho and di-ortho-substituted PCBs with the same degree of chlorination. Another important parameter that could possibly cause a low sorption affinity of ortho-substituted PCB 52 onto soil can be attributed to its low melting point compared to non-ortho-substituted PCB 77 (**Table** 6.1**)**. Research has shown that in a given class of PCBs, a congener with a higher melting point usually possesses lower aqueous solubility (Huang and Hong, 2002). The high melting point of non-ortho-substituted PCB 77 could be explained in terms of its molecular shape (planar conformation) which is responsible for the molecules to pack tightly into a crystal lattice (resulting from an increase in the cumulative strength of intermolecular London dispersion interactions). The high melting point means there is a stronger bond between the molecules, which makes it more difficult to break the molecules apart and form bonds with water resulting in low solubility and an increase in its hydrophobic character. Thus, the analyte prefers to interact more with soil than water.

The influence of co-effects of other molecules interfering with the sorption of the selected congeners was investigated in this present study. The result as shown in **Fig.** 6.4 **(**a and b**)** indicated that as more congeners are added, there is a decrease, even though minimal, in the sorption. The effect could be because more steric hindrances are caused by the molecules added to the solution, possibly due to the contortion of biphenyl rings with respect to one another. The decrease in the sorption of non-ortho-substituted PCB 77 in the presence of ortho-substituted PCB 52 could be

due to competitive effects brought on by PCB 52. This could be due to the similar soil sorption sites used by both PCBs and similar sorption mechanism (Chapter 4), which may be involved in the sorption of these molecules, leading to their competitive behaviour. Structurally similar molecules (PCB 77 and 52 are isomers with the same number of chlorines and phenyl rings) have displayed a stronger competitive effect towards the primary sorbate thereby, leading to them competing for sorption sites more strongly than dissimilar molecules (Xing *et al*., 1996; Xing and Pignatello, 1997; Pignatello, 1998; Ju and Young, 2004). Furthermore, we hypothesize that molecular mass is involved in the co-effects of structurally similar molecules. PCB 77 (shown as X on **Fig.** 6.4a) and 52 (Y on **Fig.** 6.4a) have the same molecular masses and both fit into the soil pores equally well, but because PCB 52 is di-ortho-substituted it makes it slightly more difficult to fit into the pores. This together with both being in competition results in PCB 77 being slightly less adsorbed. PCB 105 (**Fig.** 6.4a) has a higher molar mass than PCB 77 (**Table** 6.1), hence it cannot fit as easily into the soil pores. This together with its mono-substituted Cl prevents it from offering much competition to PCB 77. Thus, PCB 77 adsorption is slightly higher than when PCB 52 is present but because there may be some competition, there is a slight reduction for PCB 77 adsorption. Thus, PCB 52 is a higher competitor for PCB 77 than PCB 105. Figure 6.4b shows that the di-ortho-substituted PCB 52 (Y on **Fig.** 6.4b) is not much affected by the presence of other PCBs in the solution, as the percentage adsorption remains almost the same when other mono-substituted PCBs are in solution with it.

Faria and Young (2010), assessed the competitive effects of a binary system of 1,2-dichlorobenzene and other chlorobenzenes over a range of concentrations of competitors in three different kinds of natural soils such as Forbes, Yolo and peat soils with different characteristics. The competitive adsorption of each adsorbate was determined by measuring soil distribution normalization coefficient (K_{oc}) at equilibrium. The results revealed that adsorbates with similar chemical structures displayed a competitive behaviour similar to that of the primary pollutant. The author also noted that Forbes soil results showed a significant relationship between competitor sorbate structure and the primary contaminant K_{oc} as well as the competitor concentrations. Similar results were observed in this study between the isomers of PCB 77 and 52 and the percentage adsorption, which is related to K_{oc}. A change in the concentrations of a binary mixture of congeners with respect to non-ortho and ortho-substituted congeners was found to be less significant during sorption. This could possibly be attributed to steric effect being more important in limiting the

amount of PCB sorbed onto the soil due to the bulkiness of the molecules rather than changes in concentrations. Another important parameter for higher sorption of non-ortho PCB 77 compared to its isomer (di-ortho PCB 52) could be due to the attainment of planar conformation of PCB 77 which in turn contributes to its higher lipophilic character (high log K_{ow}) **Table** 6.1. This may possibly allow for its partitioning onto the soil particulate matter rather than being soluble in aqueous solution. Para non-substituted congeners have been reported to have higher solubility in water. This was attributed to the polar molecules forming hydrogen bonds because there are more hydrogen atoms at para positions on PCB 52 which could favourably form intermolecular hydrogen bonds compared to para substituted high electronegativity chlorine atoms such as in PCB 77. The fewer the para-substituted chlorine atoms around the phenyl rings, the closer the proximity of the hydrogen atoms to the water molecules, and the higher the tendency to form intermolecular hydrogen bonds with water. Therefore, molecules with no para-substitution become more polar which may ultimately lead to increased aqueous solubility. Meanwhile, non-ortho congeners, especially when chlorine atoms occupy the para positions, have more difficulty forming hydrogen bonds. If more chlorine atoms lie adjacent to each other, a more planar congener forms, with a higher activity coefficient in water, and lower aqueous solubility (Hutzinger *et al*., 1974; Shiu & Mackay, 1986; ATSDR, 2000; IPCS, 2003). In addition, the proximity effect caused by the presence of two chlorine atoms substituted in the para positions adjacent to each other on either of the phenyl rings is considered to limit the intermolecular hydrogen bonding in the non-ortho substituted congener of PCB 77, which could possibly reduce its water solubility.



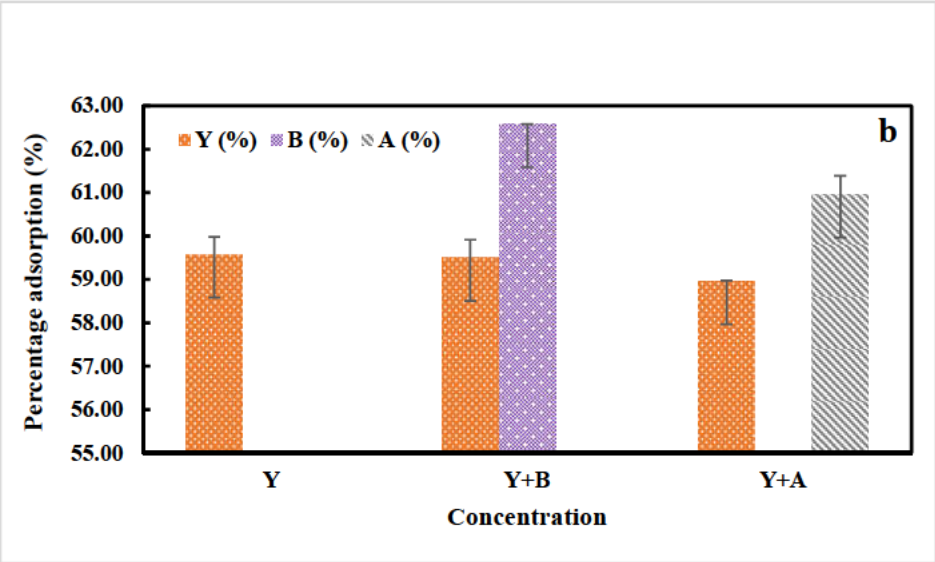


Figure 6.4 (a and b): Effect of stereochemistry on the sorption of PCBs; X (PCB 77) 3,3',4,4'-tetraCB (non-ortho); Y (PCB 52) 2,2',5,5'-tetraCB (di-ortho); A (PCB 105) 2,3,3'4,4'-pentaCB (mono-ortho); B (PCB 28) 2,4,4'-triCB (mono-ortho)

Table 6.1:

Physical and chemical properties of the PCB congeners

PCB congeners	Molecular weight, g/mol	Molecular formula	Melting point, ℃	Boiling point, ℃ (at 20 mmHg)	Solubility	Partition coefficients		Vapour pressure, mm Hg (at 25℃)	Henry's law constant, atm-m^3/mol (at 25℃)
					Water, mg/L	log K_{ow}	log K_{oc}		
PCB 28	257.54	$C_{12}H_7Cl_3$	57-58	206-207	0.0085	5.67	5.28	2.8×10^{-7}	32.20
PCB 52	291.98	$C_{12}H_6Cl_4$	87-89	268	0.046	5.84	5.91	7.3×10^{-7}	31.41
PCB 77	291.98	$C_{12}H_6Cl_4$	173	360	0.00055	6.36	4.41-5.75	4.4×10^{-8}	0.43×10^{-4}
PCB 101	326.43	$C_{12}H_5Cl_5$	77	380	0.00012	6.38	**	2.9×10^{-8}	35.50
PCB 105	326.43	$C_{12}H_5Cl_5$	**	**	0.0034	6.66	**	8.6×10^{-9}	8.24×10^{-4}
PCB 138	360.88	$C_{12}H_4Cl_6$	78.5-80	400	0.016	6.83	5.21-7.3	4.0×10^{-9}	1.07×10^{-4}
PCB 153	360.88	$C_{12}H_4Cl_6$	103-104	**	0.00091	6.92	4.75-7.68	1.9×10^{-9}	2.78×10^{4}
PCB 180	395.32	$C_{12}H_3Cl_7$	109-110	240-280	0.00031-0.0066	7.37	5.78-6.9	1.3×10^{-9}	1.07×10^{-4}

ATSDR, 2000; Mills *et al*. 2007; Dunnivant *et al*. 1992.

**Data not available

6.3.2 Effect of PCB concentrations

The effect of aqueous PCB concentrations on their sorption onto soil was investigated within the concentration range of 0.5–2.5 µg/mL. The result (**Fig.** 6.5**)** shows sorption was optimum at low solution concentration and decreased as the concentration increased. This could be attributed to the fact that as concentration was increased the pores of the expansive clays in the soil may become more saturated and the adsorption sites occupied. Therefore, PCB sorption onto the soil drastically reduced as the concentrations further increased most especially for the ortho-substituted congener. In this case, the ortho-substituted congener (PCB 52) is more hydrophilic and already has increased solubility in water. Hence, any increase in its concentration leads to more PCB 52 being soluble in water and even less interacting with soil. The sorption of PCBs could best be described to be L-type, which indicated that as more sites in the SOM are filled due to an increase in an initial PCB concentration, it becomes increasingly more difficult for bombarding PCB molecules to find a vacant site available for sorption onto the soil SOM (Giles *et al*., 1960). Similar observations were reported by Gondar *et al.* (2013) and Hundal *et al.* (2001) on the adsorption of non-ionic pesticides on soil and sorption of phenanthrene by reference smectites, respectively. This is particularly seen with PCB 77 (**Fig.** 6. 5) which is hydrophobic and prefers interactions with the soil over water. As the concentration increases, only a fixed amount of PCB 77 sorbs onto the soil resulting in the soil pores becoming blocked. No matter how much more PCB 77 is added, only that fixed amount will sorb onto the soil resulting in a constant sorption as seen in **Fig.** 6.5. On the other hand PCB 52 shows a lower K_d value due to its lower hydrophobicity compared to PCB 77. As the concentration of PCB 52 increases, more PCB 52 interacts with water, resulting in a lower K_d value. In terms of the environment, non-ortho chlorine PCBs (most toxic) are more likely to be sorbed by soil and become less available to the aquatic life but may then become more available to filter feeder organisms who source their food from surface sediment. However, ortho-substituted congeners (nonplanar) are more susceptible to aqueous solubility or when sorbed by soil they are more likely to re-suspend back to surface water or leach to the groundwater thereby posing more risk to the aquatic organisms compared to its non-ortho-substituted congener (planar) of the same isomer.

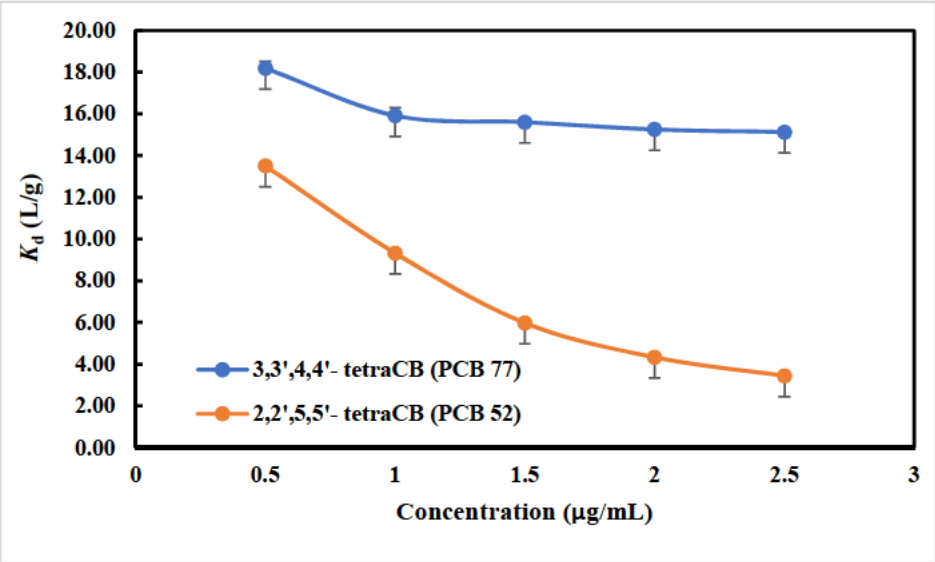


Figure 6.5: Effect of initial aqueous concentrations non-ortho (3,3',4.4'-tetraCB – PCB 77) and ortho PCBs (2,2',5,5'-tetraCB – PCB 52) on the sorption onto the soil carried out individually

6.3.3 Sorption/desorption of PCBs

The same eight PCBs were studied for their sorption/desorption capabilities. The result, as shown in **Fig.** 6.6, revealed that sorption of PCBs was found to be dependent on the number of chlorine atoms as well as the position of the chlorine atoms on the phenyl rings. Heptachloro (PCB 180) and hexachloro (PCB 153) biphenyls were found to have the highest sorption affinity for the soil among the PCB congeners. This could be attributed to their hydrophobic character and lower aqueous solubility as well as their relatively low vapour pressure at room temperature (**Table 6. 1**). One possible mechanism for the favourable interactions between hydrophobic PCBs and soil could be due to the benzene rings in PCB molecules acting as π-acceptors, which would then interact freely with the electron-rich aromatic moieties of the humic substances in soil, most especially humic acid *via* π-π electron donor-acceptor interaction (Sulaymon and Ahmed, 2008). Considering the sorption capacity of soil for trichloro biphenyl (PCB 28) and tetrachloro biphenyls (PCB 52 and 77), where both PCB 52 and 77 are isomers, non-ortho PCB 77 was noticed to have better sorption onto the soil compared to the ortho-substituted isomer (PCB 52) and PCB 28. This may not be predicted based on the differences in solubility (log K_{ow}) alone. This could be due to the ease of PCB 77 to attain a planar conformation whereas the effect of chlorine atoms at the ortho

position in PCB 52 and PCB 28 inhibits the free rotation around the 1, 1' carbon bond, (steric effect) therefore, making the molecule less flexible to interact freely with the soil particle interlayers. In comparing PCB 77 to PCB 28, both have a para-substituted chlorine atom but PCB 77 has no ortho-substituted chlorine atom, which allows for flexible interactions with the soil leading to increased sorption. In this case, it appears that hydrophobicity was found to be less important but steric effects may prove to be more significant. In addition, the partial free rotation together with fewer chlorine atoms compared to PCB 52 could be another possible reason for PCB 28 to partition more to soil than to water.

Desorption studies of PCB congeners on the soil were investigated immediately after the sorption studies at room temperature. Desorption results (**Fig.** 6.6**)** showed that the amount of PCBs desorbed from the soil were dependent on the degree of hydrophobicity, the position of the chlorine atoms and the amount of PCBs sorbed. The amount of PCB desorbed from the soil with a low degree of chlorination and di-substituted PCBs was higher than for those with highly chlorinated as well as non-ortho substituted PCBs (planar PCBs) of the same homolog. It was expected that, due to the lower solubility, low vapour pressure, and stereochemistry of PCB congeners, higher chlorinated PCBs may be stationary in soils and more readily adsorbed compared to the less chlorinated ones. Previous studies by Suzuki *et al*. (1977) and Tucker *et al*. (1975) found that lesser chlorinated biphenyls leached more into the groundwater compared to that of higher chlorinated PCBs under similar conditions, and the reasons were thought to be possibly due to them being more soluble in the aqueous phase. The present study suggests that stereochemistry of the congeners contributes significantly to the mobility and leaching of the PCB congeners.

