INVESTIGATION OF THE LEVELS OF PBDEs AND PCNs IN THE SURFACE WATER AND SEDIMENTS FROM SELECTED WATERBODIES IN THE EASTERN CAPE PROVINCE, SOUTH AFRICA

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BY

AGUNBIADE, IDOWU VICTORIA

A THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF
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UNIVERSITY OF FORT HARE
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SUPERVISOR: PROFESSOR OMOBOLA OLURANTI OKOH

JUNE 2021

FIRST DECLARATION

I, the undersigned, declare that this thesis entitled “Investigation of the levels of PBDEs and PCNs in the surface water and sediments from selected waterbodies in the Eastern Cape Province, South Africa” submitted to the University of Fort Hare for the degree of Doctor of Philosophy in Chemistry in the Faculty of Science and Agriculture, and the work contained herein is my original work with the exemption of the citations and that this work has not been submitted to any other University in partial or entirely for the award of any degree.

Name: Idowu Victoria Agunbiade
Signature: ……………………………………..
Date: …………………………………………

DECLARATION ON PLAGIARISM

I, **Idowu Victoria AGUNBIADE** student number: 201816874 hereby declare that I am fully aware of the University of Fort Hare's policy on plagiarism and I have taken every precaution to comply with the regulations.

Signature……………………………………………

Date…………………………………………

CERTIFICATION

This thesis entitled “Investigation of the levels of PBDEs and PCNs in the surface water and sediments from selected waterbodies in the Eastern Cape Province, South Africa” meets the regulation governing the award of degree of Doctor of Philosophy of the University of Fort Hare and is approved for its contribution to scientific knowledge and literary presentation.

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Prof. O.O. Okoh Date
Supervisor

ETHICAL CLEARANCE APPROVAL FOR THE STUDY

The University of Fort Hare research ethics committee confirmed that ethical clearance was not required for this study as water and sediments were the only samples involved.

DEDICATION

This thesis is dedicated to the Almighty God and my Bliss.

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My spirit, soul and body praise the Almighty God for the gift of life and for bringing to reality my dream of becoming a Ph.D holder.

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LIST OF ACRONYMS

ADD: Average daily dose

AEMREG: Applied and Environmental Microbiology Research Group

AR: Analytical reagent

ASE: Accelerated solvent extraction

AT: Average time

ATSDR: Agency for Toxic Substances and Disease Registry

BFRs: Brominated flame-retardants

CF: Conversion factor

CHA: Chatty River

CN: Chlorinated naphthalenes or chloronaphthalenes

CT: Contact time

DCM: Dichloromethane

DDT: Dichlorodiphenyltrichloroethane

DEA: Department of Environmental Affairs, South Africa

DLLME: Dispersive liquid–liquid micro extraction

DPR: Department of Petroleum Resources

DW: Dry weight

DWAF: Department of Water Affairs and Forestry, South Africa

ECP: Eastern Cape Province

ED: Exposure duration

EF: Exposure frequency

EPA: Environmental Protection Agency

ET: Exposure time

EU: European Union

FIFA: Federation International de Football Association

FRs: Flame-retardants

GC: Gas chromatograph(y)

GC-µECD: Gas chromatograph micro-electron capture detector

GIABS: Gastrointestinal absorption factor

GW: Groundwater

HF-LPME: Hollow fibre–liquid phase micro extraction
HI: Hazard index
HPLC: High performance liquid chromatography
HQ: Hazard quotient
ILCR: Incremental lifetime carcinogenic risk
ISBN: International Standard Book Number
LADD: Lifetime average daily dose
LC: Liquid chromatography
LLE: Liquid-liquid extraction
LOD: Limit of detection
LOQ: Limit of quantitation
MAE: Microwave-assisted extraction
MASE: Microwave-assisted solvent extraction
MMC: Markman Canal
MWC: Motherwell Canal
ND: Not detected
NEL: North End Lake
NPS: Non-point source
NRC: Non-carcinogenic risk
NRF: National Research Foundation
NTU: Nephelometric turbidity unit
PBDEs: Polybrominated diphenyl ethers
PCBs: Polychlorinated biphenyls
PCDDs: Polychlorinated dibenzodioxins
PCDFs: Polychlorinated dibenzofurans
PCDHs: Polychlorinated diaromatic hydrocarbons
PCNs: Polychlorinated naphthalenes
PE: Port Elizabeth
PLE: Pressurized liquid extraction
POPs: Persistent organic pollutants
PS: Point source

PSU: Practical salinity unit

CR: Carcinogenic risk

RfC: Reference concentration

RfD: Reference dose

RHP: River Health Programme

RI: Risk index

RSD: Relative standard deviation

RT: Retention time

SA: South Africa

SAMRC: South African Medical Research Council

SAWQG: South African Water Quality Guidelines

SC: Stockholm Convention

SDME: Single drop microextraction

SE: Soxhlet extraction

SEACREG: Synthetic, Environmental and Applied Chemistry Research Group

SF: Slope factor

SFE: Supercritical fluid extraction

SIM: Selective ion monitoring

SPE: Solid phase extraction

SPME: Solid-phase microextraction

SPSS: Statistical Packages for Social Sciences

SW: Surface water

SWE: Swartkops Estuary

SWR: Swartkops River

T_e: Exposure ratio

TCDD: 2, 3, 7, 8 - tetrachlorodibenzo-*p*-dioxin.

TCmX: 2, 4, 5, 6-tetrachloro-m-xylene

TDS: Total dissolved solids

TEC: Toxicity equivalent concentration

TEF: Toxic equivalent factor

TEQ: Toxic equivalency

Temp: Temperature

TF: Transfer factor (from product to the exposed skin)

Turb: Turbidity

UFH: University of Fort Hare

UNEP: United Nations Environment Programme

USA: United States of America

USEPA: United States Environmental Protection Agency

WHO: World Health Organization

µg/kg: Micrograms per kilogram

µg/L: Micrograms per litre

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GENERAL ABSTRACT

Studies have revealed that persistent organic pollutants (POPs) are omnipresent in our environment; almost all human beings have definite levels of POPs in their bodies. Even fetus and embryos are not spared; they have been found to bear certain levels of POPs. So far, there are about 28 chemicals listed as POPs among which are polybrominated diphenyl ethers (PBDEs) and polychlorinated naphthalenes (PCNs). PCN and PBDE distributions have been reported from different sources around the world, but studies relating to PCNs occurrence and distribution in Africa, especially South Africa is still minimal. PBDEs have been reported to cause diabetes, cancer, damage to reproductive system, thyroid, liver and other vital organs in the body, while PCNs have been linked to chloracne (severe skin reactions/lesions) and liver disease (yellow atrophy) in humans, chicken oedema and X-disease in cattle. Hence, this study evaluates PCN levels in water and sediment samples from three waterbodies: North End Lake (NEL), Chatty River (CHA) and Makman Canal (MMC), while PBDE levels was reported in NEL and CHA samples. The three sites are located in Port Elizabeth, Eastern Cape Province (ECP) of South Africa. The lake serves as a recreational resort while the latter two waterbodies are tributaries discharging into the Swartkop Estuary, an important estuary in ECP.

Water samples were extracted with C_{18} cartridges (solid phase), while soxhlet was employed for the extraction of sediments. Water and sediment extricates were purified and quantified with gas chromatography-micro electron capture detector (GC-µECD). Forty-seven (47) water samples and 44 sediment samples were collected in August until December 2020 from six sampling points in NEL, five points in each of CHA and MMC. All the samples were evaluated for physicochemical properties, PBDEs and PCNs using validated standard methods. The sampling period covered three South Africa seasons: August (winter), October (spring) and December (summer).

The physicochemical parameters (PP) of NEL water samples for the three seasons generally varied as follows: temperature (15.3–23°C), pH (7.9–10.3), oxidation-reduction potential, ORP (23.4-110 mV), atmospheric pressure, AP (14.52-15.56 PSI), turbidity (15.1–167 NTU), electrical conductivity, EC (114–1291 µS/cm), total dissolved solids, TDS (55-645 mg/L), total suspended solids, TSS (20–107 mg/L) and salinity (0.05–0.65 PSU). All the PPs except for turbidity and TSS are within acceptable limits. NEL sediments had moisture content (MC), organic matter (OM) and organic carbon (OC) in the range of 0.04–8.0%, 0.08–2.2%

and 0.05–1.8%, respectively. The sum of eight PCN congeners $\sum_8$PCNs and six PBDE congeners $\sum_6$PBDEs in NEL water samples ranged from 0.164–2.934 µg/L and 0.009-1.025 µg/L individually. The values for $\sum_8$PCNs and $\sum_6$PBDEs in NEL sediment samples varied from 0.991–237 µg/kg and 0.354-28.850 µg/kg, respectively. The calculated hazard quotient (HQ) corresponding to the non-carcinogenic health risk associated with PBDEs in NEL water samples was 2.0×10^{-3}-1.4×10^{-1}, while the TEQ values due to PCNs varied from 6.10×10^{-7}-3.12×10^{-3} µg/L in NEL water samples and 3.70×10^{-5}-1.96×10^{-2} µg/kg dw in sediments.

The PP values for CHA water samples include temperature (15.4–22.9°C), pH (7.7–10.5), TDS (991–1771 mg/L), TSS (6–41 mg/L), turbidity (1.0–198 NTU), EC (1981–3542 µS/cm), AP (14.60–14.80 PSI), ORP (-339.1-51.3 mV), and salinity (1.02–1.87 PSU). The EC, TDS and salinity exceeded acceptable values at certain points. The sediments of CHA have MC, OM and OC contents ranging from 0.01-10.2%, 0.2-1.3% and 0.1-0.8% in that order. Sum of $\sum_8$PCNs, $\sum_6$PBDEs in CHA water and sediment samples ranged from 0.026–1.054 µg/L, 0.007-0.079 µg/L and 0.429–1888.468 µg/kg, 0.347-6.468 µg/kg individually. The HQ in CHA water samples was 1.6×10^{-3}-7.7×10^{-3} and the estimated TEQ was 1.0×10^{-7}-6.62×10^{-5} µg/L and 1.10×10^{-5}-6.40×10^{-2} µg/kg in water and sediments, respectively.

The temperatures for MMC water samples ranged from 15.6-24.5°C, while other PPs recorded were as follows: pH (8.4-10.2), TDS (943–4002 mg/L), TSS (7-491 mg/L), turbidity (2.9-154.2 NTU), EC (1885-8004 µS/cm), AP (14.53–14.82 PSI), ORP (7.8-130 mV) and salinity (0.96-4.47 PSU). MMC's sediments recorded MC, OM and OC varying as 0.4-18.9%, 0.2-4.5% and 0.1-2.6%, respectively across the three seasons. The $\sum_8$PCNs for MMC water and sediment samples were 0.035–0.699 µg/L and 0.260–6744 µg/kg. The TEQ values in MMC water and sediment samples were 1.19×10^{-7}-1.47×10^{-4} µg/L and 4.43×10^{-5}-4.19×10^{-1} µg/kg, respectively. The results are all less than one, and this suggests that the selected water is safe.

Results showed that NEL water had highest TEQ, PCN and PBDE concentrations, while MMC sediments recorded maximum TEQ and PCN levels in this study. PBDE concentrations in NEL sediments were above the other site. In conclusion, NEL water was most polluted with both pollutants (PCNs and PBDEs), but MMC sediments contained more PCNs. There is need for the immediate remediation of these selected waterbodies.

CHAPTER ONE

GENERAL INTRODUCTION

1.0 INTRODUCTION

Water is a consequential component of life that is required for the survival of man. It constitutes 75% of human's entire body, serving as lubricant (Popkin *et al.*, 2010). It also regulates the body temperature, expels malicious toxicants from the body, aids food digestion, and conveys blood and other nutrients within the body, among other functions (Hossain, 2015). Available water for use by humans could be groundwater or surface water. Surface water (SW), found above ground level includes the salty water in the ocean and the freshwater in the creeks, estuaries, lakes, reservoirs, rivers, streams, and wetlands while groundwater (GW) occurs deeper down the Earth's surface. Examples of groundwater include aquifers, springs, shallow or deep wells. GW serves as drinking water source for some people, notably inhabitants of rural region (Nas and Berktay, 2010), because of its acceptable characteristics, even though SW is believed to be of superior quality (Affiah *et al*., 2018).

SW receives pollutants from point and non-point sources. Point source (PS) pollution originates from a distinguishable point, such as industry or sewage treatment plants, while non-point source (NPS) pollution is from a combination of multiple sources and occurs when water in the form of storm water runoff passes through the Earth's surface and washes both natural and synthetic pollutants into lakes, rivers, wetlands, etc. The water that carries non-point source pollutants may arise from natural sources such as rainfall, or from anthropogenic actions, including farm irrigation or pasture keeping (Edokpayi *et al*., 2017; Odiyo *et al*., 2012).

Human beings depend more on SW than GW for their daily water requirements, especially for drinking and farmland irrigation purposes, possibly because of its abundance and accessibility. SW is also used in thermal-power stations to cool electrical-generator and in water cycle. It provides natural habitats for marine plants (flora) and animals (fauna). The water resources of any nation play a major role in its agriculture, animal husbandry, hydro-electricity generation, industrial and recreational activities. South Africa is among the severely water-scarce nations, considering its sparse rainfall, increased human population, and water rising demand by its people for various domestic and commercial purposes (Binns *et al*., 2001).

Although, water is crucial for human survival, the consideration for clean water, which is often ignored in developing nations, is, however, more important (Khalifa and Bidaisee, 2018). The United Nations has emphasized that access to pure water and sanitation is every individual's fundamental right (Bos *et al*., 2016). Reports have shown that every individual need between 20 to 50 litres clean water daily for consumption and washing purposes. Many waterborne diseases such as cholera, typhoid, and diarrhoea, which are deleterious to human well-being, have been attributed to polluted water (WHO, 2019). For instance, diarrhoea was evaluated to cause about 829,000 human deaths yearly due to consumption of infected food and poor hygiene (WHO, 2019); these deaths would have been prevented with proper sanitation in place.

Waterbodies are negatively impaired by natural and human-induced operations, which in-turn endanger human health, impinge water quality, civic and fiscal progress (Affiah *et al*., 2018). Pollution of water may arise from discharge of wastes containing organic and inorganic contaminants, pathogenic microorganisms, radioactive substances (e.g., uranium, radon), among others. Prominent among the organic chemical contaminants are the persistent organic pollutants (POPs) comprising some pesticides, industrial chemicals such as polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), polybrominated diphenyl ethers (PBDEs), etc. Others include unintended industrial process endproducts (polychlorinated dibenzodioxins, PCDDs and polychlorinated dibenzofurans, PCDFs), and many organic solvents (Zacharia, 2019; Haffner and Schecter, 2014). The list of inorganic chemicals that are toxic include the trace metals; arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), and other substances like cyanide (CN). All these chemicals are harmful to humans, and aquatic lives when present at certain concentrations in drinking water (Valavanidis and Vlachogianni, 2010).

In this study, two groups of POPs (PCNs and PBDEs) were evaluated in the selected surface waters and sediments. PCNs belong to the chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) group; they were declared as POPs in May 2015 at the Stockholm Convention (SC) following their fulfilment of POPs criteria (Fernandes *et al*., 2017; UNEP, 2015). PCNs structures consist of naphthalene rings where the available hydrogen atoms are replaced with chlorine atoms at various positions to yield 75 congeners (Falandysz, 1998). High volumes of PCNs are applied as flame-retardants (FRs) in the production of different consumer materials. Four categories of FRs; inorganic, organophosphorus, nitrogen containing and halogenated-organic FRs totalling almost 175 have been produced industrially. The halogenated-organic FRs comprise of brominated flame-retardants (BFRs) and chlorinated flame-retardants

(Birnbaum and Staskal, 2004). The most common class of flame-retardants is the “BFRs” due to their **e**fficient action and minimal production cost (Altarawneh and Dlugogorski, 2014). Studies have revealed that BFRs are ranked as one of the best FRs globally, accounting for about 20 to 25 percent of overall FRs in use (Abbasi *et al.*, 2015). They are included in many manufactured products; rugs, padded furnishings, electrical appliances and automobiles to impart them with fire resistance property and prevent fire outbreak or possibly deaths (Qi *et al*., 2014; Zhou *et al*., 2014; Segev *et al*., 2009; Hale *et al*., 2006). Up to 5–30% by weight of PCNs are intentionally added in some manufactured products to avert fire hazards while using the products (Birnbaum and Staskal, 2004).

PCNs are released into the surroundings in the course of their industrial manufacturing and as impurities during PCB manufacturing (Brack *et al.*, 2003; Taniyasu *et al*., 2003; Yamashita *et al.*, 2003). PCN levels in PCB formulations can be up to 870 μg/g (Noma *et al.*, 2006). PCNs are unintentionally discharged during metallurgical processes, evaporation from PCN-containing products, domestic refuse burning, and other incineration processes (Helm and Bidleman, 2003). PCNs occurrence and distribution in different environmental matrices have become major concerns among environmental scientists around the world because of their toxicity on human, wildlife and the environment. All PCNs are planar chemicals that are lipid-soluble (lipophilic), they share similar structures with PCBs and 2, 3, 7, 8 -tetrachlorodibenzo-*p*-dioxin (TCDD), the most toxic compound (Falandysz, 1998).

PBDEs are toxic organobromine chemicals that also belong to the class of BFRs; they are most common due to their efficient action alongside reduced production cost. FRs are adequate in minimizing fire-related problems because of their capacity to save lives, protect valuable properties and reduce cost of fire prevention. Due to their widespread use, lipophilicity, persistence, and inert characteristics, PBDEs emission sources into the environment include; waste from electrical and electronic appliances, wastewater treatment plants, landfill sites, importation of used vehicles, and indoor surroundings (Daso *et al.*, 2010). PBDEs are now prevalent in our environment and are found both in living and non-living things all over the world. Reports have shown that PBDEs are found in human body fluids at an alarming rate (Matovu *et al*., 2019; Antignac *et al*., 2016; Dimitriadou *et al*., 2016). They pose great concern to environmental scientists because of their poisonous nature to humans (USEPA, 2010; McDonald, 2002; Hooper and McDonald, 2000).

1.1 RESEARCH JUSTIFICATION

This research was undertaken to determine the quality and pollution status of three selected waterbodies; North End Lake (NEL), Markman Canal (MMC), and Chatty River (CHA) which are all located in Port Elizabeth (PE), Eastern Cape Province (ECP) of South Africa (SA). The NEL is a surface water located between a residential and industrial part of North End, PE. NEL was formerly known as Linden or Linton Reservoir and confers appealing scenes to many homes and offices around the North End, with an average depth and length of 3 meters and 2.51 kilometers, respectively. It is used for recreational purposes, power boating, canoeing, and fishing. The lake is located beside Nelson Mandela Bay Stadium that was built for the 2010 FIFA World Cup. Water from NEL is usually purified and used for watering the vegetation growing on the coliseum. The lake has been used for recreational purposes in the city. However, as the city expands, the lake has become polluted by effluent discharges from both residential and industrial areas (Kampire *et al.*, 2015). Garcı´a-Rodrı´guez *et al.* (2007) also confirmed the pollution status of NEL. Past studies carried out on NEL include the works of Kampire *et al.* (2017, 2015) in which polychlorinated biphenyls (PCBs) residues were discovered in several tissues of fish and surface sediment samples collected from the lake.

Chatty River (CHA), Markman Canal (MMC), and Motherwell Canal (MWC) have been identified as major streamlets discharging into the Swartkops estuary (SWE). The estuary is continuously being polluted by municipal and industrial wastes originating from these waterbodies (EFA, 2009). The SWE receives liquid wastes from industries in PE and adjoining cities in ECP of SA. Its geographical area accommodates millions of people who can be impacted with these pollution sources (Binning and Baird, 2001). CHA is the biggest streamlet that flows directly into the estuary in the direction of the Swartkops Village. It is surrounded by many houses from where faeces, garbage and other effluents are discharged into the SWE. CHA moves through the populous cities of Zwide, Veeplaas, New Brighton, Bethelsdorp and Missionvale, and become polluted by their stormwater runoff and refuse discharges (Adams *et al*., 2019).