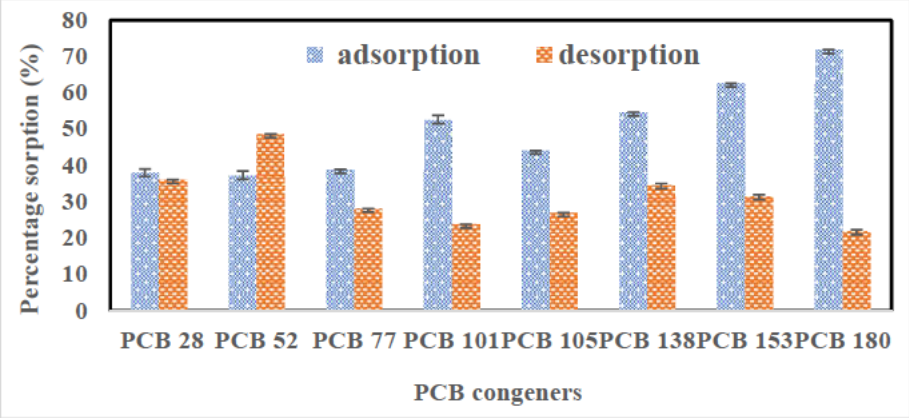


Figure 6.6: Sorption/desorption of PCB congeners

6.4 Conclusion

The effect of PCB stereochemistry on the sorption/desorption onto natural soil collected from uMngeni River of KwaZulu-Natal, South Africa was investigated in this study. The sorption/desorption of PCBs onto the soil interlayer was found to be dependent on the degree and position of chlorination on the phenyl rings, with higher chlorinated and non-ortho PCBs showing more positive and strong interactions with the SOM. The sorption of PCBs was found to be higher for the non-ortho substituted PCB (planar) compared to the ortho-substituted PCB (non-planar) of the same homolog. PCBs that did not have a para substitution were found to be more susceptible to aqueous solubility and are more likely to be re-suspended back to surface water or leach to the groundwater when sorbed by soil and may possibly pose more of a risk to the aquatic ecosystem compared to the non-ortho substituted counterpart given the same environmental conditions. An increase in the initial concentration for non-ortho-substituted hydrophobic organic pollutants such as PCB 77 are more likely to result in steady sorption by soil and become less available to the aquatic life which may then become more available to filter feeder organisms who source their food from surface sediment. However, ortho-substituted congeners may likely be susceptible to aqueous solubility as the initial concentration increases and may likely lead to less affinity to sorb to soil, and if sorbed may re-suspend back to surface water or leach to the groundwater easily consequently posing more risk to aquatic organisms.

Acknowledgments

The authors sincerely acknowledge the University of KwaZulu-Natal and School of Chemistry and Physics at UKZN for laboratory facilities.

REFERENCES

ATSDR, Toxicological Profile for Polychlorinated Biphenyls (2000). Atlanta (GA): US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Available from: http://www.atsdr.cdc.gov/ToxProfiles/tp17.pdf. *Accessed* 26/05/2018.

Ballschmiter, K.H., Froescheis, O., Jarman, W.M., Caillet, G., (1997). Contamination of the deep-sea. *Mar. Pollut. Bullet*. **34**: 288–289

Belfort, G., (1979). Selective adsorption of organic homologs onto activated carbon from dilute aqueous solutions. Solvophobic interaction approach and correlations of molar adsorptivity with physicochemical parameters. *Environ. Sci. & Technol.* **13**, (8): 939-946.

Bucheli, T. D., and Gustafsson, O., (2003). Soot sorption of non-ortho and ortho substituted PCBs. *Chemosphere.* **53**: 515–522.

Cornelissen, G., Gustafsson, O., Bucheli, T. D., Jonker, M. T. O., Koelmans, A. A., van Noort, P. C. M., (2005). Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. & Technol.* **39**:3881–3895.

Cornelissen, G., Haftka J., Parsons, J., Gustafsson ,O., (2005). Sorption to black carbon of organic compounds with varying polarity and planarity. *Environ. Sci. Technol*. **39**:3688–3694.

Cornelissen, G., Kukulska, Z., Kalaitzidis, S., Christanis, K., Gustafsson, O., (2004). Relations between environmental black carbon sorption and geochemical sorbent characteristics. *Environ. Sci. Technol*. **38**: 3632–3640

Cortes, A., Riego, J., Paya-Perez, A. B., Larsen, B., (2009). Soil sorption of co-planar and non-planar PCBs. *Toxicol. Environ. Chem*. **31-32**: 79-86.

Duinker, J. C., Hillebrand, M. Th. J., Zeinstra, T., Boon, J. P., (1989). Individual chlorinated biphenyls and pesticides in tissues of some cetacean species from the North Sea and the Atlantic Ocean: tissue distribution and biotransformation. *Aquat. Mamm*. **15**: 95 124.

Duinker, J. C., Schulz, D. E., Petrick, G., (1991). Analysis and interpretation of chlorobiphenyls: possibilities and problems. *Chemosphere*. **23**: 1009-1028.

Dunnivant, F. M., Elzerman, A. W., Jurs, P. C., Hasan, M. N., (1992). Quantitative structure-property relationships for aqueous solubilities and Henry's law constants of polychlorinated biphenyls. *Environ. Sci. Technol*. **26**, (8): 1567–1573.

Erickson, M. D., (2001). Introduction to PCB properties, uses, occurrence and regulatory history. In: Robertson, L. W., Hansen, L. G, editors. PCBs, recent advances in environmental toxicology and health effects. The University press of Kentucky. pp 11-30.

Erickson, M. D., and Kaley, R. G., II (2011). Applications of polychlorinated biphenyls. *Environ. Sci. Pollut. Res.* **18**: 135-151.

Faria, I. R.., and Young, T. M., (2010). Modeling and predicting competitive sorption of organic compounds in soil. *Environ. Toxicol. Chem*. **29**, 12: 2676–2684.

Ghosh, U., Zimmerman, J.R., Luthy, R.G., (2003). PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. *Environ. Sci. Technol*. **37**, (10): 2209–2217.

Giles, C. H., Macewan, T. M., Nakhwa, S. N., Smith, D., (1968). Studies in adsorption. Part XI.* A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.* **60**: 3973-3993.

Gondar, D., López, R., Antelo, J., Fiol, S., Arce, F., 2013. Effect of organic matter and pH on the adsorption of metalaxyl and penconazole by soils. *J. Hazard. Mater*. **260**: 627–633.

Hu, D., and Hornbuckle, K. C., (2010). Inadvertent polychlorinated biphenyls in commercial paint pigments. *Environ. Sci. Technol*, **44**, (8): 2822–2827. doi:10.1021/es902413k PMID:19957996.

Hundal, L. S., Thompson, M. L., Laird, D. A., Carmo, A. M., (2001). Sorption of phenanthrene by reference smectites. *Environ. Sci. Technol*. **35**: 3456–3461. doi: 10.1021/es001982a.

Hutzinger, O., Safe, S., Zitko, V., (1974). The chemistry of PCBs. CRC Press, Cleveland, OH. IOM, Institute of Medicine (2003). Dioxins and dioxin-like compounds in the food supply. Washington (DC): The National Academies Press. pp 769–879.

IOM, Institute of Medicine (2003). Dioxins and dioxin-like compounds in the food supply. Washington (DC): The National Academies Press.

IPCS (1993). Polychlorinated biphenyls and terphenyls. 2nd ed. Geneva, Switzerland: World Health Organization, International Programme on Chemical Safety (Environmental Health Criteria 140). Available from: http://www.inchem.org/documents/ehc/ehc/ehc140.htm. *Accessed* 03/06/2018.

Jonker, M. T. O., and Koelmans, A. A., (2002). Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations. *Environ. Sci. Technol*. **36**: 3725–3734.

Jonker, M. T. O., and Smedes, F., (2000). Preferential sorption of planar contaminants in sediments from Lake Ketelmeer, The Netherlands. *Environ. Sci. Technol*. **34**: 1620–1626.

Ju, D. Y., Young, T. M., (2004). Effects of competitor and natural organic matter characteristics on the equilibrium sorption of 1,2-dichlorobenzene in soil and shale. *Environ. Sci. Technol.* **38**: 5863–5870.

Karickhoff, S., W., Brown D. S., Scott, T. A., (1979). Sorption of hydrophobic pollutants on natural sediments. *Wat. Res*. **13**: 241-248.

Kathleen, M., McDonough, J. L., Fairey, G. V. L., (2008). Adsorption of polychlorinated biphenyls to activated carbon: Equilibrium isotherms and a preliminary assessment of the effect of dissolved organic matter and biofilm loadings. *Water Res*. 42, (3): 575-584.

King, R. S., Beaman, J. R., Whigham, D. F., Hines, A. H., Baker, M. E., Weller, D. E., (2004). Watershed land use is strongly linked to PCBs in white perch in Chesapeake Bay subestuaries. *Environ. Sci. Technol*. **38**, (24): 6546–6552.

Lorán, S., Bayarri, S., Conchello, P., Herrera, A., (2010). Risk assessment of PCDD/PCDFs and indicator PCBs contamination in Spanish commercial baby food. *Food Chem. Toxicol*. **48**: 145–151

Metcalfe, C. D., (1994). Polychlorinated biphenyls. In: Kiceniuk J. W., Ray, S., (eds) Analysis of contaminants in edible aquatic resources. VCH Press, Berlin. pp 305–338.

Mills, S. A., Thal, D. I., Barney, J., (2007). A summary of the 209 PCB congener nomenclature. *Chemosphere.* **68**: 1603–1612.

Millward, R. N., Bridges, T. S., Ghosh, U., Zimmerman, J. R., Luthy, R. G., (2005). Addition of activated carbon to sediments to reduce PCB bioaccumulation by a polychaete (Neanthes arenaceodentata) and an amphipod (Leptocheirus plumulosus). *Environ. Sci. Technol.* **39**: 2880–2887.

Okey, A. B., (2007). An aryl hydrocarbon receptor odyssey to the shores of toxicology: the Deichmann Lecture, International Congress of Toxicology-XI. *Toxicol. Sci*. **98**: 5–38.

Pignatello, J. J., (1998). Soil organic matter as a nanoporous sorbent of organic pollutants. *Adv. Colloid. Interface.* Sci **77**: 445–467.

Rao, B. H., and Asolekar, S. R., (2001). QSAR models to predict effect of ionic strength on sorption of chlorinated benzenes and phenols at sediment–water interface. *Water Res*. **35**, (14): 3391-3401.

Safe, S., (2001). Molecular biology of the Ah receptor and its role in carcinogenesis. *Toxicol. Lett*. **120**: 1–7.

Shiu, W. Y., and Mackay, D. A (1986). Critical review of aqueous solubilities, vapor pressures, Henry's Law constants, and octanol–water partition coefficients of the polychlorinated biphenyls. *J. Phys Chem*. **15**, (2): 911–29

Stegeman, J. J., Schlezinger, J. J., Craddock, J. E., Tillitt, D. E., (2001). Cytochrome P450 1A expression in mid-water fishes: potential effects of organic chemical contaminants in remote oceanic zones. *Environ. Sci. Technol*. **35**: 54-62.

Sulaymon, A. H., and Ahmed, K. W., (2008). Competitive adsorption of furfural and phenolic compounds onto activated carbon in fixed bed column. *Environ. Sci. Technol*. **42**: 392-397.

Sun, X., and Ghosh, U., (2007). PCB bioavailability control in Lumbriculus variegatus through different modes of activated carbon addition to sediments. *Environ. Sci. Technol*. **41**:4774–4780.

Suzuki, M., Aizawa, N., Okano, G., Takahashi, T., (1977). Translocation of polychlorobiphenyls in soil into plants: A study by a method of culture of soybean sprouts. *Arch. Environ. Contain. Toxicol*. **5**: 343 52.

Tanabe, S., (1988). PCB problem in the future: Foresight from current knowledge. *Environ. Pollut.* **50**: 5–28.

Tucker, E. W., Litschgi, W. J. Mees, W. M., (1975). Migration of polychlorinated biphenyls in soil induced by percolating water. *Bull. Environ. Contam. Toxicol*. **13**: 86-93.

UNEP, United Nation Environmental Programme (2001). Text of the Stockholm Convention on Persistent Organic Pollutants and implementation activities; amended 2009. United Nations Environment Programme Available from: http://chm.pops.int/ The Convention/Overview/Text of the Convention/ tabid/2232. *Accessed* 24/06/2017.

UNEP, United Nation Environmental Programme (2009). Sustainable Innovation and Technology Transfer Industrial Sector Studies: Recycling – From E-waste to Resources. United Nations Environment Programme. Available from: http://www.unep.org/ pdf/Recycling_From_e-waste_to_resources.pdf. *Accessed* 24/06/2017.

UNEP, United Nation Environmental Programme (2011). The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal. United Nations Environment Programme. Available from: http://www.basel. int/Por ta ls/4/Basel%20Convention/docs/text/BaselConventionText-e.pdf. *Accessed* 13/04/2018.

Van den Berg, M., Birnbaum, L. S., Denison, M., De Vito, M., Farland, W., Feeley, M., (2006). The 2005 World Health Organization reevaluation of human and Mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci*. **93**, (2): 223–41.

Weber, J. B., and Weed, S. B., (1974). Effects of soil on the biological activity of pesticides. In Pesticides in soil and water, ed. by W. D. Guenzi, 223-56. Madison, Wisconsin, Soil Science Society of America, Inc. pp 223-256.

WHO, World Health Organization (2010). Global Environment Monitoring System – Food Contamination Monitoring and Assessment Programme (GEMS/Food). Geneva, World Health Organization (http://www.who.int/foodsafety/chem/gems). *Accessed*, 25th May, 2018.

Wurl, O., and Obbard, J.P., (2005). Organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in Singapore's coastal marine sediments. *Chemosphere.* **58**: 925–933.

Xing, B. S., and Pignatello, J. J., (1997). Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environ. Sci. Technol.* **31**: 792–799.

Xing, B., (1997). The effect of the quality of soil organic matter on sorption of naphthalene. *Chemosphere.* **35**: 633–642.

You, J., Landrum, P. F., Trimble T. A., Lydy, M. J., (2007). Availability of polychlorinated biphenyls in field-contaminated sediment. *Environ. Toxicol. Chem.* **26**:1940–1948.

Zimmerman J. R., Gosh, U., Millward, R. N., Bridges, T. S., Luthy, R. G., (2004). Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: Physicochemical tests. *Environ. Sci. Technol*. **38**: 5458– 5464.

CHAPTER 7

MANUSCRIPT 4

Partitioning of polychlorinated biphenyls onto porewater-surface sediment systems collected along uMngeni River, KwaZulu-Natal, South Africa

Gbadebo Clement Adeyinka and Brenda Moodley*

School of Chemistry and Physics, College of Agriculture, Engineering and Sciences, University of KwaZulu-Natal, Private Bag X54001, Westville, 4000, Durban, South Africa. E-mail: adeyinkagbadebo78.ga@gmail.com
*Corresponding author; e-mail: Moodleyb3@ukzn.ac.za. Tel: +27 31 260 2796; Fax: + 27 31 2603091

ABSTRACT

This study focuses on the sorption efficiency of porewater-sediment of eight selected polychlorinated biphenyls (PCBs) most monitored in the environment as recommended by the Environmental Protection Agency. Five river sediment samples were collected along the uMngeni River of KwaZulu-Natal province of South Africa that contained different soil contents. The Walkley Black method was employed for the determination of soil organic matter in the sediments, while sediment mineralogy and morphology, as well as elemental composition, were evaluated using powder X-ray diffraction and scanning electron microscopy equipped with energy disperse X-ray, respectively. The sorption studies between porewater and sediment systems were carried out using batch adsorption experiments. The results showed that sediment samples containing high clay and silt content (site AWW and IDI) have the highest sorption percentage for all the PCBs while sites IDO and BL with high sand content sorbed the least amount of PCBs. Among the sediment physicochemical parameters, soil organic matter was observed to correlate positively and play an important role in the sorption of PCBs. Also, a decrease in the ratio of Si: (Al + Fe) was noticed to have a positive impact on the sorption of PCBs. This is the first study done on this river to critically evaluate the porewater-sediment distribution and transportation of PCBs. Sorption efficiency of sediments of known physicochemical properties similar to this study area can be predicted by the sorption results of the present study.