The MMC infiltrates into the SWE at about 6.1 km from the estuary mouth. The MMC originates from an industrial area called Markman, which houses many industries such as motor, wool, and tannery, among other industries in PE, from where liquid waste (wastewater) empties into the canal. The canal moves through a small community before accessing the SWE around a flyover (Adams *et al*., 2019). The Markman Canal carries industrial effluents from Markman community to the SWE (EFA, 2011, 2009). Past reports from the continuous monitoring of water and sediment samples of SWE and Swartkops River (SWR) have revealed a steady increase in levels of heavy metals (Adams *et al*., 2019; Binning and Baird, 2001) and certain organic pollutants like organochlorine pesticides (OCPs), PCBs and PBDEs (Olisah *et al*., 2020, 2019; Nel *et al*., 2015). In a research carried out by Phillips *et al*. (2015), more Pb and Zn were found in macrophytes and sediments of MMC and MWC than that obtained along the main course of the estuary (Phillips *et al*., 2015). However, not much has been documented on the quality of the polluting rivers and canals (CHA, MMC, MWC). Hence, the rationale for this study.

Due to the toxic nature of the POPs, they may cause deleterious impacts to the essential systems and organs in the body when present in high concentrations (Alharbi *et al*., 2018). All POPs are toxic, bioaccumulate in adipose tissues of the living organisms, persistent in the surroundings and undergo long-range atmospheric transmission, an essential property that determines their spatial distribution (Bidleman *et al.*, 2010; Schecter *et al.*, 2009). Thus, there is need for their proper monitoring in the environment, most especially in our aquatic resources.

Several PCN congeners display harmful effects related to that of TCDD; fatality, death, skin infections, cancer (Blankenship *et al.*, 2000; Jakobsson and Asplund, 2000; Villeneuve *et al.*, 2000). Some health challenges including chloracne (severe skin reactions), liver disorder, eye sores, cancers, drowsiness, migraine, blood deficiency haematuria, and vomiting were recorded among people who accidentally encountered PCNs (CICAD, 2001).

Bioassay studies of PBDEs on rats and mice have experimentally linked PBDEs with endocrine and thyroid disorder, cancer (caused by penta and decabromodiphenyl ether), liver toxicity, developmental toxicity, diabetes and other health issues (ATSDR, 2017; Birnbaum and Staskal, 2004). PBDEs have shown intense toxicity and are proven endocrine disruptors that interrupt normal thyroid hormone function in human beings, which may cause adverse neurobehavioural impairements and cancer (ATSDR, 2017; Birnbaum and Staskal, 2004; Darnerud, 2003; McDonald, 2002).

Several published reports are available on PBDEs distribution across the globe in surface water, air, soil, sediment, sewage sludge, indoor dust, landfill leachates, fish and other marine animals, to mention a few (Qiu *et al*., 2020; Liu *et al*., 2015; Sun *et al*., 2015; He *et al*., 2014;

Zhu *et al*., 2014; Moon *et al*., 2012a; Clarke *et al*., 2010). In addition, their occurrences in human hair, milk, blood and adipose tissues have been documented (Matovu *et al*., 2019; Dimitriadou *et al*., 2016; Kucharska *et al*., 2015; Abdallah and Harrad, 2014; Moon *et al*., 2012b; Kim *et al*., 2005). The levels of PBDEs have been evaluated in certain Provinces of SA (Abafe and Martincigh, 2016, 2015a, b; Daso *et al*., 2016, 2015, 2013a, b, 2012; Darnerud *et al*., 2011; Olukunle and Okonkwo, 2015; Olukunle *et al*., 2015, 2012; La Guardia *et al*., 2013; Odusanya *et al*., 2009; Polder *et al*., 2008). Apart from the work of Olisah *et al*. (2020a, b), there is scarcity of information on this pollutant in ECP.

Similarly, PCN distributions have been recorded in certain environmental samples around the globe (Mao *et al*., 2020; Dat *et al*., 2019, 2018; Hu *et al*., 2019; Gewurtz *et al*., 2018**;** Kim *et al*., 2018; Xue *et al*., 2016; Mahmood *et al*., 2014; Schiavone *et al*., 2010). However, studies relating to PCN occurrence or distribution in Africa as a continent (Hogarh *et al*., 2012); and even SA as a nation is minimal. Very little information exists on the environmental concentrations, fate and PCN emissions within the Republic of South Africa.

Without mincing words, this research is the foremost to investigate PCNs incidence within South Africa, and this will provide reference figures for PCNs and PBDEs assessment from aqueous samples in ECP, which is believed to have the second largest land mass in the Republic (RHP, 2004).

1.2 RESEARCH HYPOTHESIS

The research hypothesis is that PBDEs and PCNs are found in surface water and sediments of the selected bodies of water. This hypothesis was tested by measuring the pollutants' levels in the samples and comparing with findings from previous studies and approved International Standards.

1.3 AIM AND SPECIFIC OBJECTIVES

The study was aimed at investigating PBDE and PCN occurrences and concentrations in surface water and sediments of North End Lake, Markman Canal and Chatty River all located in Port Elizabeth, Eastern Cape Province of South Africa.

The specific objectives were to:

a) validate existing analytical methods for PBDE and PCN determinations in surface water and sediments;

b) evaluate relevant physicochemical variables such as pH, temperature, turbidity, electrical conductivity, salinity, total dissolved and suspended solids of surface water samples collected from all the locations;

c) assess the physicochemical parameters such as moisture content, organic matter and carbon of the sediments collected from the study sites;

d) determine PBDE and PCN levels in water and sediment samples from the study sites;

e) study the seasonal variations of these compounds in the environmental matrices; and

f) estimate the possible human health risks due to these pollutants.

1.4 THESIS SYNOPSIS

This Thesis is a compendium of both past and recent studies on distribution and fate of two halogenated flame-retardants (PBDEs and PCNs) in our environment with emphasis on their incidence in surface water and sediments of three waterbodies (North End Lake, Markman Canal and Chatty River). Their seasonal variations and probable health risks were estimated in these stated matrices. The Thesis comprises of seven independent chapters.

Chapter 1: This chapter gives a concise general introduction about the types, importance and pollution sources of water in our environment. General features of POPs and specific properties of the two selected pollutants along with their adverse health effects are enumerated. Brief history of the studied sites, the aim, specific objectives and justification for this study are also stated.

Chapter 2: This chapter reviews past studies on the occurrence and analytical methods employed for PCNs quantification in human and environmental matrices as published in Environmental Pollutants and Bioavailability, 32:1, 154-174, DOI: 10.1080/26395940.2020.1829992.

Chapter 3: This chapter contains reports on PBDEs prevalence in humans and the environment with emphasis on South Africa. It was submitted to Environmental Science and Pollution Research journal as a manuscript and is under revision.

Chapter 4: This chapter validates previously published and developed chemical analytical methods for PCNs and PBDEs extraction and quantification from aqueous and solid environmental samples, using GC-µECD.

Chapter 5: This chapter evaluates the variations of water physicochemical parameters, PCN and PBDE concentrations in three Port Elizabeth surface water sources. The associated risks with these pollutants in the water samples are also estimated.

Chapter 6: The environmental concentrations of PCNs and PBDEs in sediment samples of lake, river and canal are determined in this chapter.

Chapter 7: General discussion, recommendations, conclusion and contibutions of this study to knowledge are presented in this chapter.

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CHAPTER TWO

LITERATURE REVIEW

A review on occurrence and analytical procedures for the evaluation of polychlorinated naphthalenes in human and environmental matrices

(Published in Environmental Pollutants and Bioavailability)

Abstract

Polychlorinated naphthalenes are organochlorine compounds which are made up of the naphthalene ring system, in which up to eight hydrogen atoms were substituted with chlorine atoms, yielding 75 chlorinated compounds referred to as “congeners”. They were considered as persistent organic pollutants (POPs) in May 2015 at the Stockholm Convention owing to their toxicity, persistence, bioaccumulation and potential for long-range transport in the environment. PCNs were invented in the early 1900s to be applied as flame-retardants in consumer products and as insulating liquids for capacitors due to their excellent insulating properties and low reactivity. Flame-retardants have emerged as an effective solution in minimizing fire-related problems. However, their negative environmental impacts have become of great concerns, given that they are toxic and ubiquitous. While chloracne and liver damage have been associated with human exposure to PCNs, other toxic effects have also been reported in both humans and animals. Different analytical methods for the evaluation of PCNs in various environmental samples were reviewed in this article. The liquid-liquid extraction method is frequently used for water analysis than the solid phase extraction because of its affordability, while the soxhlet extraction method is mostly considered for determinations in other environmental matrices. The gas chromatography is generally employed for the separation of PCNs, while the identification or quantification is usually performed by mass spectrometry. Their levels in human and some environmental samples across the globe and the factors influencing the distribution are also mentioned. Reported data revealed that the highly toxic congeners (CNs 66, 67 and 73) are prevalent in most human and food samples. There is need for proper and continuous monitoring of these pollutants in our environment.

Keywords: Persistent organic pollutants; flame-retardants; polychlorinated naphthalenes; bioaccumulation; toxicity; congener.

2.0 Introduction

Persistent organic pollutants (POPs) are chemical compounds that withstand environmental decomposition from chemical, biological, and photolytic processes (Ritter *et al.,* 1995). They all have four key characteristics in common: they are environmentally persistent, toxic, undergo long-range transport in the atmosphere, and bio-accumulate in adipose tissues of living organisms (Ritter *et al.,* 1995). POPs include the first twelve "Dirty Dozen" which are the highly toxic chemicals and the "Nasty Nine". The dirty dozen comprises of eight pesticides, two industrial chemicals, and two unintended industrial by-products; they are used in agriculture, industry, and some household products such as pesticides, solvents, and even pharmaceuticals. The nasty nine include polycyclic aromatic hydrocarbons and brominated flame-retardants (BFRs) (Haffner and Schecter, 2014).

Polychlorinated naphthalenes, which are mostly semi volatiles, were included on the list of banned POPs at the seventh meeting of the Conference of the Parties to the Stockholm Convention in May 2015 because of their hazardous, bioaccumulation and persistent tendencies in the environment (UNEP, 2015). They were previously applied in high volumes as flame-retardants in various household products. They constitute up to 5–30% by weight in some manufactured products and are added intentionally to prevent fire-related damages during the products usage. Over 175 types of flame-retardants (FRs) are now commercially available. They are divided into four classes, which are the inorganic, organophosphorus, nitrogen-containing and halogenated-organic FRs. The latter group includes brominated and chlorinated flame-retardants (Birnbaum and Staskal, 2004).

Naphthalenes are organic compounds that may be replaced with halogens in about eight positions. Chlorinated naphthalenes or chloronaphthalenes (CN) which are often called polychlorinated naphthalenes (PCNs) are a class of organochlorine chemicals made up of the naphthalene ring system, in which one to eight hydrogen atoms have been substituted with chlorine atoms, yielding 75 chlorinated compounds referred to as "congeners" (UNEP, 2017a; Helm *et al.*, 2006; Falandysz, 1998). PCN general structure and numbering as described by certain authors (UNEP, 2017; Falandysz, 1998) are displayed in Figure 2.1.

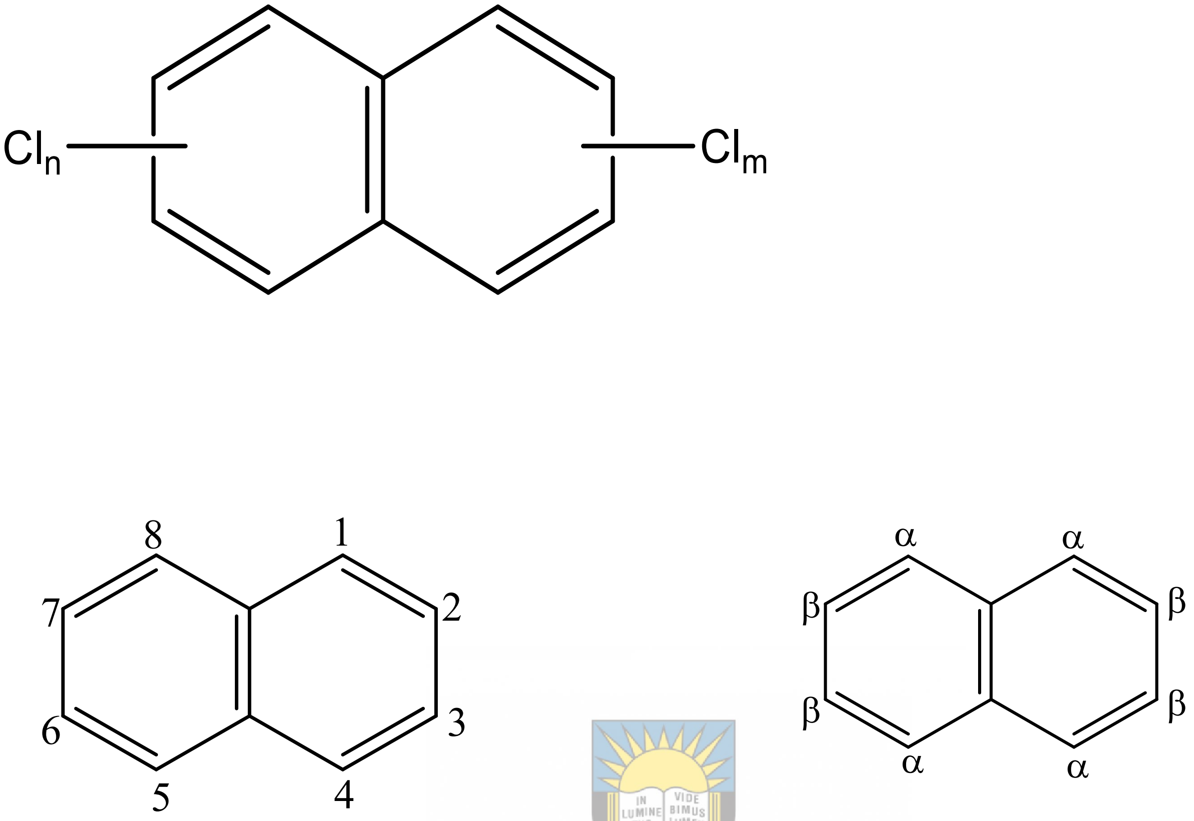

Figure 2. 1 General structure of polychlorinated naphthalenes (where m + n = 1 to 8) (Source: UNEP, 2017a; Falandysz, 1998)

PCNs were invented in the early 1900s to be applied as flame-retardants in consumer products and insulating liquids for capacitors due to their excellent insulating properties and low reactivity (Hanari *et al*., 2004). The generic molecular formula is $C_{10}H_{8-n}Cl_n$; where *n* ranges from 1 to 8. Commercially manufactured PCNs are impure materials, which are usually mixtures of many congeners, comprising of fine liquids, strong waxes, and solids. Liquid PCNs dissolve almost in all organic solvents, while strong waxes or solid PCNs dissolve in halogenated aromatic liquids, chlorinated paraffin, plasticizers, petroleum waxes, and naphtha (Kucklick and Helm, 2006).

They are divided into eight homologue groups based on positioning and numbering systems of the chlorine atoms as mono- to octa chloronaphthalenes as shown in Table 2.1. The mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, and octa-CNs have 2, 10, 14, 22, 14, 10, 2, and 1 congeners, respectively (Jakobson and Asplund, 2000; Falandysz, 1998). Table 2.2 describes the scientific names for the 75 PCN congeners (Hanari *et al*., 2020).

Table 2. 1 List of PCN Homologues

Congener group	Acronym	Molecular formula	No. of individual congeners
Monochloronaphthalenes	MonoCN	$C_{10}H_7Cl$	2
Dichloronaphthalenes	DiCN	$C_{10}H_6Cl_2$	10
Trichloronaphthalenes	TriCN	$C_{10}H_5Cl_3$	14
Tetrachloronaphthalenes	TetraCN	$C_{10}H_4Cl_4$	22
Pentachloronaphthalenes	PentaCN	$C_{10}H_3Cl_5$	14
Hexachloronaphthalenes	HexaCN	$C_{10}H_2Cl_6$	10
Heptachloronaphthalenes	HeptaCN	$C_{10}HCl_7$	2
Octachloronaphthalenes	OctaCN	$C_{10}Cl_8$	1

Source: Jakobson and Asplund, 2000; Falandysz, 1998

Table 2. 2 PCN congeners' scientific names

PCN No	IUPAC	PCN No	IUPAC	PCN No	IUPAC
Monochlorinated naphthalenes (MonoCN)		26	2,3,6-TriCN	52	1,2,3,5,7-PentaCN
1	1-MonoCN	Tetrachlorinated naphthalenes (TetraCN)		53	1,2,3,5,8-PentaCN
2	2-MonoCN	27	1,2,3,4-TetraCN	54	1,2,3,6,7-PentaCN
Dichlorinated naphthalenes (DiCN)		28	1,2,3,5-TetraCN	55	1,2,3,6,8-PentaCN
3	1,2-DiCN	29	1,2,3,6-TetraCN	56	1,2,3,7,8-PentaCN
4	1,3-DiCN	30	1,2,3,7-TetraCN	57	1,2,4,5,6-PentaCN
5	1,4-DiCN	31	1,2,3,8-TetraCN	58	1,2,4,5,7-PentaCN
6	1,5-DiCN	32	1,2,4,5-TetraCN	59	1,2,4,5,8-PentaCN
7	1,6-DiCN	33	1,2,4,6-TetraCN	60	1,2,4,6,7-PentaCN
8	1,7-DiCN	34	1,2,4,7-TetraCN	61	1,2,4,6,8-PentaCN
9	1,8-DiCN	35	1,2,4,8-TetraCN	62	1,2,4,7,8-PentaCN
10	2,3-DiCN	36	1,2,5,6-TetraCN	Hexachlorinated naphthalenes (HexaCN)	
11	2,6-DiCN	37	1,2,5,7-TetraCN	63	1,2,3,4,5,6-HexaCN
12	2,7-DiCN	38	1,2,5,8-TetraCN	64	1,2,3,4,5,7-HexaCN
Trichlorinated naphthalenes (TriCN)		39	1,2,6,7-TetraCN	65	1,2,3,4,5,8-HexaCN
13	1,2,3-TriCN	40	1,2,6,8-TetraCN	66	1,2,3,4,6,7-HexaCN
14	1,2,4-TriCN	41	1,2,7,8-TetraCN	67	1,2,3,5,6,7-HexaCN
15	1,2,5-TriCN	42	1,3,5,7-TetraCN	68	1,2,3,5,6,8-HexaCN
16	1,2,6-TriCN	43	1,3,5,8-TetraCN	69	1,2,3,5,7,8-HexaCN
17	1,2,7-TriCN	44	1,3,6,7-TetraCN	70	1,2,3,6,7,8-HexaCN
18	1,2,8-TriCN	45	1,3,6,8-TetraCN	71	1,2,4,5,6,8-HexaCN
19	1,3,5-TriCN	46	1,4,5,8-TetraCN	72	1,2,4,5,7,8-HexaCN
20	1,3,6-TriCN	47	1,4,6,7-TetraCN	Heptachlorinated naphthalenes (HeptaCN)	
21	1,3,7-TriCN	48	2,3,6,7-TetraCN	73	1,2,3,4,5,6,7-HeptaCN
22	1,3,8-TriCN	Pentachlorinated naphthalenes (PentaCN)		74	1,2,3,4,5,6,8-HeptaCN

23	1,4,5-TriCN	49	1,2,3,4,5-PentaCN	Octachlorinated naphthalene (OctaCN)	
24	1,4,6-TriCN	50	1,2,3,4,6-PentaCN	75	1,2,3,4,5,6,7,8-OctaCN
25	1,6,7-TriCN	51	1,2,3,5,6-PentaCN		

Source: Hanari *et al*., 2020.