Key words: Partitioning, polychlorinated biphenyls, sediments, porewater, batch adsorption, uMngeni River

7.1 Introduction

Polychlorinated biphenyls (PCBs) are one of the priority organic pollutants most investigated in the environment due to their historical toxicity and health effects on both humans and wildlife as implemented by agencies in developed countries such as the US Environmental Protection Agency (USEPA), European Commission (EC) and the State Environmental Protection Administration (SEPA) in China (Bi *et al*., 2002). Since the early 1920s, PCBs have had wide commercial applications such as dielectric and heat exchange fluids, due to their general inertness, thermal stability and high resistance to both acids and alkalis (Afghan and Chau, 1989; Buccini, 2003; Wang *et al*., 2005). Due to the possible health implications and environmental impacts of PCBs, their usage and production are severely restricted and totally banned in many countries and intergovernmental organizations worldwide. For instance, Sweden, USA, Norway, Finland and Denmark restricted the usage and production of PCBs in 1972, 1977, 1980, 1985, and 1986, respectively while in Russia production was only stopped in 1993 (ATSDR, 2000; Breivik *et al*., 2002). In 2004, many countries under the Stockholm Convention (SC) on POPs finally signed the treaty that prohibited further production and usage of hazardous persistent organic pollutants (POPs) such as PCBs (UNEP, 2004). Commercial PCB mixtures have a characteristic colour ranging from clear to light yellow oils or resins with no tendency to crystallize, even at low temperatures (WHO, 2003). Less chlorinated PCBs are more volatile than those with a higher degree of chlorination. Their solubility decreases as the number of chlorine atoms on the phenyl rings increase thereby enhancing the hydrophobic tendency of the congeners. Even though the production and usage of PCBs has been stopped years ago, recent studies show that some levels of PCBs are still present in the environment. Zhang *et al.* (2003) reported total concentrations of 21 PCBs in the range of 15.1-57.9 ng/g and 0.2-2.5 ng/g in sediment and soil of Minjiang River in China while Tolosa *et al*. (1995) also reported 12 PCB congeners in sediment in Rhone prodelta in France in the range 38.3-228.5 ng/g. Traceable levels of PCBs were also reported in soil and sediment in parts of Africa. Barakat *et al.* (2002) revealed that sediment collected in the Alexandria Harbour, Egypt were found to contain 0.9-1211 ng/g for the sum of 96 total PCB concentrations and Barhoumi *et al.* (2013) reported 0.8-14.6 ng/g of total PCB concentration for 10 PCBs in sediment of Bizerte lagoon of Tunisia. Sediment and soil of central South Africa was reported to contain 0.12-1.80 and 0.3-4.70 ng/g, respectively (Nieuwoudt *et al*., 2009). The current presence of PCBs could be attributed to their persistence and hydrophobic nature especially in soil and

sediment that is a major reservoir for the hydrophobic pollutants. The remobilization and suspension of PCBs in the environment is still very possible due to the role of soil organic matter (SOM) and particulate organic matter (POM) in the surface and underground water as well as changes in the environmental conditions, such as, pH and temperature. In order to understand the mobility and transportation of PCBs between different environmental compartments, the partitioning of these pollutants must be evaluated. Non-polar PCB congeners have very low water solubility. However, the presence of particulate matter in porewater systems can have a significant effect, hence encouraging the solubility of hydrophobic PCBs into the water/porewater beyond the predictable solubility levels (Brownawell and Farrington, 1985; Chiou *et al.,* 1986; Chin and Gschwend, 1990). Although, several investigations have been conducted on the PCB concentrations and other hydrophobic contaminants in surface water and soil/sediment systems, there is still insufficient data on the fate and mobility as well as behaviour of PCBs in the water-soil/sediment compartment. Qiao *et al*. (2008) investigated the partitioning behaviour of PAHs between sediment and the water system of Taihu Lake (a shallow lake) of China. The authors noted that the partitioning coefficient (log K_{oc}) between surface water and sediment for the selected 16 EPA PAHs with log $K_{ow} < 5$ showed a linear realtionship with their log K_{ow} values. This indicated that hydrophobic PAHs tend to partition favourably to soot particles found in natural sediment compared to being soluble in aqueous solution. Gdaniec-Pietryka *et al*. (2013) studied the remobilization of seven indicator PCB congeners from sediment using three series of the model water-sediment system. The outcome of their investigation revealed that the solubility of individual PCBs did not affect the desorption of PCBs from the sediment. Rather, the dissolved PCBs were readily transported in running waters. However, suspended and colloidal material was found to be a major reservior for the hydrophobic PCBs in lotic aquatic environments. The remobilization of these PCBs from the sediment system to the aqueous phase with respect to their aqueous solubility was reported to be limited thereby reducing the risk of secondary pollution. South Africa is currently facing a serious water stress in due to global climate change. To solve the problem of water shortage, the best possible remediation approach is urgently needed. Thus, the study of partitioning of organic pollutants is important because this process controls the distribution, transport, and transformation of organic pollutants between the aqueous phase and soil or sediment in the aquatic environment. Partitioning affects the remediation and biological uptake as well as microbial degradation of organic pollutants such as PCBs in the aquatic

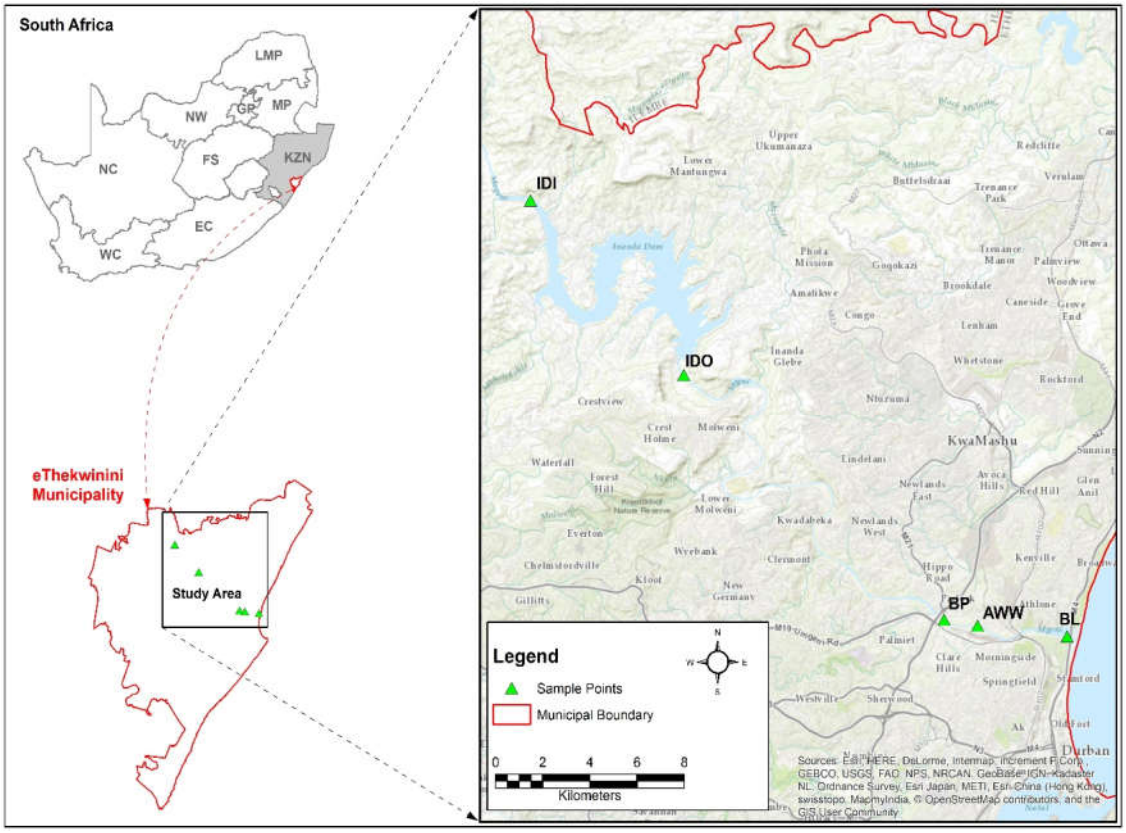
environment. The aim of this present study was to evaluate the partitioning of selected PCB congeners between real porewater and sediment samples collected along the uMngeni River, KwaZulu-Natal province, South Africa. The objective of this work was to apply previous knowledge from batch adsorption from a model soil sample to real water samples and critically examine the role of porewater and sediment physicochemical and geochemical properties, based on the sorption of eight selected PCB congeners in real samples collected from five selected sites along the uMngeni River. This river is located in sub-Saharan agro-ecological zones of KwaZulu-Natal province, South Africa. The selected congeners were chosen based on their prevalence in the environment and the reported toxicity cases on both humans and animals. In addition, the EPA has categorized these congeners as hot spot pollutants to be frequently studied in the environment due to their potential health effects. This is the first study done on uMngeni River to critically evaluate and understand the composition of soil/sediment minerals, organic materials and water particulate matter and also to assess the possible threat these pollutants might pose to safe water deliveries. The outcome of this study will help to ascertain to what extent these properties influence the distribution and transportation of organic pollutants such as PCBs along this river, which serves as a major source of water particularly to people of this province and it will also provide a base line assessment on a global scale.

7.2 Materials and methods

7.2.1 Study sites and sample collection

The study area, (uMngeni River) is one of the major rivers in South Africa and the largest river in KwaZulu-Natal. It is approximately 232 kilometres (144 miles) long with a catchment area of 4,432 square kilometres (1,711 sq miles) on a coordinate of 29°48′36″S 31°02′08″E and serves as a major source of water to the people of the province. Sediments used in this study were collected from five locations along the uMngeni River in September, 2017: (1) Inanda dam inlet (29° 39'05.20" S 30° 48'06.24" E), (2) Inanda dam outlet (29° 42'55.74" S 30° 52'07.69" E), (3) Business park (29° 48'19.05" S 30° 58'58.08" E), (4) Northern wastewater treatment works effluent and discharge point into the uMngeni River (29° 48'27.01" S 30° 59'51.05" E) and (5) Blue lagoon (29° 48'41.03" S 31º 02'12.05" E). The sampling map is shown in **Fig**. 7.1. The sediment samples were characterized by substantial differences in their physicochemical properties i.e. differences in the level of clay, organic matter content and water pH. A previous study by Gakuba *et al.* (2015) on

this river revealed that some trace levels of targeted PCBs are still present during the study period with a total of eight PCB concentrations found in the range of 6.910-21.69 ng/mL, 40.67-252.3 ng/mL and 102.6-427.8 ng/g (dw) in surface water, porewater and surface sediment, respectively. The result revealed that sediment was a major reservoir for the hydrophobic PCBs among the three-environmental media studied. River sediments were collected from the selected sites as identified by global positioning system (GPS) of the locations along the river, using a stainless-steel corer into a 1 L amber glass bottle whose cap was lined with aluminium foil. The physicochemical parameters of the river water were measured onsite as shown in **Table** 7.1. The bottles were stored in a container with ice to maintain a relatively low temperature during transportation to the laboratory.



IDI = Inanda Dam Inlet, IDO = Inanda Dam Outlet, BP = Business Park, AWW = After Waste Water Treatment Plant, BL = Blue Lagoon

Figure 7.1: Sampling sites for uMngeni River, KwaZulu-Natal, South Africa. (Created using ArcMap10.4 version)

7.2.1.1 Porewater separation

Porewater from the sediment samples were all separated within 24 h after samples were collected. Sediment samples were centrifuged at 6000 rpm for 20 min, the pore water was decanted and vacuum filtered using 0.4 µm cellulose acetate filter paper. The pore water collected was stored in a 100 mL amber glass bottle and preserved with 0.01% NaN_3 to minimize bacterial growth prior to batch adsorption experiments.

7.2.1.2 Separation and characterization of sediment samples

After the porewater was isolated, the sediment samples were air dried at room temperature in the fume hood for six days thereafter broken up manually using a marble mortar and pestle and sieved using 425 µm mesh size. Sediment particles that passed through the 425 µm sieve were collected in the receiver, and mixed manually to achieve homogeneity and stored in the amber glass bottle under air tight conditions prior to batch adsorption experiments. The contents of organic matter and cation exchange capacity (CEC) in sediment samples were determined by the Walkley Black method (Walkley and Black, 1934; Tiessen and Moir 1993; Nelson and Sommers 1996; Chan *et al*., 2001; Schumacher 2002), and the barium chloride compulsive exchange method as described by Gillman and Sumpter 1986 and modified in 2011 and recommended by the Soil Science Society of America, respectively. The elemental analysis for CEC was determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Perking Elmer Precisely Optima 5300 DV). The details of these procedures were discussed in chapter 4. The soil mineralogy, macro-morphological properties and qualitative elemental analysis were determined using low angle powder X-Ray diffractometer (XRD) (PANalytica EMPYREAN, Netherland-Holland) using Kα radiation of Cu operated at 40 kV and 40 mA and the spectra were analyzed using Highscore Plus software and quantified using Rietveld, and scanning electron microscopy (SEM) equipped with energy disperse X-ray (EDX), respectively. The results are shown in **Table** 7.2 and **Fig**. 7.2. Particle size analysis on each sediment sample was performed by the sieve pipette method.

7.2.2. Reagents and chemicals

Further information regarding reagents and chemicals used were given in chapters 3 and 4 of this thesis.

7.2.3 Adsorption experiments

Batch sorption experiments were conducted to investigate the partitioning of PCBs between pore water solution and sediment samples. A 1 g sample of each sediment sample was weighed into a stainless steel centrifuge tube together with a 10 mL aliquot of porewater containing 10% of 0.01 mol/L $CaCl_2$, ($CaCl_2$ was added to improve centrifugation and to minimize the CEC). The solution pH for all samples (as measured on site, **Table** 7.1) was maintained to prevent the influence of pH on the sorption of PCBs. The experiment was conducted at room temperature at 25±1ºC. Preliminary investigation of both porewater and sediment samples was conducted to determine the concentration level of PCBs of interest using our established method for the routine monitoring of PCBs in the environment. The results indicated that the concentration detected in all the sites were below the detection limit of the instrument, and therefore the standard addition method was used for the batch adsorption experiments in this study. An aliquot of a 0.5 µg/mL PCB mixture was added to the porewater/sediment solution which was then placed on a LABCOM orbital shaker for 24 h at a speed of 350 rpm to allow for partitioning of the PCBs to the sediment interlayer surfaces. Previous preliminary investigations on the sorption of PCBs onto different soil particle grain sizes (chapter 4) revealed that a 24 h equilibration period was sufficient for the PCBs to sorb onto the soil containing soil organic matter (SOM) up to 11.92 mg/g and cation exchange capacity of up to 7.90 Meq/100 g. The values for both SOM and CEC obtained in this current study for all the sediment samples across the sites were all less than 11.92 mg/g and 7.90 Meq/100 g, respectively. The SOM and CEC values obtained in this current study are shown in **Table** 7.1. The quality control measures followed the same experimental procedures as described in chapters 3 and 4 of this thesis with the percentage recoveries found to be between 76% – 101% for the selected PCBs. All experiments were conducted in triplicate. The partition coefficient (K_d) and percentage sorption were determined using **Eqs**. (7.1) and (7.2), respectively.

$$K_{\mathrm{d}} = \left(\frac{C_{\mathrm{o}} - q_{\mathrm{e}}}{q_{\mathrm{e}}}\right)\frac{V_{\mathrm{o}}}{m} \qquad (7.1)$$

$$A_{\mathrm{ti}} = \frac{M_{\mathrm{s}}^{\mathrm{ads}}(t_i)}{M_{\mathrm{o}}} \times 100 \qquad (7.2)$$

where, K_{d} is the partition coefficient (L/g), C_{o} (mg/L) is the initial concentration, q_{e} (mg/L) is the aqueous concentration at the equilibrium, V_{o} (L) is the volume of the solution used and m (g) is the mass of the soil. M_{o} (mg) is the mass of the test substance in the test tube at the beginning of the experiment and was determined using the following expression: $M_o = V_o \cdot C_o$. $M_{\mathrm{s}}^{\mathrm{ads}}$ (mg) is the mass of the test substance adsorbed onto the soil and was determined using the expression $M_{\mathrm{s}}^{\mathrm{ads}} = M_{\mathrm{o}} - C_{\mathrm{aq}}^{\mathrm{ads}} t_{\mathrm{i}} \cdot V_{\mathrm{o}}$, where t_i is time at equilibrium and $C_{\mathrm{aq}}^{\mathrm{ads}}\, at\, t_i$ is the concentration of the adsorbed substances in aqueous phase (mg/L) at time t_{i} (s) which is further used to determine the percentage adsorption of the PCBs onto the soil samples after the batch adsorption experiments.

Table 7.1:

Physicochemical properties of the river water and sediment samples

Soil	Organic matter composition (n = 3)			CEC, Meq/100 g (n = 3)	%Soil particle grain sizes					Water physicochemical parameters				Si / Al +Fe (Ratio)
	%OC	%TOC	%SOM		Clay	Silt	Fine sand	Medium sand	Coarse sand	pH	Water temp, ^{o}C	TDS, ppm	Conductivity, µs	
IDI	1.06	1.66	4.92	3.61	18.58	19.93	18.84	19.96	22.68	7.7	21.40	274.00	4.89×10^{2}	0.77
IDO	0.13	0.51	1.52	1.18	1.88	14.22	21.34	27.33	36.62	9.4	21.20	195.40	3.47×10^{2}	1.98
BP	0.91	1.47	4.37	2.32	4.85	18.82	18.57	30.34	29.41	6.8	21.10	301.50	5.22×10^{2}	8.33
AWW	1.79	2.55	7.57	4.15	13.90	30.43	27.92	19.49	8.59	6.8	21.90	771.20	1.38×10^{3}	0.48
BL	0.17	0.56	1.67	2.72	1.13	12.79	25.59	25.59	3.30	7.9	20.90	28 350	5.07×10^{4}	1.95

7.2.4. GC-MS analysis

Comprehensive information about GC-MS parameters for this study is provided in chapters 3 and 4 of this thesis.

7.3 Results and discussion

7.3.1 Water/sediment physicochemical parameters

The physicochemical properties of water and sediments used in this study are shown in **Table** 7.1. The pH of the river water was relatively neutral (6.8–7.9) except for IDO, which was alkaline (9.4). The pH values for the selected sites in this current study could possibly favour the sorption of PCB congeners onto the sediment system except for IDO. This is based on results presented in chapter 4 that investigated the role of aqueous pH. A low solution pH could lead to small molecules of organic matter (humic substances) combining to give large aggregates due to bonding between the organic matter and the mineral surface, which could ultimately encourage the adsorption of hydrophobic organic pollutants. An increase in the solution pH may cause destruction of the organic matter or increase the dissociation/ionization of the functional groups on SOM, which could lead to an increase in the charge of the SOM structure and cause a disappearance of the hydrophobic sites in the soil. In addition, the loosely coiled structures and smaller fractions of hydrophobic regions may still be present in sediment, though some of these may be too small to act as binding sites for PCBs, which may ultimately lead to a reduction in the sorption of PCBs. The water temperature was measured on site and ranged between 20.90 to 21.90°C. The lower temperature recorded at these sites could possibly have a significant effect on the sorption of PCBs onto the sediment as the vapour pressure of these hydrophobic pollutants are expected to be lower at low temperature which would discourage the solubility of pollutants in the water column, therefore, increasing its movement towards soil organic matter.