The occurrence of PCNs has been widely studied in various matrices around the world; air (Mao *et al*., 2020; Hu *et al*., 2019; Dat *et al*., 2018; Die *et al*., 2016; Xue *et al*., 2016; Hogarh *et al*., 2013, 2012; Odabasi *et al*., 2012; Jaward *et al*., 2004), fish and seafoods (Gewurtz *et al*., 2018; Kim *et al*., 2018; McGoldrick *et al*., 2018; Isosaari *et al*., 2006), foods (Fernandes *et al*., 2019, 2011, 2010; Domingo *et al*., 2003), biota (McGoldrick *et al*., 2018; Helm *et al*., 2008; Hanari *et al*., 2004), human samples (Li *et al*., 2020; Jin *et al*., 2019; Fromme *et al*., 2015; Schiavone *et al*., 2010; Park *et al*., 2010; Kunisue *et al*., 2009; Witt and Niessen, 2000; Lunden and Noren, 1998), sediment (Dat *et al*., 2019; McGoldrick *et al*., 2018; Li *et al*., 2017; Lega *et al*., 2017; Kukucka *et al*., 2015; Zhang *et al*., 2015a; Mahmood *et al*., 2014a; Pan *et al*., 2012, 2011; Castells *et al*., 2008; Helm *et al*., 2008; Marvin *et al*., 2002), water (Mahmood *et al*., 2014a; Ishaq *et al*., 2009; Marti and Ventura, 1997), and sewage sludge samples (Zhang *et al*., 2014). Nevertheless, there are limited studies relating to PCN occurrence in water samples.

The procedures for sample collection, pre-treatment, extraction, purification (clean-up) and instrumental analysis for PCNs are comparable with other organo-halogenated chemicals such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). Scientists and researchers have developed and validated several analytical methods for PCN analysis. Owing to their lipophilic nature, poor water solubility and their minute concentrations in water, their isolation from aqueous matrices has been commonly achieved using solid phase extraction (Marti and Ventura, 1997), and conventional liquid–liquid extraction (LLE) method (Mahmood *et al*., 2014a). Extraction of PCNs from air, solid and other environmental samples has usually been performed using soxhlet extractor with dichloromethane (Mao *et al*., 2020; Dat *et al*., 2019, 2018; Mahmood *et al*., 2014a), or other organic solvents (McGoldrick *et al*., 2018; Lega *et al*., 2017). Other developed methods for extracting PCNs from environmental samples include accelerated solvent extraction or pressurized liquid extraction systems (Hu *et al*., 2019; Kim *et al*., 2019; Gewurtz *et al*., 2018; Lega *et al*., 2017; Li *et al*., 2016), and sonication (Odabasi *et al*., 2017).

In the same manner with PCB, conventional gas chromatography (GC) with electron capture detection has been severally used in the past for the partitioning and separation of discrete PCN congeners. However, gas chromatograph coupled with mass spectrometer is now preferred owing to its different advantages (Fernandes *et al*., 2017). This chapter provides a summary of occurrence, distribution, and fate of PCNs in the environment in relation to their physicochemical properties. Human exposure to PCNs, routes of exposure and their attendant health effects, methods of extraction, analysis and detection in the environment and human samples are also discussed in this review.

2.1 Physicochemical properties and applications of PCNs

2.1.1 Physicochemical properties of PCNs

The physicochemical properties of PCNs are comparable to those of PCBs, PCDDs, and PCDFs in terms of good thermic balance, satisfactory weather stability, insulating features, low combustibility, and inertness. All these favours their application as insulating liquids in capacitors, generators, and non-conducting wires in the electrical industry (Fernandes *et al*., 2017). PCNs possess small to medium volatility, which decreases as the chlorine content increases (Jakobson and Asplund, 2000). The physicochemical properties of the congeners depend on the numbering and positioning systems of the chlorine atoms within the CN organic molecule (Environment Canada, 2011; Falandysz, 2003; Blankenship *et al*., 2000). The essential physical and chemical properties of PCNs include; water solubility (S_W), vapour pressure (P_V), octanol-water partition coefficient (Kow), Henry's law constant (K_H), melting point (MP), and boiling point (BP). S_W, P_V, and K_H values are prone to reduction from mono- to octa-CNs, while Kow, MP and BP increase from mono- to octaCNs (Environment Canada, 2011). However, Kow, octanol-air partition coefficient (K_{oa}), K_H and air-water partition coefficient (K_{aw}) are important variables for describing their environmental fate (Puzyn and Falandysz, 2007).

Partition coefficients describe how a solute is distributed between two immiscible phases at equilibrium. The octanol–air partition coefficient is the ratio of a solute concentration in octanol to the solute concentration in air at equilibrium. One of the most important parameters for describing how the semi-volatile compounds partition between the atmosphere and other environmental matrices (soil, vegetation, aerosols, etc.) is their octanol-air partition coefficient (log K_{oa}) (Meylan and Howard, 2005). Pollutant concentrations in soil are linked with soil organic carbon (SOC), leading to repeated soil–air exchange. However, non-volatile chemicals with higher log Koa are less impacted by SOC content, as they are static in soils with considerable attraction for the soil and have minimum capacity to reabsorb into the atmosphere (Sweetman *et al*., 2005). Su *et al*. (2002) obtained K_{oa} values for 27 CN congeners by interpolation of known Koa values using isothermal capacity factors on three gas chromatographic columns having different polarity at temperature range of 10°C to 50°C. The partition coefficients were determined indirectly, but the major challenge with the analysis is the high cost and long duration for capacity factors measurement on multiple GC columns. Harner and Bidleman (1998) estimated log K_{oa} values for 24 PCNs as a function of temperature from 0 to 50°C. Their study revealed a clear trend of increasing values as the level of chlorination increased. The values increased by more than three (3) orders of magnitude from di- to hexachlorinated homologue groups. Wania and Mackay (1996) viewed K_{oa} values as ideal for evaluating the partitioning properties of POPs in the environment. They proposed that K_{oa} values should be evaluated from the ratio of K_{ow} and K_{aw} since experimentally determined K_{oa} values are available for few compounds. Based on these ratios, pollutants with K_{oa} between 10^6 and 10^8 have reasonably high environmental mobility, while those with K_{oa} of 10^8-10^{10} have low mobility (Wania and Mackay, 1996). The congeners with less chlorine substitution demonstrate tendency to engage in long-range transport in the atmosphere from the temperate to Artic regions. This is somewhat attributed to their relatively high air-water partition coefficient (log K_{aw}) values that support partitioning in air. However, heavier and highly chlorinated congeners engage mostly in long-range oceanic transport. Less volatile compounds do not return to the atmosphere after their deposition on the surface of the earth (soils, oceans, rivers etc.) (Wania, 2006). Hence, the contribution from the oceans is often higher than through the atmospheric transport, even though their solubility decreases as the level of chlorination increases. Congeners that are more volatile are highly susceptible to changes in the rate at which they degrade in air. K_{ow} and K_{aw} have shown marked influences on organic matrices (soils and sediments) and air (Wang *et al*., 2020).

The octanol-water partition coefficient (log Kow) is another variable used in the estimation of the environmental fate of organic compounds. Studies have shown its relationship with water solubility, soil/sediment adsorption coefficients, toxicities, and bioconcentration factors for aquatic organisms (Yeh and Hong, 2002; Harner and Bidleman, 1998). Kow are measured using direct experimental methods, reverse-phase high-performance liquid chromatography and thin-layer chromatography (RP-HPLC and RP-TLC), or generator-column technique (Yeh and Hong, 2002; Harner and Bidleman, 1998). Yeh and Hong (2002) obtained Kow at 25°C for 12 PCB congeners using generator-column/extractor-column method, and GC-ECD instrument. Their log Kow values ranged from 6.47 to 7.15 and increased as the molecular weights increased. POPs, being mostly hydrophobic, have K_{ow} ranging between 10^4 and 10^8, and find their ways into the aquatic environment via atmospheric transport or from different tributaries, thus recording much higher level in freshwater column than in the marine water (Gioia *et al*., 2011). Just like PCBs, highly chlorinated congeners of PCN are prone to deposit often in soils and sediments, given their higher K_{ow}. As the octanol-water partition coefficient increases with the degree of chlorination and molecular weight, their potential to become partitioned to soils and sediments also increases. The experimental estimation of partition coefficients in a complex system can be an expensive, difficult, and time-consuming process (Yeh and Hong, 2002).

Henry's law constant (K_H) (or air-water partition coefficient, K_{aw}) is the ratio of a compound's partial pressure in air to the concentration of the compound in water at a given temperature. The higher the K_H value at a given pressure, the lower is the solubility of the gas in the liquid. Experimentally determined data for these variables are available for few congeners due to lack of high purity materials required for PCN analysis, long duration, and high costs of the experiments (Puzyn and Falandysz, 2007; Yeh and Hong, 2002). As a result, Puzyn and Falandysz (2007) applied extrapolative and reliable quantitative structure-property relationship (QPSR) models to evaluate log K_{ow}, log K_{oa}, log Kaw, and K_H for 75 PCN congeners as; 3.93-6.68, 5.93-11.64, −1.68 to −5.21, and 0.02-51.24 respectively. The variation of these physicochemical properties with temperature influences POPs environmental behaviour and transportation (van de Plassche and Schwegler, 2002). Almost all POPs are volatile; this facilitates their evaporation and deposition in air, soil and water at normal atmospheric temperatures. Hot temperatures promote organic pollutants' evaporation from the Earth's surface in equatorial and humid zones, while cold temperatures at high latitudes aid their deposition from the atmosphere on soil and water. This in turn favours their adsorption on suspended solids, and are eventually removed by rain; thereby permitting POPs persistence in the environment. Similarly, cool temperatures reduce POPs vapourization from water, thereby increasing their liquefaction and partitioning from gaseous to liquid phase on the Earth's surface. Semi-volatiles like PCNs are partitioned into water, snow, ice, soil or vegetation (Wania and Mackay, 1996).

Chlorinated naphthalenes (CN) are lipid-loving compounds (highly lipophilic); their water solubility generally decreases as the molecular weight increases while their boiling and melting point increase as the chlorine content increases. They are insoluble in water except for mono- and di-CNs; the water solubility is 2870 µg/L for 2-CN and 924 µg/L for 1-CN. This reduces for higher chlorinated congeners, which vary from 85-862 µg/L for di-CNs to 65 µg/L for tri-CNs and 0.08 µg/L for octa-CN. They are mainly soluble in organic solvents such as benzene, dichloromethane, diethyl ether, hexane, isooctane, petroleum ether, and toluene (Jakobson and Asplund, 2000). Their lipophilic nature is responsible for their bioaccumulation in humans and across the food web (Falandysz, 2003). The degree of bioaccumulation rises with the chlorination level of the CN, but octa-CN shows little or no bioaccumulation due to its poor water retention (CICAD, 2001). Higher tendency to resist biotransformation is demonstrated by chlorinated naphthalenes lacking adjacent carbon atoms unsubstituted with chlorine, and such CNs usually bioaccumulate along the food chain. The higher the number of unsubstituted adjacent carbons, the higher its susceptibility to metabolic degradation. The following chloronaphthalenes belong to this group: CN42, CN52, CN58, CN60, CN61, CN64, CN66, CN67, CN68, CN69, CN71, CN72, CN73, CN74, and CN75 (UNEP, 2012; Falandysz, 2003).

The boiling point ranges from 260ºC (mono-CN) to about 440ºC for octa-CN. The melting point also varies from -2.3ºC for mono-CN to 192ºC for octa-CN, and molecular weight from 162.61 g/mol for mono to 404 g/mol for octa-CN (van de Plassche and Schwegler, 2002**)**. The commercial PCNs are crystalline solids or waxes with the exception of 1-monoCN, which is liquid at normal room temperature (Jakobsson and Asplund, 2000). Vapour pressure depicts the propensity of liquids and solids to change into a gas (for liquids to vapourize and solids to sublime) (Wania and Mackay, 1996). Vapor pressure for 2-mono-CN is 2.53 Pascal (Pa), 1-mono-CN (5.59 Pa), di-CN (0.352 Pa), and 5×10^{-7} Pa at 25ºC for octa-CN. Their vapour pressures range from low to moderate; and decrease with increase in their degree of chlorination. The rate at which the congeners with high level of chlorination volatilize from water to soil would be possibly small as a result of the trend in their vapour pressure. Meanwhile, those that are less chlorinated would readily volatilize (Falandysz *et al*., 2001). The least molecular weights' CN congeners (mono- and di-CNs) have low melting points and high vapour pressure.

With the application of QPSR model, atmospheric persistence characterized by half-life is 2 days for mono-CN, di-CNs (5 days), tri-CNs (10 days), tetra-CNs (19 days), penta-CNs (39 days), hexa-CNs (79 days), hepta-CNs (163 days), and octa-CN (343 days) (Puzyn *et al*., 2008). These properties promote their easy vapourization and long-range atmospheric transport (LRAT) in air from source to distant region (Falandysz, 2003). They are later deposited into water and terrestrial surfaces across the globe (Environment Canada, 2011; Hanari *et al*., 2004; Helm *et al*., 2004). PCNs have tendency to cause extensive environmental pollution, owing to their long half-lives in air and water (mobile media) and due to their partitioning in substantial amount into those media, however, they are released more into air than water (Environment Canada, 2011).

Dominant species in air are the low molecular weight CNs, with tri- and tetra-CNs recording up to 80% and 90-95% of the overall mass in ambient and arctic air, respectively (van de Plassche and Schwegler, 2002). CNs in air may linger there for a long time or partition into soil by deposition (Environment Canada, 2011). In the aquatic environment, di- to octa-CNs have tendency to persist in water, while tri- to hepta-CNs persist more in the soil and sediment, depending on their homologue groups (UNEP, 2012; Environment Canada, 2011). Fate of POPs, including PCNs are monitored in the aquatic systems by sediment studies, which could provide useful information regarding their historical patterns and original composition rather than using biological samples (van de Plassche and Schwegler, 2002).

High bioconcentration factor (BCF), log $K_{ow} \geq 3$, or log $K_{oa} \geq 5$ is an indication that an organic substance possesses a potential for bioaccumulation. Other signs of possible bioaccumulation include molecular mass below 700, high tendency for adsorption, hydrolysis and/or degradation (Tamis *et al*., 2009). Biomagnifications are also bound to happen when log $K_{oa} \geq 5$ in several mammals (UNEP, 2012). PCNs generally have log K_{ow} values in the range of 4.2 to 8.5 and log K_{oa} is between 5.9 and 11.6 in aquatic and air-breathing organisms (ECHA, 2017; UNEP, 2012). Vapour pressure and water solubility of PCNs decrease as the degree of chlorination increases, hence lipophilicity and log K_{ow} (>5) of tri- to octa-CNs are very high (UNEP, 2017b, 2013a). Log K_{ow} of 7.5–8.5 for hexa- to octa-CNs are equally high. Their major route of exposure is food ingestion, especially fish consumption for humans. Aquatic organisms considerably consume organic substances with low water and high fat solubility; thus, enhancing their bioaccumulation. PCNs accumulate in the breast milk and adipose tissues with considerable level of fats (Environment Canada, 2011; van de Plassche and Schwegler, 2002). Other factors contributing to their bioaccumulation include slow metabolism or elimination from the body of the prey organisms (Tamis *et al*., 2009). Some physicochemical parameters of PCNs are displayed in Table 2.3.

Table 2. 3 Physicochemical Properties of PCNs

CN groups	Molecular weight	Boiling point (°C)	Melting point (°C)	Solubility (µg/L)	log Kow [a]	log Koa [a]	log Kaw [a]	K_H[a](Pam^3/ mol)	half-life[a] (days)
Mono- CN	162.61	260	-2.3–60	924-2870	3.93-3.97	5.93-6.02	-2.05 to -2.01	22.21-24.48	2
Di- CN	197	285–298	37–138	85– 862	4.20-4.67	6.55-7.02	-2.83 to -1.93	3.67-29.15	5
Tri- CN	231.5	274	68–133	16.7-65	4.59-5.50	7.19-7.94	-3.35 to -1.68	1.11-51.24	10
Tetra- CN	266	NA	111–198	3.7-8.3	5.14-6.10	7.88-8.79	-3.54 to -1.78	0.71-40.66	19
Penta- CN	300.4	313	147–171	7.3	5.67-6.49	8.79-9.40	-3.73 to -2.30	0.46-12.45	39
Hexa- CN	335	331	194	0.11	6.02-6.68	9.62-10.17	-4.13 to -3.04	0.19-2.27	79
Hepta- CN	369.5	348	194	0.04	6.48-6.57	10.68-10.81	-4.34 to -4.11	0.11-0.19	163
Octa- CN	404	365	198	0.08	6.43	11.64	-5.21	0.02	343

Source: [a]Puzyn and Falandysz, 2007; UNEP, 2013a; CICAD, 2001. NA=Not available

2.1.2 Applications of PCNs

PCNs are commercially produced to be utilized in different applications because of their good insulating, water-resistant, fireproof, mucus-repellent properties, as well as satisfactory cohesion and affinity for other components. They serve the same purposes as PCBs due to their comparable structural resemblance (UNEP, 2017a). PCNs were extensively manufactured between 1930 and 1950 to be used in cable and capacitor production as flame-retardants (Jakobsson and Asplund, 2000). PCBs and PBDEs were also employed in cables production as flame-retardants. PCNs are widely used in paints, textile and paper industries, as raw materials in dye-making, as fungicides in wood, plasticizing agents, oil supplements, molding materials for amalgam, and lubes/grease for graphite wires (Helm *et al*., 2006; CICAD, 2001). They were applied in chloroprene rubber (Yamamoto *et al*., 2016; Yamashita *et al*., 2003), used by military as inert artillery (Hewitt *et al*., 2011), as sealants and putty in building construction until sometime in 2000 (UNEP, 2013b; Yamashita *et al*., 2003).

2.2 Sources of PCNs in the environment

Like all other POPs, PCNs possess toxic characteristics, withstand degradation and bio-accumulate in adipose tissues of both animals and humans. They are conveyed from their production sites into far distances worldwide by wind, water, other moving species and accumulated overtime in our terrestrial and aquatic ecosystems (UNEP, 2017a).

Polychlorinated naphthalenes occur universally in both living and non-living things, and bio-accumulate in fatty tissues of humans (Zhang *et al*., 2015a; Domingo, 2005; Falandysz, 2003). They are discharged into our surroundings through various industrial processes similar to PCDD and PCDF during their commercial production and as by-products in the production of PCB (Taniyasu *et al*., 2003; Yamashita *et al*., 2003, 2000). PCN levels in PCB formulations exist in small quantity and can be up to 1% (UNEP, 2017a). Other means through which they are inadvertently released include; manufacturing of chlorine through chloralkali process (Weber *et al*., 2008; Brack *et al*., 2003), or chlorinated solvents such as chlorinated methane (Zhang *et al*., 2015b), metallurgical processes (copper ore roasting, metals smelting, and refinery), evaporation from PCN-containing products (CICAD, 2001), disposal and burning of PCN-containing products, and other combustion processes (Odabasi *et al*., 2017; Helm and Bidleman, 2003; CICAD, 2001).