High conductivity values ranging between 347 to 5070 µs/cm and total dissolved solids (TDS) of 195.40 to 28350 mg/L values were recorded for the sites during the sampling period. The high conductivity values could be due to the relatively low rainfall at the time of sampling, which could possibly influence the hydrological condition of the sites resulting in a slower flow of water, which could possibly lead to more sediment settling onto the riverbed during the sampling period. Among the sites, both AWW and BL were found to have high values for both the conductivity and TDS

compared to other sites, and this could be attributed to the direct input from the waste treatment plant into the uMngeni River. In addition, high conductivity and TDS values obtained at the BL site could be attributed to the direct influence of the close proximity of the Indian Ocean at this site, which contributes significantly to the salt concentration recorded here. Our preliminary investigation on the role of ionic strength on the sorption of PCBs onto soil, in the presence of $CaCl_2$, revealed that changes in the aqueous ionic concentrations did not have much effect on the sorption of PCBs (chapter 4).

The sediments physicochemical characteristics such as SOM, CEC and sediment particle grain sizes such as clay, silt and sand content are shown in **Table** 7.1. It was observed that both IDI and AWW sites have the highest SOM, CEC and clay percentage of 4.92 and 7.57, 3.61 and 4.15, and 18.58 and 13.90, respectively and IDO had the lowest value of 1.52, 1.18 and 1.88 and highest sand content of about 85.29% among the sites. Both SOM and clay content have been reported to have direct influence on the sorption of hydrophobic organic pollutants onto the soil/sediment (Karapanagioti *et al*., 2001; Huang *et al*., 2013; Smaranda *et al*., 2014; Olu-Owolabi *et al*., 2015; Qi and Zhang, 2015;). The results of chapter 4 in this work also confirms this. Hence, the 2 sites, IDI and AWW are expected to have highest partitioning of the PCBs studied.

7.3.2 Soil morphological and mineralogical properties

The SEM micrographs **Fig**.7.2, revealed evidence of a compact matrix in AWW and IDI sediment samples, which were well dispersed and had large pore spaces between the particles. A porous system and aggregate formats with a clear discontinuous structure were found in IDO and BL sediment samples. Organo-mineral aggregates of extracellular polysaccharide (Si ---O_2 bonds) and mineral particles were noticed in all the sediment samples. The EDX results showed the presence of elements silicon (Si), oxygen (O) and aluminium (Al) in higher quantities and trace amounts of K, Fe, Mg, Na, Ca, minerals as well as a smaller amount of Ti in the sediment samples.

The mineralogical composition of sediment samples was evaluated using XRD (**Table** 7.2 and **Fig**. 7.3). Minerals detected included, quartz, albite, microcline, chlorite, muscovite, kaolinite, calcite, halite, illite, mica, microcline (intermediate), microcline (maximum) montmorillonite-(Li), and vermiculite. Comparison of mineralogical data of sediment samples can provide valuable insight

into the signature characteristics of sediment inputs to sorption of pollutants in the environment. Mineralogical data generated for the sediment samples are in the form of percentage of mineral components for each of the sampling sites. The results showed that the sediment samples consist of mineral matter, which accounted for the larger percentage of the samples. Among these minerals, quartz was dominant and the value ranged between 23.10-69.80%. In addition, clay forming minerals such as albite, microcline, muscovite, chlorite, illite, mica, microcline (intermediate) microcline (maximum), montmorillonite-(Li) and vermiculite were also found in sediment samples along the sites. The clay minerals present as characterized using the XRD diffraction pattern and analyzed using Highscore Plus software are illite $(KH_3O)(AlMgFe)_2(SiAl)_4O_{10}[(OH)_2,(H_2O])$, albite,$(NaAlSi_3O_8)$, montmorillonite $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2{\bullet}n(H_2O)$, kaolinite $(Al_2Si_2O_5(OH)_4)$, calcite $(CaCO_3)$, and quartz (SiO_2). The elements Si, Al, Na, Fe and K in the sediment samples were similar to that identified in the EDX spectrum.

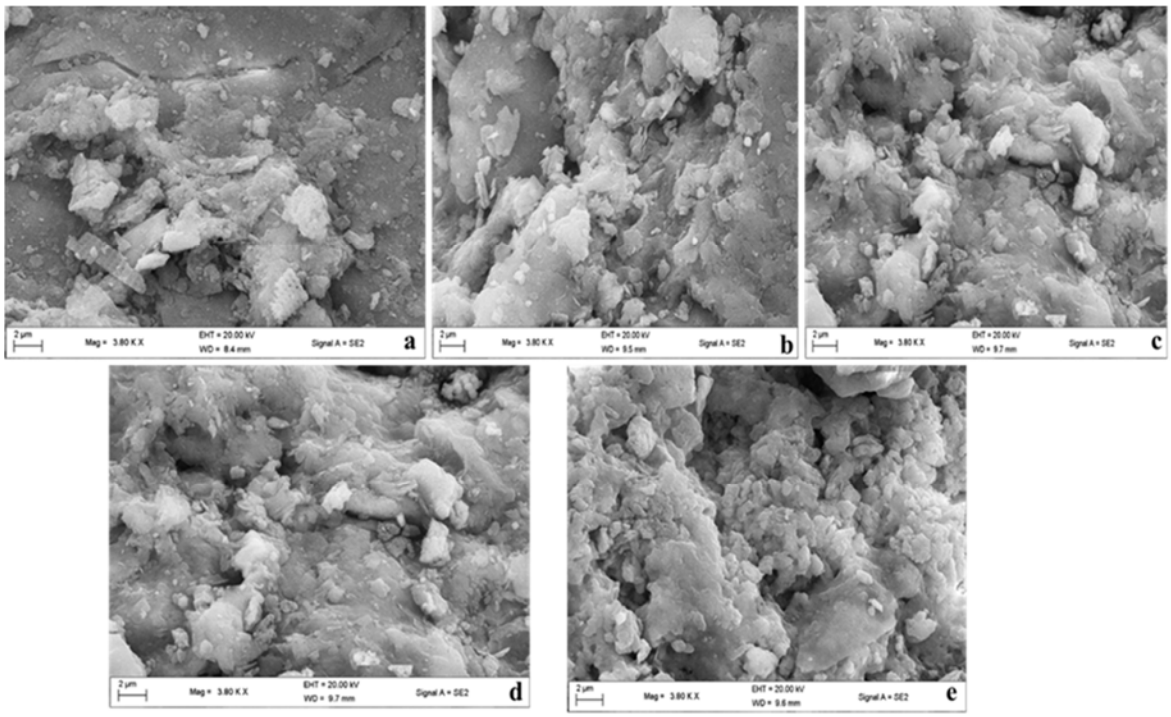


Figure 7.2: Typical scanning electron microscopy (SEM) images of sediments. (a) IDI; (b) IDO; (c) BP; (d) AWW and (e) BL

Table 7.2:

Mineralogical composition of sediments collected along uMngeni River

Soil	%Sediment Mineralogy												
	Albite	**Calcite**	**Halite**	**Illite**	**Kaolinite**	**Mica**	**Microcline (intermediate)**	**Microcline (maximum)**	**Montmorillonite-(Li)**	**Muscovite 2M 1**	**Quartz**	**Vermiculite**	**Vermiculite 2M**
IDI	14.6	-	-	6.2	42.2	-	7.0	-	-	-	29.3	-	0.7
IDO	43.1	-	-	-	2.3	3.5	-	26.4	0.9	-	23.1	0.7	-
BP	16.8	-	-	-	-	-	-	11.5	0.7	7.6	62.8	-	0.6
AWW	17.1	-	-	14.3	-	-	7.2	-	1.0	-	60.4	-	-
BL	19.2	1.2	3.8	-	1.2	-	-	-	-	2.3	69.8	2.6	-

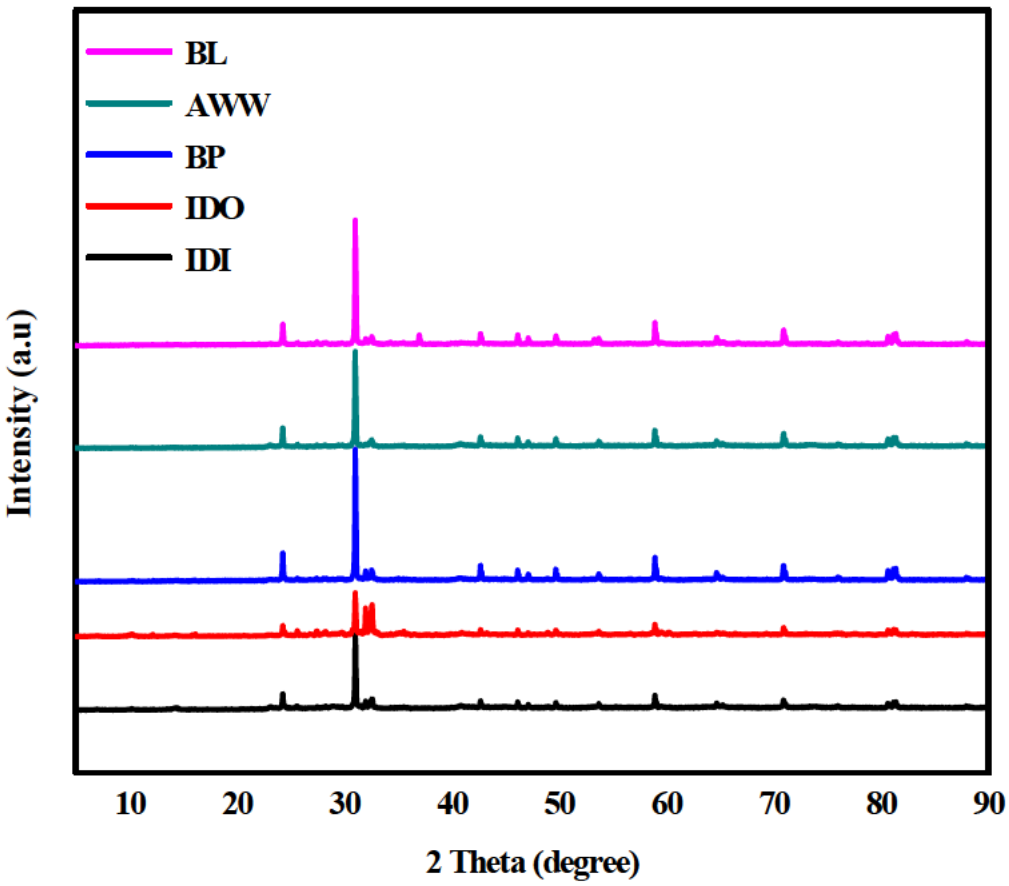


Figure 7.3: X-ray diffractogram patterns of sediment samples

7.3.3 Sorption study

Sorption experiments were performed between porewater and sediment fractions for all the site samples. A 1 g of sediment to 10 mL porewater was used for the sorption studies and a known concentration of PCB standard mixture was added to the solution/sediment and equilibrated for 24 h while maintaining the pH of river water. Standard addition was adopted in this study due to the non-detection of the targeted PCBs. The experiment was performed at room temperature. The results of the batch experiments are shown in **Fig**. 7.4. Due to different physical and chemical characteristics exhibited by the different sites, the sorption capacity of the sediment at the individual locations differed. The sorption of PCB concentrations by these sediments indicated by different physicochemical properties resulted in significant differences in their adsorptions. A relatively higher sorption affinity was observed in the sediment of AWW, IDI and BP compared to

sediments of BL and IDO, which were found to sorb less PCBs. The results revealed that the five sediments had varying geochemical compositions as seen from **Table** 7.1. IDO and BL sites were sandier with relatively low clay and silt content, as well as low SOM content. In contrast, AWW, IDI and BP contained relatively more clay and silt with higher concentrations of SOM. PCBs, being non-polar compounds, have a relatively stronger affinity for SOM interaction, which is very strongly dominated by non-specific van der Waals interactions due to its diminished π-electron density by electron withdrawing substituents such as Cl atoms. The order of sorption of all the PCBs on each of the sediments was AWW > IDI > BP > BL > IDO, which is the order of abundance of SOM content, (clay + silt): sand ratio in the sediments. Sediments with larger values of (clay + silt): sand ratio were able to sorb PCBs more efficiently (**Fig**. 7.4). Sediments that have a greater clay content would decrease the mobility of the PCBs towards the aqueous phase.

Another important parameter that could possibly affect the sorption of hydrophobic PCBs onto the soil/sediment system in this study is the presence of sediment mineral constituents (sediment mineralogy composition). From the XRD results shown in **Table** 7.2, it was observed that sediment sample AWW contained major mineral components such as montmorillonite, illite, and kaolinite. Bailey and White (1970) reported that montmorillonite is an expandable clay with a 2:1 structure and illite is a non-expandable 2:1 clay that has an octahedral aluminium layer, incorporated between tetrahedral silicon sheets. The ratio of 2:1 indicates that there are more Si sites than Al, and the high Si: Al ratio on both montmorillonite and illite surface. While kaolinite is a clay with a 1:1 arrangement, that contains an octahedral aluminium layer overlying tetrahedral silicon sheets. The ratio of 1:1 for kaolinite indicates an equal amount of Si and Al sites. Higher surface areas have been reported for both montmorillonite and illite (8×10^6 m^2/kg and 10^5 m^2/kg) compared to lower surface area reported for kaolinite (3×10^4 m^2/kg) (Bailey and White 1970). Surface area is one of the soil parameters that affects the sorption of HOCs, where an increase in surface area would encourage the sorbate to hold tightly to the sorbent surface interlayer. An increase in surface area of sorbent will indicate an availability of more potential sites at the surface of the sorbent into which sorbate molecules can favourably interact. Sorption is a surface phenomenon, which involves the transfer of sorbate molecules to the interlayer surface sites of the sorbent. Therefore, the expanded structure and high surface areas possessed by both montmorillonite and illite could allow for higher sorption affinity for the HOCs. The presence of these important parameters

together with others could also be a contributing factor responsible for the higher sorption of PCBs exhibited by AWW, IDI and BP sediments.

Shen, (2000) reported the role of atomic ratio of Si: (Al + Fe) on the sorption capacity of soil to non-polar polyethylene glycol mono-p-nonylphenyl ether (A_9PE_{10}). The author found a positive correlation between soil with a higher value of Si:(Al + Fe) ratio and the adsorption of A_9PE_{10}. A similar hypothesis was tested in this present study (shown in **Table** 7.1) but a contrary observation was noticed on the sorption of hydrophobic PCBs. Sediment particles with the lowest value of Si:(Al + Fe) ratios were found to have better sorption capacity for all the PCB congeners investigated in this study. It is noted that commercial soil (bentonite and kaolinite) and natural red soil collected from the B-horizons site in Southern Taiwan were used for the study done by Shen, (2000) while the sediment investigated in this present study was collected from a natural river in South Africa located in the sub-Saharan African region, which has different geological and physicochemical properties. The elements Si, Al, and Fe in the natural soil are capable of forming their respective oxides in solution such as SiO_2, Al_2O_3, and Fe_2O_3, respectively. The SiO_2 is a strong Bronsted acid while Al_2O_3 and Fe_2O_3 are strong Lewis acids. The decrease in the ratio of Si:(Al+Fe) means there are more Al and Fe contributing to the system resulting in an increase in the acidic strength of the solution and a corresponding decrease in solution pH. A decrease in solution pH results in the presence of hydrogens that maintain the acid functionality on the carboxylic acid present in the soil organic matter, resulting in a more hydrophobic material. As more hydrophobic sites are created on the soil surface interlayer, there would be a high affinity for hydrophobic PCBs to sorb onto the soils. Another possible reason could be due to an increase in more pores being created by the octahedral surface of Al and Fe to the tetrahedral surface of Si sheet, thereby resulting in more sites available for PCB sorption. Presently this is the first study to report information on this important parameter regarding the sorption of hydrophobic PCBs onto the natural sediment interlayer. Although, this may not be the only factor controlling the distribution and transportation of pollutants in the environment since sediment and pollutant interactions involve some complex mechanisms.

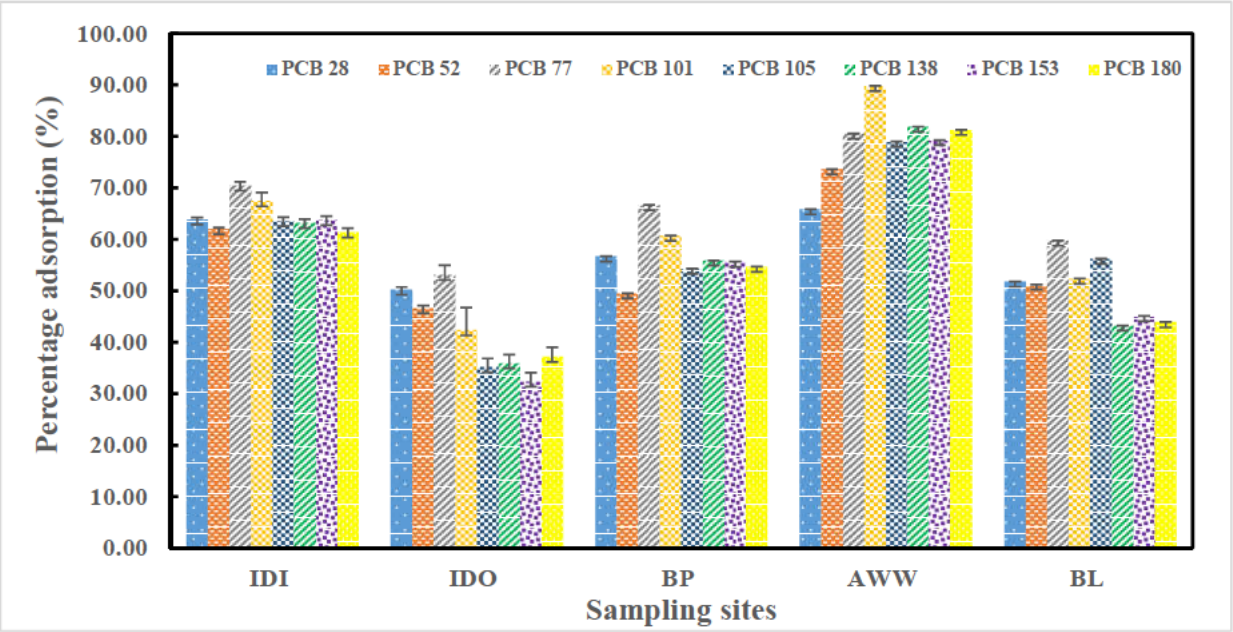


Figure 7.4: Sorption of PCB congeners onto sediment particle interlayer samples collected from different sites along the uMngeni River

7.3.3.1 Statistical analysis of the data

The Pearson correlation (R^2 and p-values) measures the strength of the relationship between two variables. The larger the R^2 value, the stronger the relationship that exists between the two variables while the lower the p-value the more significant the relationship. A p-value less than 0.01 indicates a very strong significant difference, less than 0.05 signifies that there is a significant difference and values greater than 0.05 mean a very weak significant difference. The percentage sorption of PCBs onto the sediment interlayer with sediment physicochemical parameters such as SOM, pH, clay, silt and sand contents was subjected to the Pearson Correlation Test **Table** 7.3 using the SPSS statistical software package version 25.0 (SPSS, 2017). The results indicated that the percentage sorption of PCBs onto the sediment interlayer at all sites was positively correlated with sediment physicochemical parameters, particularly SOM and silt while negatively correlated with sand content at all sites. The average R^2 values ranged between 0.936 to 0.985, which indicated that there is a linear correlation between SOM and PCB sorption. In addition, the p-values between SOM and PCB sorption in most cases were less than 0.05 and 0.01, respectively at all sites. This

showed that there is a strong significant relationship between SOM and PCB interactions for the sorption process, as compared to other sediment physicochemical parameters in this study. Considering the PCB congeners, the p-values are becoming smaller and R^2 values increase as the number of chlorine atoms increases on the PCB. This shows that there is a linear correlation between the hydrophobic character of PCBs and SOM in the sediment. The less chlorinated PCB 28 and PCB 52 displayed the lowest p- and R^2 values, meaning that less chlorinated PCBs have more preference for water compared to the higher chlorinated counterparts. PCB 77, which has the same number of chlorine atoms as PCB 52, also had a lower p- and high R^2 values. This could be attributed to the presence of para-substituted chlorine atoms in PCB 77 and its planar stereochemistry (coplanar conformation), which allowed for its free rotation, thereby increasing its hydrophobic character with stronger affinity for SOM sorption. In addition, there is a strong relationship between PCB sorption and clay with R^2 values ranging between 0.792 and 0.931 but there exists a weak significant difference because all the values of p are greater than 0.05 (between 0. 72 to 0.110) except for PCB 28, which has its p-value at 0.021, which is more significant at this level. Similar results were reported by Huang *et al*. (2013) on the adsorption of atrazine onto clay, where the authors reported that no relationship existed between atrazine and clay with a reported p-value of 0.942. Silt showed a positive correlation and a significant difference in the relationship with PCBs but sand was negatively correlated with all the PCBs. The result of a nonlinear relationship between PCBs and sand indicated that less PCBs were sorbed by sites with a high percentage of sand such as IDO and BL, which may encourage possible desorption of PCBs into the aqueous solution.

Table 7.3:

Pearson correlation coefficients between percentage sorption of PCB congeners and sediment physicochemical parameters in uMngeni River, KwaZulu-Natal, South Africa

Parameter	SOM	pH	Clay	Silt	Sand	PCB 28	PCB 52	PCB 77	PCB 101	PCB 105	PCB 138	PCB 153	PCB 180
SOM	1	-0.776	0.778	0.973**	-0.933*	0.947*	0.936*	.983**	.983**	0.976**	0.985**	0.970**	0.971**
pH		1	-0.446	-0.667	0.586	-0.693	-0.871	-0.795	-0.842	-0.840	-0.829	-0.855	-0.873
Clay			1	0.694	-0.937*	0.931*	0.823	0.844	0.802	0.826	0.814	0.815	0.792
Silt				1	-0.899*	0.883*	0.838	0.916*	0.914*	0.900*	0.918*	0.889*	0.894*
Sand					1	-0.987**	-0.899*	-0.942*	-0.917*	-0.927*	-0.926*	-0.926*	-0.904*

* Significant at p = 0.05 level, ** significant at p = 0.01 level

7.4 Conclusion

The sorption capacities of five selected river sediment samples collected along uMngeni River of KwaZulu-Natal, South Africa were investigated in this study. The sorption was observed to be dependent on the physicochemical parameters of the sites such as SOM, clay, silt and sand content, pH, and sediment mineralogy as well as the elemental composition. It was established that SOM, silt and clay contents played a major role in the sorption of PCBs while sediment mineral compositions such as montmorillonite, illite, and kaolinite were also important. The ratio of Si: (Al + Fe) on the sediment mineral surface and PCB sorption was investigated and the outcome of the study showed a significant contribution to the sorption of the PCB congeners in this study. The statistical consideration of the results indicated that Pearson correlation coefficient and p-values for SOM were positive and showed a very strong significant relationship between SOM and pollutant sorption for all the PCBs investigated in this study. Sand content and pH were found to be negatively correlated and less significant in the sorption of PCBs. Sites with a high percentage of clay + silt:sand ratio such as AWW and IDI sorbed more PCBs compared to sites IDO and BL which have less clay + silt:sand ratio.

Based on the outcome of this study, the sorption of hydrophobic pollutants such as PCBs is controlled by the geological composition of the soil/sediment of the studied area. For sediment with high SOM with p-values less than 0.01, the strong binding between hydrophobic PCB molecules and soil/sediment organic compounds can prevent the PCBs being released, thus reducing its bioavailability to aquatic organisms (with the exception of filter feeders). Soil/sediment with a large percentage of sand may possibly allow or permit the pollutants to leach into the groundwater or resuspend the pollutants back to the surface water very easily and increase the pollution load of river water with high bioavailability of the pollutants to aquatic life and humans using polluted water as a source of drinking water.

Acknowledgments

The authors sincerely acknowledge the University of KwaZulu-Natal and School of Chemistry and Physics at UKZN for laboratory facilities.

REFERENCES

Afghan, B. K. and Chau, A. S. Y., (1989). Analysis of trace organics in the aquatic environment. Boca Raton, FL, CRC Press. pp 33-68.

ATSDR (Agency for Toxic Substances and Disease Registry), (2000). Toxicological Profile for Polychlorinated Biphenyls (PCBs). Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Atlanta, Georgia. Available http://www.atsdr.cdc.gov/ToxProfiles/ tp17.pdf. *Accessed* 21/04/2016.

Bailey, G. W. and White, J. L. (1970). Factors influencing the adsorption, desorption and movement of pesticides in soil. *Residue Rev*. **82**: 29-92.

Barakat, A. O., Kim, M., Qian, Y., Wade, T. L. (2002). Organochlorine pesticides and PCBs residues in sediments of Alaxandria Harbour, Egypt. *Mar. Pollut. Bull*. **44**: 1421- 434.

Barhoumi, B., LeMenach., K., Dévier., M-H., El megdiche, Y., Hammami, B., Ameur, W.B., Hassine, S.B., Cachot, J., Budzinski, H., Driss, M.R. (2013). Distribution and ecological risk of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in surface sediments from the Bizerte lagoon, Tunisia. *Environ. Sci. Pollut. Res. Int.* **21**: 6290-6302.

Bi, X. H., Chu, S. G., Meng, Q. Y., Xu, X. B., (2002). Movement and retention of polychlorinated biphenyls in a paddy field of WenTai area in China. *Agr. Ecosyst. Environ*. **89**, (3): 241-252.

Breivik, K., Sweetman, A., Pacyna, J. M., Jones, K. C., (2002). Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 1. Global production and consumption. *Sci. Total. Environ*. **290**, (1-3): 181-198.

Brownawell, B. J. and Farrington, J. W., (1985). Partitioning of PCBs in marine sediments,.In Sigleo, A. C., and Hattori, A. (eds.), Marine and Estuarine Geochemistry. Lewis Publishers, Inc., Chelsea, Michigan. pp 97–120.

Buccini, J., (2003). The development of a global treaty on persistent organic pollutants (POPs). In: Fiedler H (ed) The hand book of environmental chemistry, on persistent organic pollutants, 3rd edn. Springer-Verlag, Berlin/Heidelberg. pp 14-29.

Chan, K.Y., Bowman, A., Oates, A., (2001). Oxidizable organic carbon fractions and soil quality changes in an oxic paleustalf under different pasture leys. *Soil Science.* **166**: 61- 67.

Chiou, C. T., R. L. Malcolm, T. I. Binton, D. E. Kile, D. E., (1986). Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environ. Sci. Technol*. **20**: 502-508.

Gakuba, E., Moodley, B., Ndungu, P., Birungi, G., (2015). Occurrence and significance of polychlorinated biphenyls in water, sediment pore water and surface sediments of uMngeni River, KwaZulu-Natal, South Africa. *Environ. Monit. Assess*. **187**: 568, doi 10.1007/s10661-015-4790-1.

Gdaniec-Pietryka, M., Mechlinska, A., Wolska, L., Galuszka, A., Namiesnik, J., (2013). Remobilization of polychlorinated biphenyls from sediment and its consequences for their transport in river waters. *Environ. Monit. Assess*. **185**: 4449-4459.

Huang, Y., Lin, Z., He, Y., Zang, F., (2013). Quantifying effects of primary parameters on adsorption-desorption of atrazine in soil. *J. Soils and Sediments*. **13**: 82-93

Karapanagioti, H. K., Childs, J., Sabaini, D., (2001). Impacts of heterogeneous organic matter on phenanthrene sorption: different soil and sediment samples. *Environ. Sci. Technol*. **35**: 4684–4698.

Nelson, D.W. and Sommers L. E., (1996). Total carbon, organic carbon, and organic matter. In: Methods of Soil Analysis, Part 2, 2nd ed., A.L. Page *et al*., Ed. Agronomy. **9**: 961-1010. Am. Soc. of Agron. Inc. Madison, WI.

Nieuwoudt, C., Quinn, L., Pieters, R., Jordaan, I., Visser, M., Kylin, H., Borgen, A. N., Giesy, J. P., Bouwman, H., (2009). Dioxin-like chemicals in soil and sediment from residential and industrial areas in central South Africa. *Chemosphere*. **76**: 774-783.

Olu-Owolabi, B. I Diagboya, P. N., Adebowale, K. O., (2015). Sorption and desorption of fluorene on five tropical soils from different climes. *Geoderma.* **239–240**: 179–185.

Qi, Y. and Zhang, T.C., (2016). Sorption and desorption of testosterone at environmentally relevant levels: Effects of aquatic conditions and soil particle size fractions. *J. Environ. Eng*. **142**: 1-9.

Qiao, M. and Huang, S., Wang, Z., (2008). Partitioning characteristics of PAHs between sediment and water in a shallow lake. *J. Soils Sediments***. 8**: 69-73.

Schumacher, B. A., (2002). Methods for the determination of total organic carbon (TOC) in soils and sediments. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-02/069 (NTIS PB2003-100822), Las Vegas, ERASC.

Shen, Y-H., (2000). Sorption of non-ionic surfactants to soil: the role of soil mineral composition. *Chemosphere*. **41**: 711 – 716.

Smaranda, C., Bulgariu, D., Malutan, T., Gavrilescu, M., (2014). The evaluation of the factors affecting sorption of pentachlorophenol in soil. *Soil Agron.* **57**, (2): 133-138.

Tiessen, H. and Moir, J.O., 1993. Total and organic carbon. In: Soil Sampling and Methods of Analysis, M.E. Carter, Ed. Lewis Publishers, Ann Arbor, Michigan. pp 187-211.

Tolosa, I., Bayona, J. M., Albaiges, J., (1995). Spatial and temporal distribution, fluxes and budgets of organochlorinated compounds in northwest Mediterranean sediments. *Environ. Sci. Technol*. **29**: 2519-2527.

UNEP/GEF/Kalmar, United Nations Environment Programme, on POPs Högskola, Invemar, (2004). Global International Water Assessment (GIWA), Caribbean Sea/Colombia and Venezuela, Central America & Mexico GIWA Regional Assessment 3b, 3c, Kalmar Sweden. *Accessed,* 12/09/ 2017.

Walkley, A. and Black, I. A., (1934). An examination of the Degtjareff method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science*. **63**: 251-263.

Wang, Y. J., Cheng, H., Edwards, R. L., He, Y. Q., Kong, X. G., An, Z. S. J., Wu, Y., Kelly, M. J., Dykoski, C. A., Li, X. D., (2005). The Holocene Asian Monsoon: Links to solar changes and North Atlantic climate, *Science*. **308**: 854– 857.

WHO, World Health Organization (2003). Polychlorinated biphenyls: Human health aspects. (Concise international chemical assessment document; 55). Geneva, 2003

Zhang, Z. L., Hong, H. S., Zhou, J.L., Huang, J., Yu, G., (2003). Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. *Chemosphere.* **52**: 1423-1439.

CHAPTER 8

GENERAL CONCLUSION AND RECOMMENDATIONS

8.1 GENERAL CONCLUSION

The partitioning of eight indicator PCBs representing non-ortho-substituted (planar PCB) to tetra-substituted (nonplanar PCB) congeners between aqueous solution and natural soils collected from uMngeni River of KwaZulu-Natal province of South Africa as well as factors that affect their partitioning were investigated in this study. The amount of PCBs sorbed by soil was found to increase with an increase in contact time reaching an equilibrium within 8 h. The partitioning of PCBs onto the soil or sediment was said to be highly dependent on the soil or sediment physicochemical properties such as SOM content, CEC, the carbon to nitrogen ratio (C/N ratio) of the soil, BET surface area, pore volume and pore size distribution present as well as soil or sediment particle grain sizes. Among the soil or sediment physicochemical properties investigated, SOM was found to be the most significant factor influencing the partitioning of the hydrophobic PCBs in this study. It was evident that HA availability in the aqueous phase was found to encourage the solubility of hydrophobic PCBs in water, thereby reducing the partitioning onto the inter-surface layer of soil. Furthermore, the ratio of Si: (Al + Fe) on the sediment mineral surface and PCB partitioning showed a significant contribution to the partitioning of the PCB congeners in this study. The soil or sediment mineral compositions such as montmorillonite, illite, and kaolinite were also found to be important. The results of kinetic studies on the partitioning of PCBs on the soils investigated was found to follow a pseudo-second order, suggesting that the mechanism of partitioning of the selected PCB congeners occurred *via* multi-step processes between aqueous solution and soil active components. Low solution pH values favoured the partitioning of PCB congeners most especially the most hydrophobic ones, due to the hydrophobic interactions between the PCB congeners and the organics moieties present in the soil. Ionic strength was found to be less significant in the partitioning of PCBs between aqueous solution and soil particle grain sizes. The partitioning of PCBs onto the soils was said to be temperature driven, where low aqueous temperatures encouraged more partitioning of hydrophobic PCBs onto the soil. Thermodynamic studies showed that the PCB interaction with soil particle sizes was a spontaneous process with a negative value of $\Delta G°$. The role of initial PCB concentration on the partitioning

was found to be L-type, and indicated that an increase in the PCB concentrations in the aqueous phase make it more difficult for PCB molecules to find a vacant site available for sorption onto the soil SOM. In addition, sorption of PCBs best fitted with the Freundlich isotherm, indicating that a heterogeneous surface interlayer on the soil was most suited for the partitioning of hydrophobic PCB congeners. Stereochemistry of the PCB congeners was found to be another important parameter controlling the sorption/desorption processes where the presence of compounds possessing a similar molecular structure served as a competitor to each other, thereby determining the fate of PCB sorption onto the soil surface interlayers. PCBs that did not have a para substitution (more ortho-substituted congeners) were found to be more susceptible to aqueous solubility even as the initial concentration increased and were more likely to be re-suspended back to surface water or leach to the groundwater when sorbed by soil.

Generally, based on the outcome of this study, the following important points are highlighted:

Soil or sediment containing larger proportions of soil organic matter, mineral components and high ratio of clay/silt to sand content as well as soil or sediment rich in high HA concentration are more likely to hold hydrophobic pollutants within soil interlayer surfaces. This then discourages leaching and re-suspension of pollutants to the groundwater and surface water thereby posing less of a risk of PCB contamination to aquatic organisms. However, soil or sediment with a large percentage of sand are more likely to contain less humic acid (lipophilic substance) and discourage the partitioning of hydrophobic pollutants onto the soil or sediment. This will allow or permit the pollutants to leach into the groundwater or resuspend the pollutants back to the surface water very easily and increase the pollution load of river water with high bioavailability of the pollutants to aquatic life and humans using polluted water as a source of drinking water.

Less chlorinated/ortho-substituted organic pollutants (PCBs) were found to be more susceptible to aqueous solubility and are more likely to be re-suspended back to surface water or leach to the groundwater when sorbed by soil and consequently may possibly pose more risk to the aquatic ecosystem relative to the non-ortho-substituted/highly hydrophobic counterpart given the same environmental conditions.