2.2.1 Advertent industrial production of PCN

Polychlorinated naphthalenes are industrially produced by heating liquefied naphthalene and chlorine gas under moderately high heat in the presence of iron (III) or antimony (V) chloride catalyst. The raw stock formed is reacted with sodium carbonate (Na_2CO_3), or sodium hydroxide (NaOH), made to undergo fractionation and refined with activated clay (van de Plassche and Schwegler, 2002). The final products are mixtures of liquids, waxes and high melting points solid CNs. They were previously manufactured as technical mixtures and sold using diverse trade names including; Halowax, Nibren wax, Perna wax and Basileum, Seekay wax, Clonacire, Cerifal materials ((Falandysz, 2003; Falandysz *et al*., 2000; Jakobsson and Asplund, 2000). The manufacturing and usage of Halowax (produced by Koppers Company of Pittsburg, USA) supersede other mixtures. Halowax technical mixtures are made up of chlorine contents in the range of 22-70% by weights (CICAD, 2001). The various types and percentage chemical compositions of Halowax mixtures are summarized in Table 2.4. The production of PCNs through chlorination of molten naphthalene with gaseous chlorine is a nucleophilic and electrophilic substitution reaction; these reactions aid PCNs production with chlorine in central (α-) positions (1, 4, 5, 8-positions). Some PCN congeners are substituted at α-positions; CNs-46 (1,4,5,8-TetraCN), 59 (1,2,4,5,8-PentaCN), 65 (1,2,3,4,5,8-HexaCN), 71 (1,2,4,5,6,8-HexaCN), 72 (1,2,4,5,7,8-HexaCN), 74 (1,2,3,4,5,6,8-HeptaCN), and 75 (1,2,3,4,5,6,7,8-OctaCN) (Falandysz, 1998).

The synthesis of PCNs was first reported in 1833; but the production and usage of PCNs became significant in the early 20th century, though the precise amount produced was unknown. Nearly 150,000 metric tons (10% of the Worldwide PCBs production) was assumed generated (Falandysz, 1998). Many countries intentionally stopped PCNs manufacturing and application between the 1970s and 1980s because of reported toxicity and bio-accumulative nature in our surroundings. PCNs were then replaced with other compounds such as polyesters and polycarbonates in the capacitor and cable industries. PCNs are still found in substantial amount in the environment till date, in spite of their little or no production at commercial quantity (Li *et al*., 2020). Products containing PCNs were still on sale openly in Japan commercial stores until early 2000s (Yamamoto *et al*., 2016; Yamashita *et al*., 2003), but the production of PCNs was assumed to have stopped (UNEP, 2013b).

PCNs were incorporated into consumer products (electronics, furniture, textiles, paints, etc.) to serve as flame-retardants and other purposes. The extended lifespans of these flame-retarded products into which they have been blended initiate their continuous discharge from products and after discarding as waste into environment for many years or centuries (de Wit *et al*., 2010; CICAD, 2001).

Table 2. 4 Approximate compositions of halowax mixtures

Trade names	**Major constituents**	**Minor constituents**	**CN compositions (% by weight)**	**Boiling points (^{O}C)**	**Melting points (^{O}C)**
Halowax 1000	mono-diCN (26% Cl)	Tri-heptaCN	60 mono, 40 di	250	33
Halowax 1001	di-pentaCN (50% Cl)	Mono, hexa, heptaCN	10 di, 40 tri, 40 tetra, 10 penta	308	98
Halowax 1013	tri-pentaCN (56% Cl)	Mono-di, hexa-heptaCN	10 tri, 50 tetra, 40 penta	328	120
Halowax 1014	tetra-hexaCN (62% Cl)	Mono-tri, hepta- octaCN	20 tetra, 40 penta, 40 hexa	344	137
Halowax 1031	mono-diCN (22% Cl)	Tri-octaCN	95 mono, 5 di	250	25
Halowax 1051	hepta-octaCN (70% Cl)	Mono-hexaCN	10 hepta, 90 octa	-	185
Halowax 1099	di-penta CN (52% Cl)	Mono, hexa-octa	10 di, 40 tri, 40 tetra, 10 penta	315	102

Source: CICAD, 2001.

2.2.2 Formation of PCN during cooking processes

Studies have shown that humans become exposed to PCNs and similar POPs through food consumptions (Fernandes *et al*., 2019, 2017, 2011, 2010; Domingo *et al*., 2003), while Domingo (2011) reviewed on the impact of cooking operations on certain POPs and heavy metals in foods. Their surveys revealed that the cooking effects are dependent mainly on the food types involved and the cooking methods employed. It was envisaged that any cooking procedures that extricate fat from the food would lower POP concentrations in the prepared food, considering the fact that POPs (PCDD/Fs, PCBs, PBDEs, PCDEs, and PAHs) are related with the fatty part of any foods (Domingo, 2011). Another study proposed that PCNs could be produced from cooked food (Dong *et al*., 2013). Two cooking oils (olive and peanut oils) believed to be PCN free was fried with sucralose (a synthetic sweetener) at elevated temperature. Sucralose thermally decomposed at high temperature to release chlorine, while carbon originated from the cooking oils to produce PCN. PCN concentrations recorded in the olive and peanut oil fumes were 240 and 490 pg/g, respectively. Their findings proposed that the heating of cooking oil in the presence of sucralose-initiated chlorine and PCNs generation. PCNs generation in the course of cooking was attributed to the production of polycyclic aromatic hydrocarbons (PAHs), and presence of various kinds of chlorine-based compounds in foods, food preservatives and seasonings that facilitated the production (Dong *et al*., 2013). Production of other POPs during cooking procedures have been reported (Alomirah, 2010; Farhadian *et al*., 2010).

2.2.3 Inadvertent production of PCN from other industrial processes

PCNs are accidentally produced and discharged through different industrial and other thermal processes (Liu *et al*., 2014a, b). Denier van der Gon *et al.* (2007) reported in their study that combustion was the major source of PCNs emitted into the atmosphere in Europe. Industrial combustion, as well as waste incineration, remain the leading routes of PCN entrance into our present-day ecosystem (Liu *et al*., 2010; Jansson *et al*., 2008; Nadal *et al*., 2007; Takasuga *et al*., 2004). Discharges of PCNs were studied in various industrial thermal processes such as refuse burning (Takasuga *et al*., 2004; Noma *et al*., 2006), manufacturing of iron and steel (Liu *et al*., 2012a, b), nonferrous melting procedures (Jiang *et al*., 2019, 2015; Nie *et al*., 2012a, b, 2011), coking processes (Liu *et al*., 2010) and manufacturing of cement (Liu *et al*., 2011). The volume of PCN discharged during various steps of secondary copper smelting processes in a China factory has recently been reported (Jiang *et al*., 2019). The secondary copper smelter composed of three major steps; feeding–fusion, oxidation, and deoxidation steps. It was revealed that total PCN discharges reduced in this sequence: feeding–fusion step (65% of total PCN emissions) > oxidation step (27%) > deoxidation step (8%). This shows that the feeding–fusion step contributed more to PCN released into the environment during copper melting operations. PCN concentrations in the stack gas samples for the three stages ranged from 477.0–762.5 ng/m^3 (Jiang *et al*., 2019).

Elevated amount of unwanted PCNs (427 kg/year in 2010) was reported during the manufacturing of chlorinated methane in China (Zhang *et al.*, 2015b). During the production of these chlorinated solvents, which are usually evaporated, the unwanted PCNs are removed from the solvents. Great magnitudes of PCN were formed alongside PCDD/PCDFs and other unwanted POPs in the course of chlorine manufacturing through chloralkali electrolysis process (Weber *et al*., 2008; Brack *et al*., 2003; Kannan *et al*., 1998). The investigation of PCNs profile in soil, sediment, and biota samples gathered around a chlor-alkali factory implied that PCN congeners are formed during the chlor-alkali process (Kannan *et al*., 1998).

Studies in countries such as USA, UK, Germany, Japan, France, and China have indicated the presence of PCNs in certain PCB mixtures. Huang *et al*. (2015) reported total concentration of 1,307 µg/g PCN from a Chinese PCB insulating oil sample in Zhejiang Province, China, while Yamashita *et al*. (2000) recorded PCN total concentrations of 5.2-730 µg/g from eighteen commercial PCB formulations. The occurrence of PCN in PCB formulations can be expounded by the more reactive properties and halogenation (chlorination) of naphthalene that happened concurrently with chlorination of biphenyl during PCBs production, since commercial biphenyl contains naphthalene, which is more reactive than biphenyl (Fernandes *et al*., 2017; Falandysz, 1998).

The accidental discharge of PCNs from these industrial and thermal processes have resulted in their occurrence in humans and our environment. Li *et al*. (2020) recorded maximum value of 2497 pg/g lipid in human milk samples from 19 Provinces of China; they argued that industrial discharge of PCN from thermal processes was the major source of PCN found in the analysed milk samples.

2.3 Toxic effects of PCNs

Sets of thermodynamic data obtained by Falandysz *et al.* (2001) on 75 CN congeners indicated that their continuous deleterious effects on living organisms steadily increased from mono - CN to octa – CNs.

Previous comparative studies on PCNs, PCDDs, PCDFs and PCBs showed that PCNs have similar and even higher toxic equivalency (TEQ) than others (Park *et al.,* 2010; Kannan *et al*., 2001a; Kannan *et al.*, 1998). All CN congeners are planar compounds that dissolve easily in lipids (lipophilic) and they structurally resemble the highly poisonous 2, 3, 7, 8 - tetrachlorodibenzo-*p*-dioxin (TCDD). Several of them exhibit toxicity similar to those of the TCDD with poisonous effects, which include mortality, embryo toxicity, hepatotoxicity, immunotoxicity, dermal lesions, and carcinogenicity (Jakobsson and Asplund, 2000; Blankenship *et al.,* 2000; Villeneuve *et al.,* 2000; Falandysz, 1998). Some PCNs caused induction of ethoxyresorufin O-deethylase (EROD) and aryl hydrocarbon hydroxylase (AHH) just like harmful planar PCBs; HexaCNs 67, 68, 69 and HeptaCN 73 are powerful inducers of EROD and AHH (Falandysz, 1998). The dioxin-like toxicity of PCNs depends on the planar structure and substitution of chlorine at lateral (β) positions (2, 3, 6, 7) of the naphthalene ring (Falandysz, 1998). Based on this assertion, there are seven PCN congeners which have their lateral positions filled with chlorine; CNs- 48 (2,3,6,7-TetraCN), 54 (1,2,3,6,7-PentaCN), 66 (1,2,3,4,6,7-HexaCN), 67 (1,2,3,5,6,7-HexaCN), 70 (1,2,3,6,7,8-HexaCN), 73(1,2,3,4,5,6,7-HeptaCN), 75 (1,2,3,4,5,6,7,8-OctaCN). Although CNs-68 (1,2,3,5,6,8-HexaCN) and -69 (1,2,3,5,7,8-HexaCN) show reasonably high dioxin-like toxicity, they both have one carbon at the β-position which is not substituted with chlorine (Falandysz, 1998).