Changes in the environmental conditions such as pH and temperature may possibly alter the secondary pollution of river water. The presence of organic pollutants in alkaline soils having less

organic matter content in a tropical hot climatic condition could increase the chances of leaching and remobilization of organic pollutants causing ground and surface water contamination.

8.2 RECOMMENDATIONS

Based on the results and knowledge obtained in this study, the following recommendations are suggested:

- The co-effect of PCB congeners on the sorption was investigated in this study. Competitive interaction behaviour on the sorption among the PCBs requires further investigations possibly with molecular modelling in order to further confirm the mechanism of interaction involved between non-ortho-substituted (planar) and ortho-substituted (nonplanar) PCB congeners on their sorption onto different environmental media.
- Sorption of hydrophobic PCBs as well as various factors that affect their sorption were investigated in this study. The results show that a change in the environmental parameters and sorbate properties are cabable of causing a potential change in quality of surface and ground water with resultant effects on aquatic life. Therefore, this study suggests that thorough ecological risk assessment studies should be conducted on this river to ascertain the risk and toxic level of these pollutants to the aquatic life that depend on this river.
- The sorption behaviour of respresentative tri-chloro to hepta-chloro biphenyls as well as non-ortho and ortho-substituted congeners on the sorption between aqueous solution and soil or sediment systems have been investigated in this study. The study on the sorption of less chlorinated (mono/di-chloro) and higher (octa/deca-chloro) chlorinated PCB congeners should also be carried out to further establish their sorption behaviour compared to those investigated in this study.
- Sorption studies of related hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons and organochlorine pesticides are important as well and their sorption behaviours would add to the knowledge generated in this study. In addition, the outcome of this study further suggests a similar investigation of polar organic emerging contaminants like pharmaceutical and personal care products, which may have different stereochemistries and chemical characteristics. This is important because they have a

potential to pose similar or more severe toxic effects to both aquatic ecosystems and higher animals as well as humans in the environment.

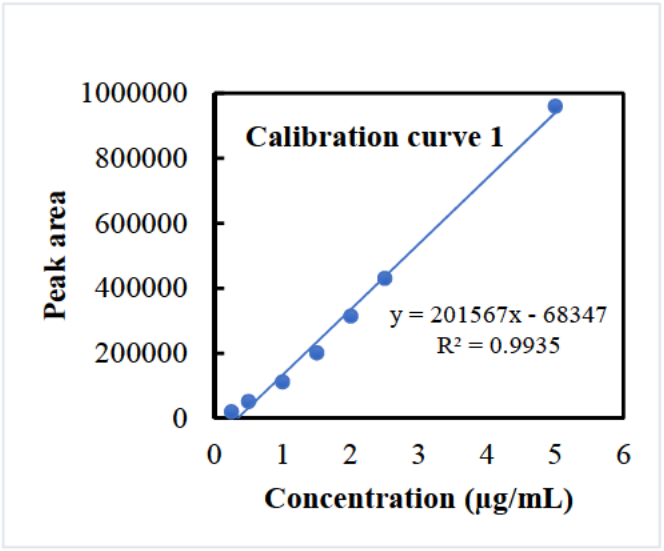
APPENDICES

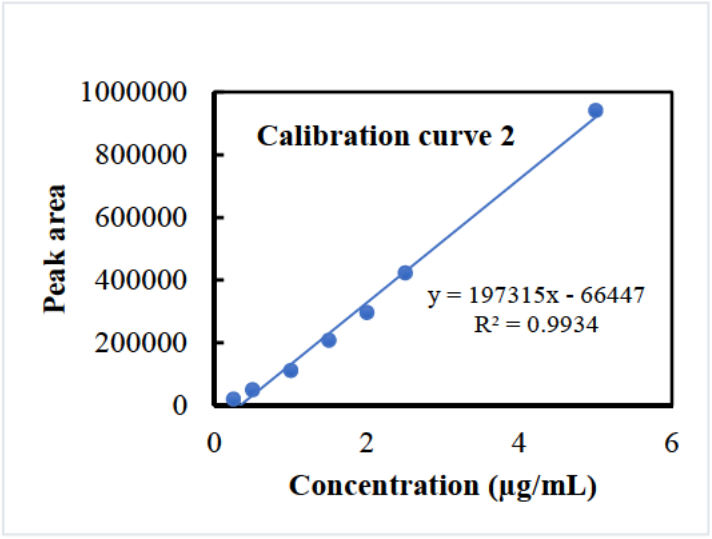
APPENDIX A: Examples of peak area table, calibration curves, and pseudo-second order kinetic fitting for PCB representatives

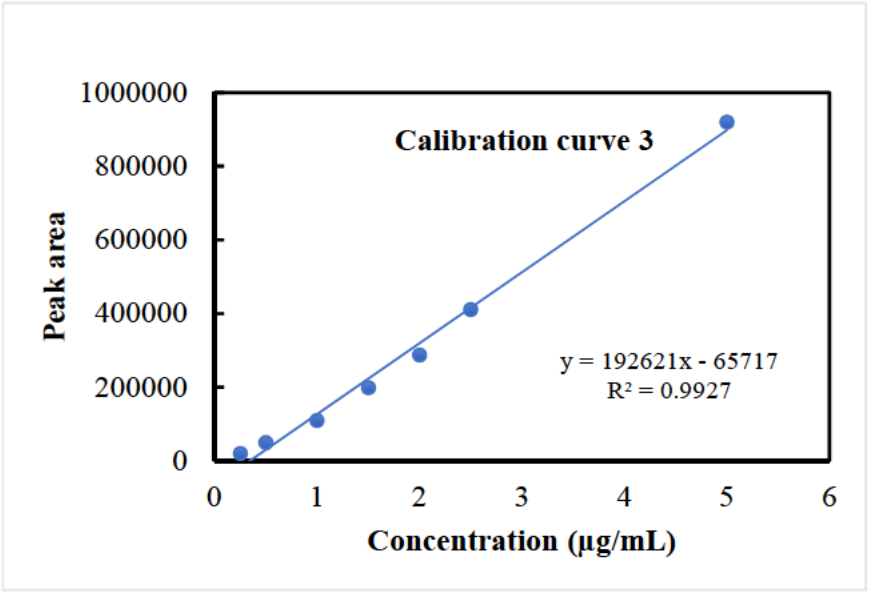
A1 Example of peak areas (PCB 153)

Conc. µg/mL	Peak area 1	Peak area 2	Peak area 3
0.25	20367	20159	19847
0.5	51430	50028	49714
1	112723	111331	109778
1.5	201538	208109	198463
2	314933	296689	287347
2.5	430636	422971	411014
5	959918	941344	919740

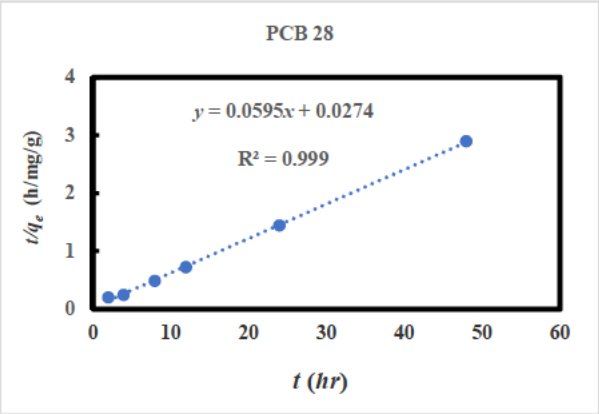
A 2 Example of calibration curves (PCB 153)

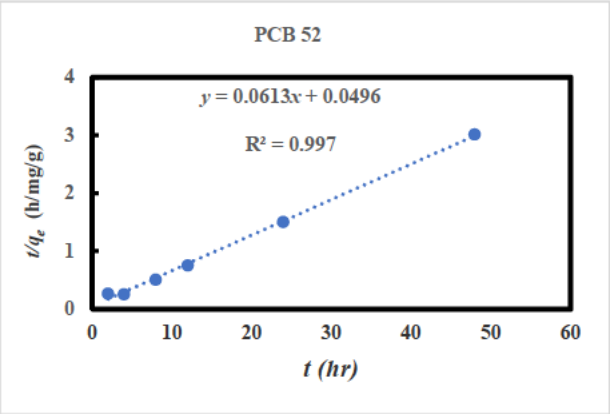


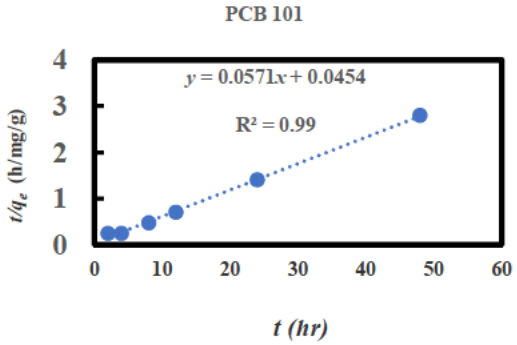


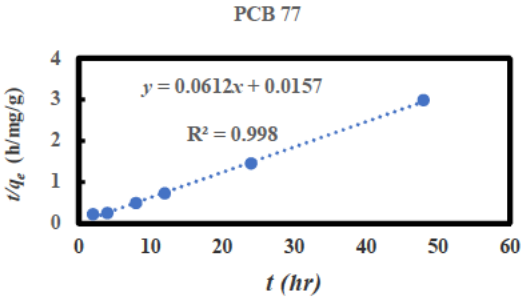


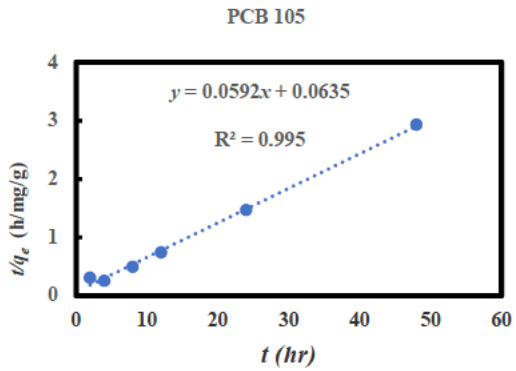
A 3 Pseudo-second order kinetic data for all 8 PCB congeners at the initial concentration of 2.0 µg/g and pH 6.5

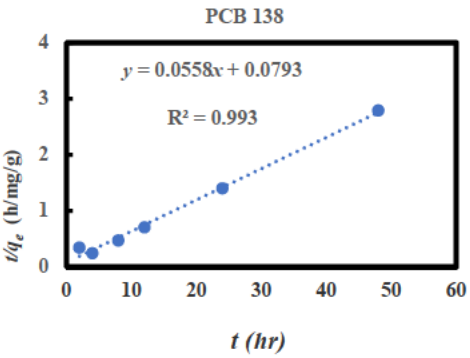


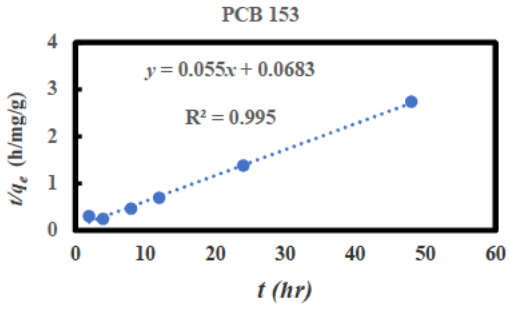


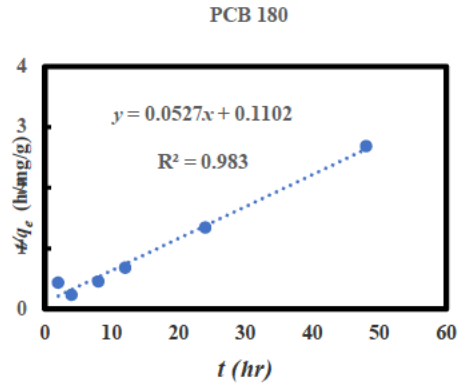





PCB 105
y = 0.0592x + 0.0635
R² = 0.995
t/qe (h/mg/g)
t (hr)
0
1
2
3
4
0
10
20
30
40
50
60

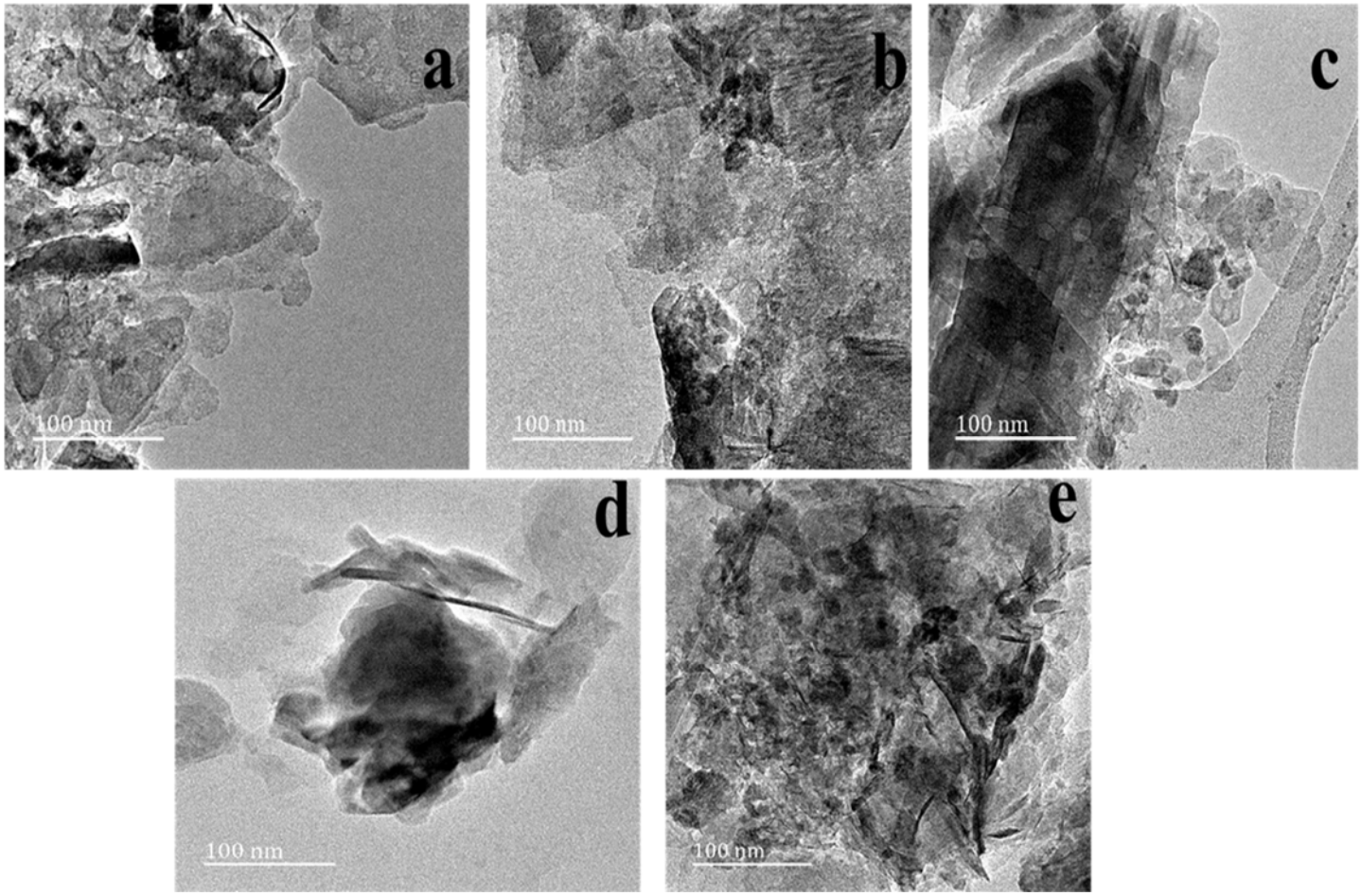

PCB 138
y = 0.0558x + 0.0793
R² = 0.993
t/qe (h/mg/g)
t (hr)
0
1
2
3
4
0
10
20
30
40
50
60


PCB 153
y = 0.055x + 0.0683
R² = 0.995
t/qe (h/mg/g)
t (hr)
0
1
2
3
4
0
10
20
30
40
50
60

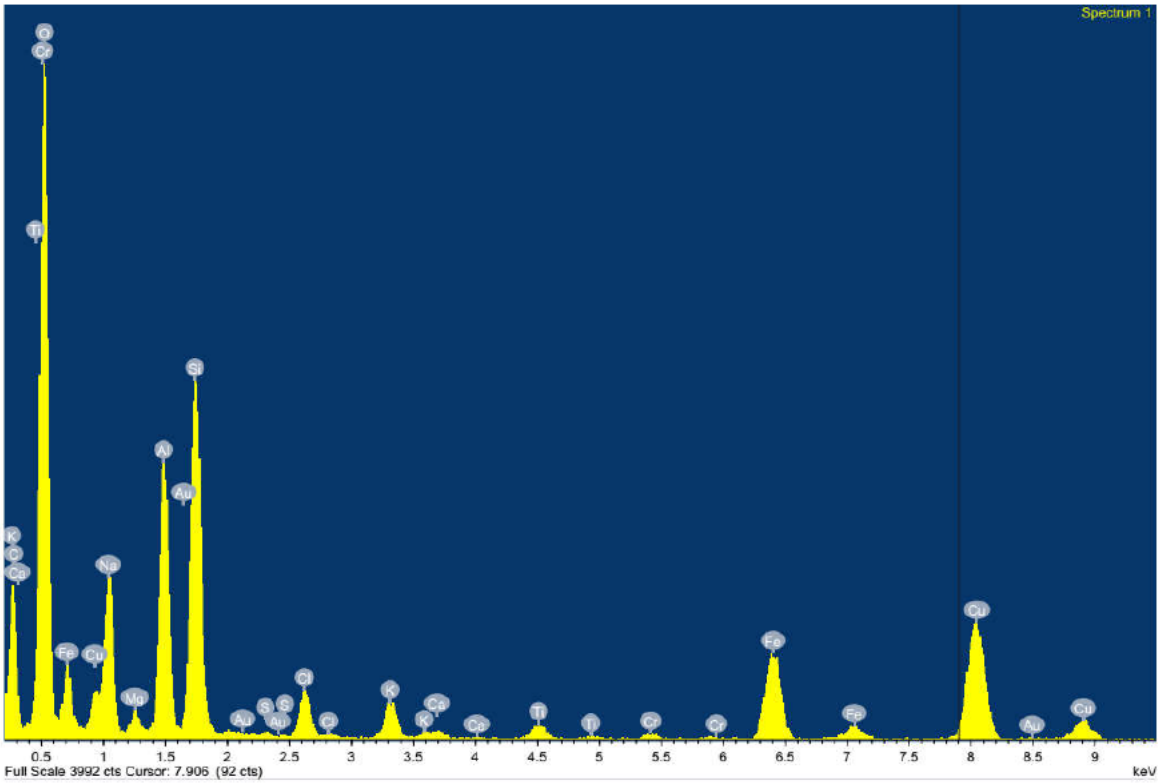

PCB 180
y = 0.0527x + 0.1102
R² = 0.983
t/qe (h/mg/g)
t (hr)
0
3
4
0
10
20
30
40
50
60

APPENDIX B: HRTEM/EDX, SEM/EDX for soil particle grain sizes and sediment samples

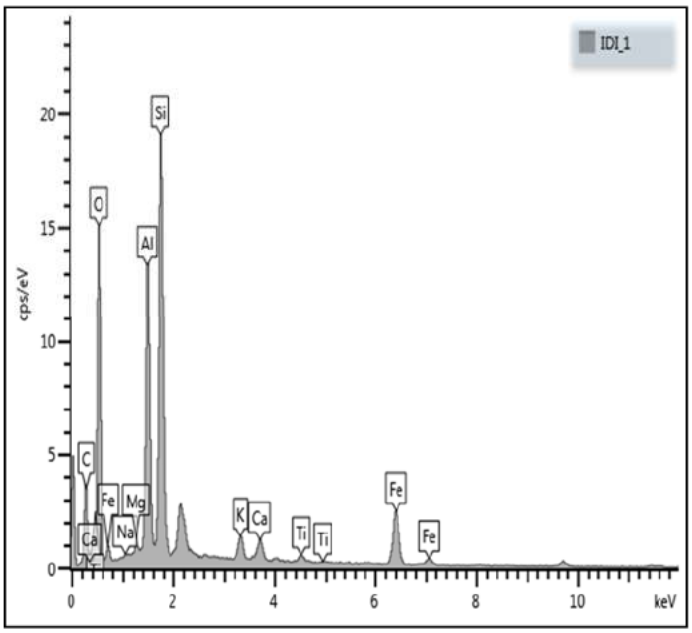
B 1 HRTEM images of soil particle grain sizes. (a) 75 µm soil; (b) 100 µm soil; (c) 200 µm (d) 300 µm soil; (e) 425 µm soil.

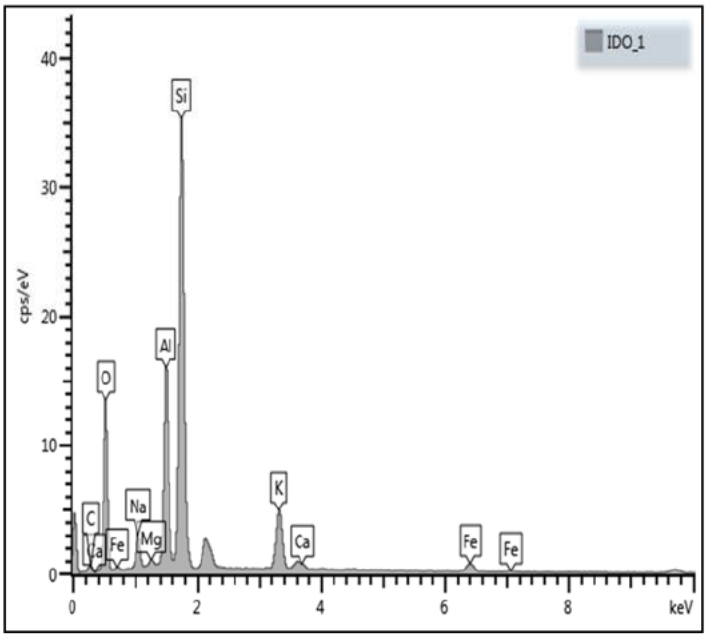


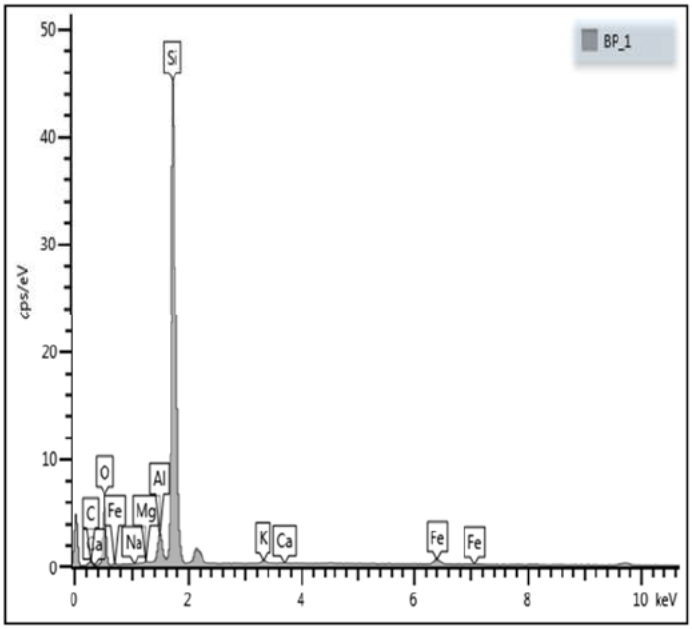
B 2 HRTEM-EDX of representative soil particle grain sizes

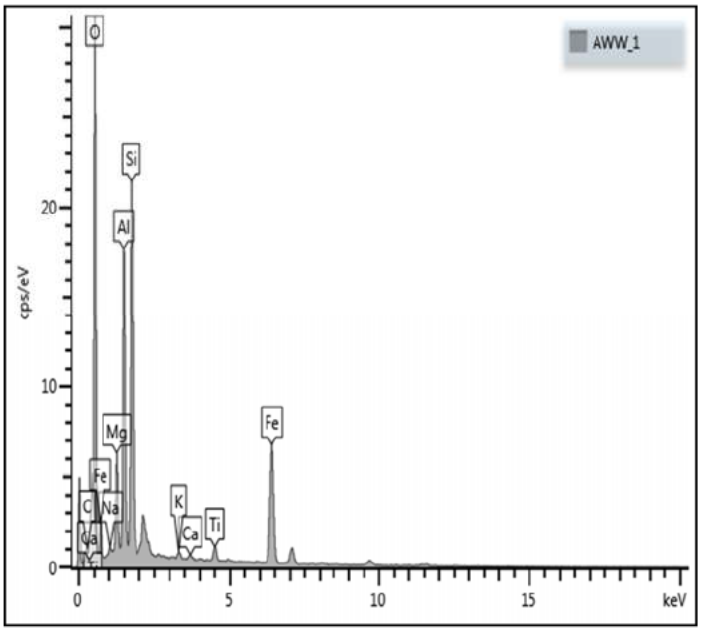


B 3 SEM-EDX of representative sediment samples collected along uMngeni River



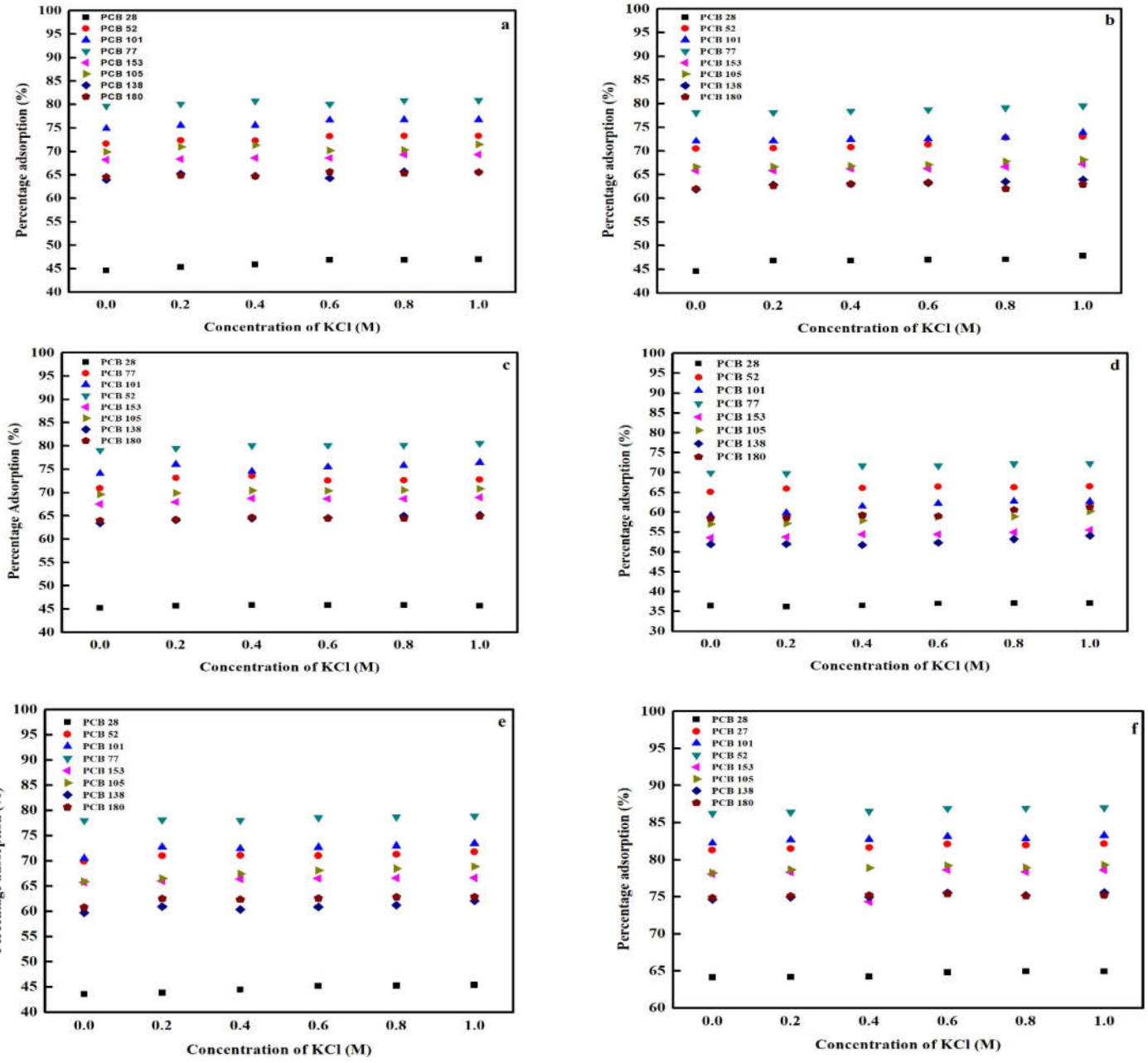



BP_1
cps/eV
keV
Si
O
C
Fe
Mg
Al
Na
K
Ca
Fe
Fe

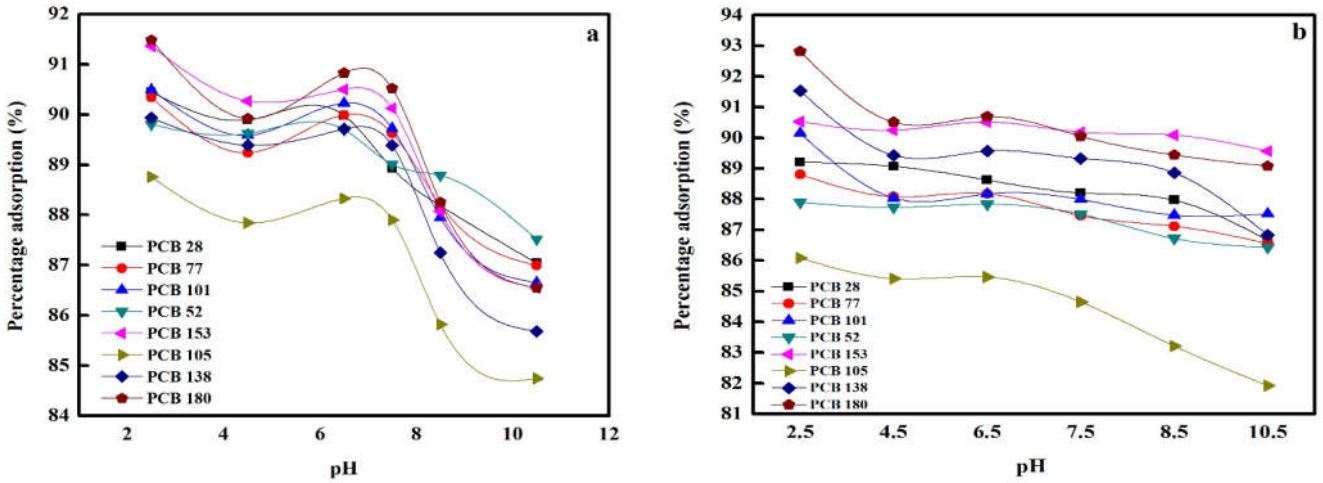

AWW_1
cps/eV
keV
O
Si
Al
Mg
Fe
C
Na
K
Ca
Ti
Fe

APPENDIX C: Effect of ionic strength, pH and temperature on the sorption of PCB congeners

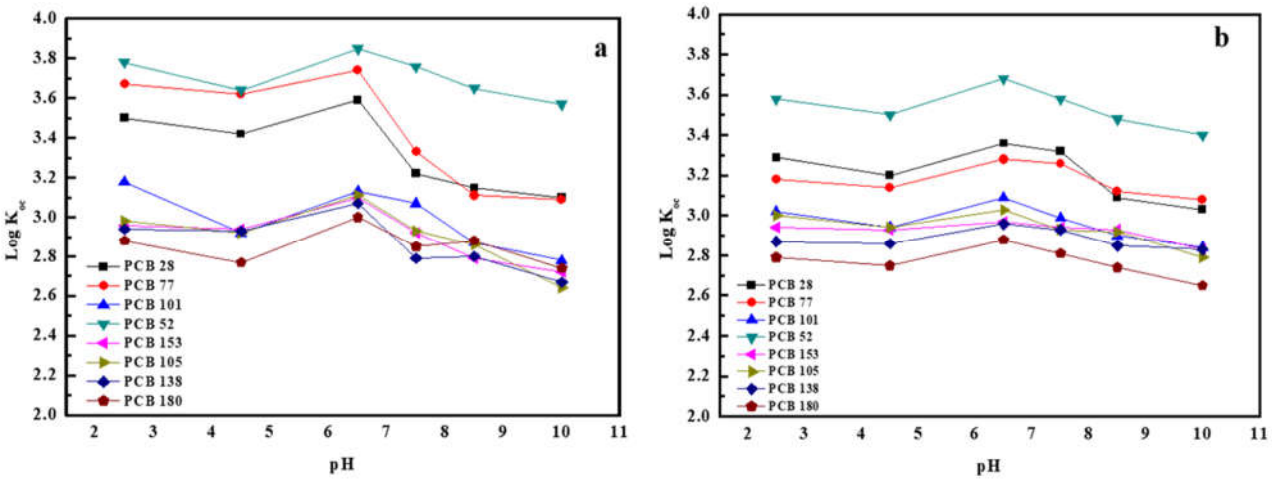
C 1 Effect of ionic strength on the sorption of PCBs between water and individual soil grain particle sizes. (a) 75 µm; (b) 100 µm; (c) 200 µm; (d) 300 µm; (e) 425 µm and (f) Mixtures of soil particle grain sizes.



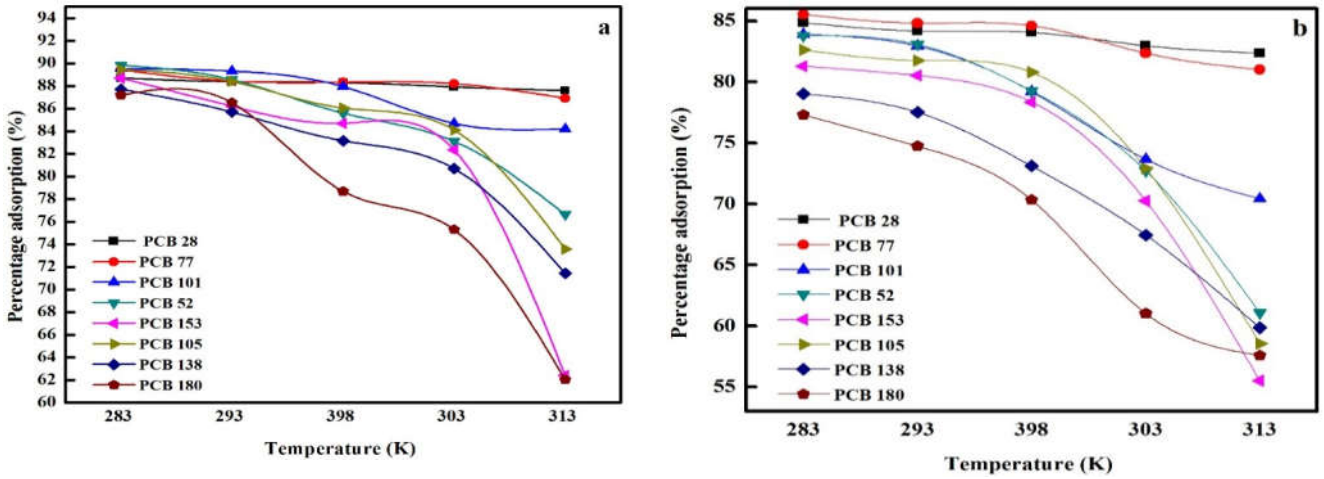
C 2 Effect of pH on the sorption of PCBs between aqueous solutions of $CaCl_2$ on different soil particle grain sizes. (a); 300 µm soil (b) 425 µm soil.



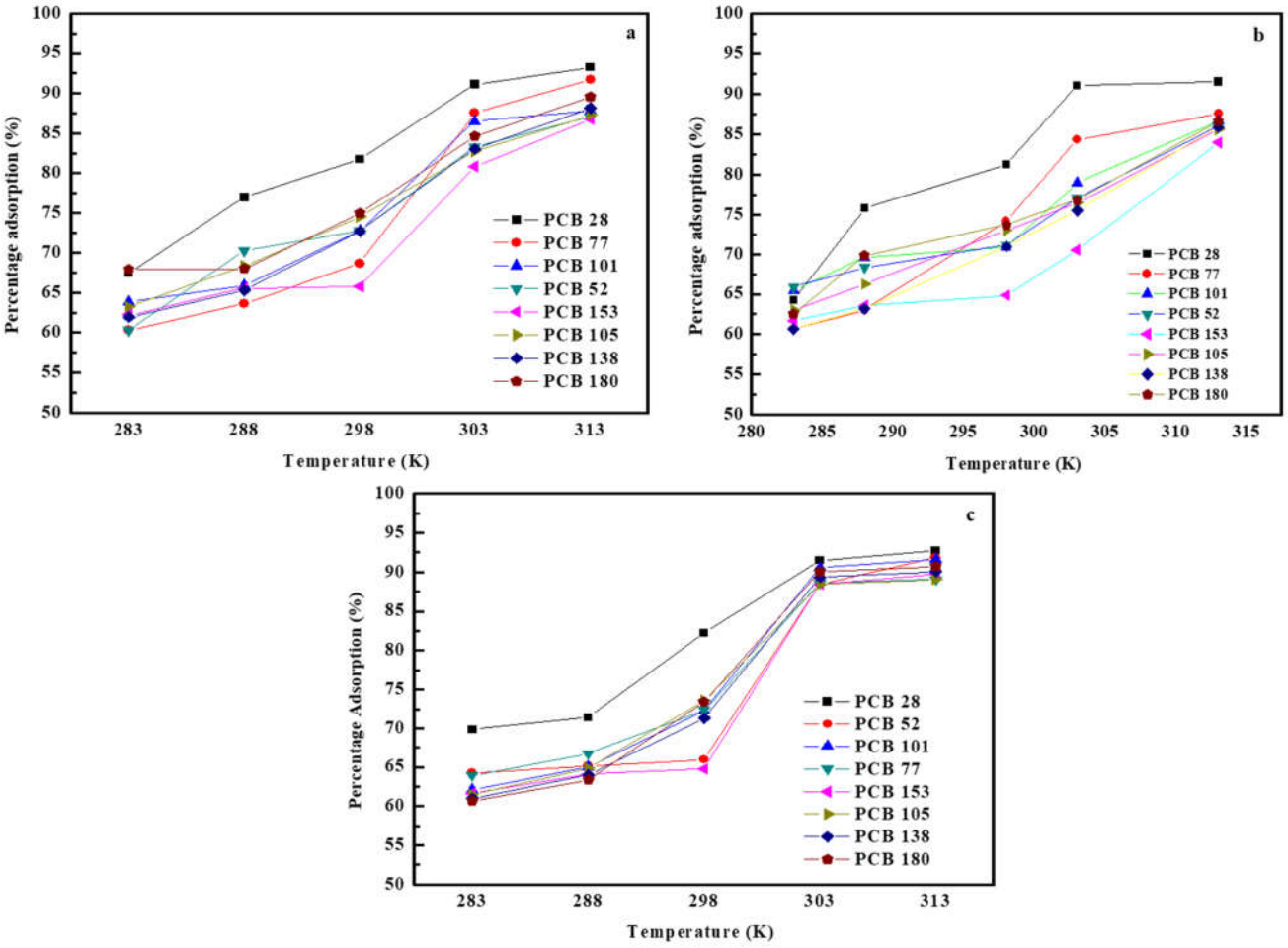
C 3 Effect of pH on the sorption of PCBs between aqueous solutions of humic acid on different soil particle grain sizes



C 4 (a-b) Effect of temperature on the partitioning of the PCBs between aqueous solution and various soil particle sizes. (a) 200 µm; (b) 300 µm.



C 5 (a-c): Effect of temperature on the partitioning of the PCBs between aqueous solution of humic acid and various soil particle sizes



APPENDIX D: Thermodynamic studies

D 1 Thermodynamic studies of the interaction of PCBs with water and soil particle sizes.

Parameters PCB 52	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol
283	18.52	-6.87	16.99	-6.66	8.85	-5.13	5.17	-3.86	4.73	-3.66
293	17.80	-7.01	15.44	-6.67	7.76	-4.99	4.91	-3.87	4.73	-3.78
298	16.80	-6.99	12.70	-6.30	5.94	-4.42	3.82	-3.32	4.72	-3.84
303	14.16	-6.68	6.23	-4.61	4.92	-4.02	2.66	-2.47	3.28	-2.99
313	11.87	-6.44	5.05	-4.22	3.28	-3.09	1.57	-1.17	3.23	-3.05
$\Delta H°$, kJ/mol	-11.39		-33.23		-25.09		-30.48		-10.99	
$\Delta S°$, kJ/(mol.K)	-15.41		-92.40		-69.65		-92.42		-25.24	
Parameters PCB 77	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol
283	14.96	-6.27	13.14	-6.06	8.46	-5.02	5.91	-4.18	6.24	-4.31
293	14.06	-6.46	11.32	-5.91	7.63	-4.95	5.58	-4.19	5.96	-4.35
298	13.30	-6.55	10.21	-5.76	7.57	-5.02	5.49	-4.22	5.90	-4.40
303	12.40	-6.60	7.39	-5.04	7.48	-5.07	4.66	-3.88	5.00	-4.05
313	11.59	-6.76	5.22	-4.30	6.65	-4.93	4.27	-3.78	4.49	-3.91
$\Delta H°$, kJ/mol	-6.54		-23.32		-5.46		-8.47		-8.48	
$\Delta S°$, kJ/(mol·K)	-0.52		-60.10		-1.56		-14.84		-25.14	
Parameters PCB 101	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol
283	18.11	-6.77	18.82	-6.90	8.55	-5.05	5.21	-3.88	7.24	-4.66
293	17.76	-7.01	15.72	-6.71	8.37	-5.17	4.86	-3.85	6.44	-4.54
298	17.64	-7.11	15.68	-6.82	7.30	-4.93	3.81	-3.31	6.02	-4.45
303	11.63	-6.18	8.93	-5.51	5.54	-4.31	2.80	-2.59	4.86	-3.98
313	9.99	-5.99	6.46	-4.85	5.34	-4.36	2.38	-2.26	4.67	-4.01
$\Delta H°$, kJ/mol	-16.05		-27.53		-13.39		-21.27		-11.78	

Δ*S*°, kJ/(mol·K)	-31.64		-71.72		-28.96		-60.70		-25.02	
Parameters PCB 105	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol
283	20.19	-7.07	19.62	-7.37	8.48	-5.03	4.75	-3.67	7.93	-4.87
293	19.77	-7.27	18.49	-7.49	7.63	-4.95	4.48	-3.65	7.66	-4.96
298	17.93	-7.15	16.57	-7.36	6.17	-4.51	4.20	-3.56	6.16	-4.50
303	12.33	-6.33	7.92	-5.78	5.29	-4.20	2.69	-2.49	3.92	-3.44
313	10.43	-6.10	1.45	-2.60	2.79	-2.67	1.41	-0.90	3.53	-3.29
Δ*H*°, kJ/mol	-17.90		-62.60		-26.93		-30.07		-22.65	
Δ*S,*° kJ/(mol·K)	-37.30		-191.78		-76.04		-91.31		-61.88	
Parameters PCB 138	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol
283	15.93	-6.51	13.43	-6.11	7.14	-4.63	3.77	-3.12	6.52	-4.41
293	15.32	-6.65	13.16	-6.28	6.00	-4.36	3.44	-3.01	6.19	-4.44
298	13.44	-6.44	10.90	-5.92	4.94	-3.96	2.72	-2.48	4.56	-3.76
303	9.50	-5.67	4.10	-3.56	4.18	-3.60	2.07	-1.84	3.50	-3.15
313	7.93	-5.39	2.75	-2.63	2.50	-2.39	1.49	-1.04	2.92	-2.78
Δ*H*°, kJ/mol	-18.76		-43.13		-25.60		-24.04		-21.88	
Δ*S*°, kJ/(mol·K)	-42.37		-128.29		-73.21		-72.95		-63.75	
Parameters PCB 153	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol
283	17.65	-6.75	15.84	-6.89	7.86	-4.85	4.34	-3.46	7.35	-4.69
293	16.32	-6.80	14.79	-6.98	6.26	-4.47	4.13	-3.46	6.91	-4.71
298	14.47	-6.62	12.99	-6.80	5.54	-4.24	3.62	-3.19	6.17	-4.51
303	11.57	-6.17	6.68	-5.40	4.67	-3.88	2.36	-2.16	3.70	-3.30
313	8.91	-5.69	3.20	-4.01	1.66	-1.32	1.25	-0.57	3.35	-3.15
Δ*H*°, kJ/mol	-17.47		-40.63		-35.96		-31.22		-21.82	

Δ*S*°, kJ/(mol·K)	-37.13		-118.08		-108.07		-96.14		-59.58	
Parameters PCB 180	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol
283	19.42	-6.98	12.26	-5.90	6.80	-4.51	3.41	-2.88	4.02	-3.28
293	15.11	-6.62	11.97	-6.05	6.43	-4.53	2.96	-2.64	3.83	-3.27
298	11.51	-6.05	6.01	-4.44	3.69	-3.24	2.37	-2.14	3.25	-2.92
303	10.18	-5.84	1.59	-1.16	3.05	-2.81	1.56	-1.13	2.55	-2.36
313	7.43	-5.22	1.15	-0.36	1.63	-1.28	1.36	-0.80	2.11	-1.95
Δ*H*°, kJ/mol	-24.11		-66.78		-36.69		-24.93		-17.10	
Δ*S*°, kJ/(mol·K)	-60.31		-212.07		-112.15		-77.24		-48.13	

D 2 (a-g) Thermodynamic studies of the interaction of PCBs with aqueous solution of humic acid and soil particle sizes

Parameters (a) PCB 52	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol	K_d	Δ*G*°, kJ/mol
283	2.067	-4.863	1.90	-4.480	1.65	-3.875	1.70	-3.991	2.07	-4.882
293	2.258	-5.407	2.37	-5.672	2.01	-4.817	1.95	-4.674	2.16	-5.168
298	3.328	-8.245	2.80	-6.940	2.47	-6.122	2.93	-7.252	2.24	-5.541
303	4.536	-11.427	4.62	-11.648	4.10	-10.339	3.78	-9.523	4.20	-10.569
313	4.728	-12.302	4.80	-12.484	4.62	-12.014	4.10	-10.672	4.63	-12.053
Δ*H*° (kJ/mol)	73.584		76.490		76.930		64.514		67.947	
Δ*S*° (kJ/mol.K)	276.174		285.278		284.023		241.513		254.475	

Parameters (b) PCB 77	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol
283	2.058	-4.841	1.79	-4.215	1.64	-3.865	2.23	-5.244	2.04	-4.802
293	2.249	-5.384	1.90	-4.541	2.61	-6.256	2.45	-5.861	2.31	-5.521
298	2.837	-7.029	2.01	-4.983	2.82	-6.986	2.68	-6.649	2.78	-6.899
303	4.201	-10.583	4.02	-10.131	3.69	-9.292	3.16	-7.972	4.22	-10.622
313	4.390	-11.424	4.32	-11.252	4.05	-10.532	3.94	-10.245	4.27	-11.118
ΔH°, kJ/mol	63.482		68.191		55.892		40.233		60.798	
ΔS°, kJ/(mol.K)	240.158		253.244		213.038		159.670		230.921	

Parameters (c) PCB 101	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol
283	1.649	-3.880	1.72	-4.038	2.04	-4.799	2.19	-5.149	1.86	-4.372
293	2.564	-6.139	1.77	-4.238	2.23	-5.346	2.56	-6.126	2.15	-5.148
298	2.632	-6.521	2.12	-5.255	2.82	-6.978	2.66	-6.600	2.78	-6.883
303	4.474	-11.270	4.20	-10.590	3.99	-10.058	3.31	-8.347	4.46	-11.227
313	4.620	-12.023	4.64	-12.071	4.12	-10.725	4.01	-10.422	4.60	-11.968
ΔH°, kJ/mol)	73.886		79.047		56.860		42.253		74.483	
ΔS°, kJ/(mol.K)	275.568		290.491		216.954		166.920		277.422	

Parameters (d) PCB 105	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol
283	2.047	-4.817	1.821	-4.284	1.971	-4.637	1.949	-4.585	1.790	-4.211
293	2.644	-6.332	2.164	-5.181	2.447	-5.859	2.264	-5.421	2.133	-5.108
298	2.764	-6.849	2.282	-5.655	2.959	-7.331	2.832	-7.017	2.883	-7.143
303	4.191	-10.558	3.996	-10.065	3.638	-9.165	3.111	-7.838	4.199	-10.578
313	4.473	-11.640	4.346	-11.310	4.068	-10.587	3.902	-10.154	4.268	-11.107
$\Delta H°$, kJ/mol	60.581		65.304		51.995		46.667		67.378	
$\Delta S°$, kJ/(mol.K)	231.021		244.432		200.351		180.688		252.521	

Parameters (e) PCB 138	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol	K_d	$\Delta G°$, kJ/mol
283	1.660	-3.906	1.786	-4.203	1.835	-4.318	1.686	-3.967	1.735	-4.083
293	2.370	-5.675	2.043	-4.891	2.173	-5.203	1.967	-4.710	2.050	-4.909
298	2.536	-6.284	2.109	-5.226	2.814	-6.972	2.671	-6.617	2.695	-6.677
303	4.277	-10.774	4.014	-10.112	3.662	-9.226	3.038	-7.653	4.303	-10.841
313	4.645	-12.087	4.336	-11.284	4.164	-10.836	3.930	-10.228	4.389	-11.423
$\Delta H°$, kJ/mol	74.636		66.969		59.516		54.630		72.293	
$\Delta S°$, kJ/(mol.K)	277.347		249.536		224.985		206.254		268.925	

Parameters (f) PCB 153	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol
283	1.645	-3.869	2.012	-4.733	1.863	-4.384	1.806	-4.250	1.804	-4.244
293	1.715	-4.107	2.758	-6.604	2.201	-5.269	2.006	-4.803	2.057	-4.926
298	1.894	-4.692	2.876	-7.126	2.218	-5.496	2.132	-5.283	2.125	-5.264
303	4.198	-10.576	3.841	-9.677	3.474	-8.751	2.633	-6.632	4.201	-10.582
313	4.572	-11.898	4.319	-11.238	4.012	-10.441	3.747	-9.750	4.355	-11.334
ΔH°, kJ/mol	79.218		54.189		53.025		44.027		68.408	
ΔS°, kJ/(mol.K)	290.358		208.947		201.648		168.907		254.783	

Parameters (g) PCB 180	**75 µm**		**100 µm**		**200 µm**		**300 µm**		**425 µm**	
Temperature	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol	K_d	ΔG°, kJ/mol
283	1.923	-4.525	1.734	-4.079	2.416	-5.685	1.896	-4.462	1.693	-3.983
293	2.408	-5.766	2.177	-5.213	2.418	-5.789	2.572	-6.158	1.985	-4.752
298	2.652	-6.570	2.583	-6.399	2.997	-7.424	2.888	-7.156	2.869	-7.108
303	4.416	-11.125	4.103	-10.336	3.809	-9.596	3.142	-7.916	4.389	-11.057
313	4.795	-12.477	4.375	-11.385	4.326	-11.258	4.003	-10.416	4.478	-11.654
ΔH°, kJ/mol	73.684		68.747		50.729		46.478		76.623	
ΔS°, kJ/(mol.K)	275.310		256.637		197.557		180.788		283.923	