2.3.1 Toxic effects on enzymes

Studies have shown that PCNs caused induction of cytochrome P-450 enzymes (Kilanowicz and Skrzypinska-Gawrysiak, 2010; Kilanowicz *et al*., 2009). While exposure of some rats to PCN has resulted in the induction of these enzymes in the livers, kidneys and lungs of these animals, the induction efficiency of any compound is dependent on the extent of chlorination, substitution pattern and planarity of the molecule (Jakobsson and Asplund, 2000).

2.3.2 Toxic effects on animals and humans

Studies have revealed hexachloronaphthalenes (HxCNs) as the most dangerous PCN congeners; majorly hexaCNs 66, and 67 (Falandysz, 1998). Some of the dangerous effects noticed after administering HxCNs on rats include; oxidative stress, heme biosynthesis disruption, accumulation of fats in the liver (hepatic steatosis), blood disorders (hematological disturbances), liver damage (hepatotoxicity), loss of appetite (anorectic effect), among other effects (Klimczak *et al*., 2018; Kilanowicz *et al*., 2009). Chicken oedema (characterized by loss of feathers) and X-disease (bovine hyperkeratosis) in cattles, characterized by symptoms such as vitamin A deficiency, hyper salivation, skin thickening

(Pachyderma), hair loss and occasional deaths, have all been linked to PCN exposure in animals (Jakobsson and Asplund, 2000).

Certain harmful health effects such as chloracne (severe skin reactions), liver disease, cirrhosis of the liver, irritation of the eyes, fatigue, headache, anemia, hematuria, and nausea have all been reported in human beings who were occupationally exposed to PCNs, with likelihood of such workers being in danger of different kinds of cancers (CICAD, 2001). Their poisonous effects are mainly due to penta-, hexa- and hepta-CNs, that display dioxin-like effects on liver cell lines in humans and animals (Blankenship *et al.*, 2000; Villeneuve *et al.*, 2000).

2.4 Determination of PCNs

The procedures for sample collection, extraction, clean up and PCN analytical techniques are comparable with other organo-halogenated chemicals (Kucklick and Helm, 2006).

2.4.1 Sample collection and storage

2.4.1.1 Air samples

Several researchers have reported occurrences of PCNs in various environmental matrices. Air samples are collected with either high-volume air samplers (Mao *et al*., 2020; Dat *et al*., 2018; Xue *et al*., 2016; Jaward *et al*., 2004), or polyurethane foam disk passive air samplers (PUF-PAS) (Hu *et al*., 2019; Xu *et al*., 2014; Hogarh *et al*., 2012). In all the studies, the samplers are installed at the sampling locations for a specific length of time and are enclosed in an aluminum foil inside an airtight polyethylene bag when the time is due, then stored at less than 5°C for analysis. The limitation with the use of the classical high-volume air samplers for collecting semivolatile organic compounds (SOCs) in air is the high cost of the equipment, skilled employee, and electricity requirement before operation. Its deployment in remote regions is also considered uneconomically viable (Harner *et al*., 2006; Pozo *et al*., 2004). The introduction of these PUF-PAS was a significant development in the universal surveillance of PCNs in air (Kucklick and Helm, 2006). PUF-PAS is simple to operate, cheap, requires no electricity and can be used globally on a wide range even in deserts (Harner *et al*., 2006; Pozo *et al*., 2006, 2004).

2.4.1.2 Water and sediment samples

Water samples are usually collected into amber glass bottles with a teflon-lined screw cap placed in an ice chest and held at 4^{o}C until analysed (Mahmood *et al*., 2014a; Marti and Ventura, 1997). The amber glass bottles are recommended for aqueous samples to avert direct contact with sunbeams (USEPA, 2007). Soil or sediment samples are usually collected with a stainless-steel grab sampler (Li *et al*., 2017; Zhang *et al*., 2015a; Castells *et al*., 2008; Kannan *et al*., 2001b), or gravity core equipment (Dat *et al*., 2019; McGoldrick *et al*., 2018). The samples are kept in either aluminium-covering glass containers (Dat *et al*., 2019), glass jar (Kannan *et al*., 2001b), aluminium foil (Wang *et al*., 2012), or polyethylene bags (Mahmood *et al*., 2014a). The choice of sampling instrument for soil or sediment samples depends on certain factors; research aim/objectives, instrument accessibility, sample properties, type or size, sampling site location, depth and size, among other considerations. Surface sediment required for evaluating horizontal partitioning of sediment properties are routinely collected by grab samplers, while core samplers are suitable for collecting underground sediments needed for appraising the extent of pollution, geological dating, histories, or characteristics of a site. Core samplers span from simple equipment that can be operated by hand to complex equipment which require crane, gearwheel or electricity supply for operation. Sample contamination is minimal during core sampling, but this may be laborious, time consuming and require some level of expertise. The grab samplers are portable, affordable, adaptable in all environments, and are easily operated (USEPA, 2001). The samples are air or freeze-dried, ground, sieved and stored in amber glass bottles until analysis (Zhang *et al.*, 2015a; Mahmood *et al*., 2014a; Yamashita *et al*., 2000).

2.4.1.3 Fish and other biota samples

Either gill netting, trap netting and/or electrofishing usually collect fish and other biota from aquatic environment. They are conveyed on ice in a clean polyethylene bag to the laboratory, before storage at −20°C for study (Gewurtz *et al*., 2018; Kannan *et al*., 2000a; Falandysz *et al*., 1996). Fishing equipment can be either simple or complex, but all employ procedures such as gilling and tangling (gill nets and trammel nets), trapping (traps, pound nets), filtering (trawls, seines), hooking and spearing (hook and line, harpoons) and pumping (fish pumps) for fish harvesting (Boopendranth, 2012).

2.4.1.4 Human samples

Human breast milk samples are expressed and donated by voluntary nursing mothers to evaluate PCN levels in human milk and their possible health hazards to breastfed babies. The liquid samples are stocked in a freezer at about −20°C pending extraction and further analysis (Li *et al*., 2020; Pratt *et al*., 2013). Blood samples from voluntary healthy contributors are routinely collected with vein puncture cannula, needle and syringe. The samples must be centrifuged immediately after venipuncture to get plasma portion and preserved in refrigerator until analysis (Jin *et al.,* 2019; Fromme *et al*., 2015). Human adipose (fatty) tissues are collected usually from donors during cosmetic surgery (liposuction or lipectomy) process and stored immediately in cleansed glass bottles inside a refrigerator (Schiavone *et al*., 2010; Kunisue *et al*., 2009)

2.4.2 PCN extraction methods

2.4.2.1 Water and sediment samples

PCNs are extracted from water samples by liquid-liquid extraction (LLE) method in separating funnel using different organic solvents including acetone, hexane, and DCM (Mahmood *et al*., 2014a; Marti and Ventura, 1997) and by solid-phase extraction (SPE) (Marti and Ventura, 1997). The LLE method has few disadvantages in that it is laborious, and consumes more time and solvents compared to SPE which requires less attention, time and solvents, but the SPE is seldom used due to its higher cost when compared to LLE (Adeniji *et al*., 2017; Johnson, 2011). Higher recovery of up to 100% is obtained in LLE when compared to the use of automated SPE cartridges (55-66% recovery) (Marti and Ventura, 1997). Another development is the use of instrument for extracting PCN from environmental samples; some studies employed pressurized liquid extraction (PLE), or accelerated solvent extraction (ASE). Zhang *et al*. (2015a) reportedly utilized ASE for sieved sediment samples, while Mahmood *et al*. (2014a) applied soxhlet extraction (SE) method with DCM in a separate study. Yamashita *et al*. (2000) also employed SE method with toluene after freeze-drying the sediment samples. Sediment samples from Laojie River of Northern Taiwan after being freeze-dried were also extracted using soxhlet apparatus with DCM as extractant (Dat *et al*., 2019). SE seems to be the most widely used method for isolation of PCNs from different solid environmental matrices due to its high yield and low cost. The samples can be extracted in wet form after blending with dehydrated sodium sulphate (Na_2SO_4) or diatomaceous earth, or after freeze- or air-drying (Kucklick and Helm, 2006).

However, SE method is gradually becoming obsolete with the recent introduction of a faster automated PLE extraction system which has been applied for PCN extraction in sediments (Zhang *et al*., 2015a; Horii *et al*., 2004), and in air specimens (Hu *et al*., 2019). Nevertheless, most laboratories still employ

SE method for solid and biota samples because it is cheaper when compared with the fast but expensive automated systems.

PLE is an automated sample preparation scientific procedure that merges high temperature and pressure with aqueous solvents to bring about fast and effective separation of samples of interest (analytes) from other solid or semisolid matrices. It is a new procedure that uses lesser solvents and time for analysis when compared to other classical solvent extraction methods. Its advantages include high sample yield, reduced cost of labour, low solvents usage, analysis error and time (Vazquez-Roig and Picó, 2015; Noorashikin and Sanagi, 2009).

Commercial biphenyl is reported to contain naphthalene (Fernandes *et al*., 2017; Falandysz, 1998), hence PCNs are routinely found as contaminants in commercial PCB formulations (Huang *et al*., 2015; Yamashita *et al*., 2000). The percentage of PCNs in PCBs technical formulations was estimated to be about 0.087% (Falandysz, 1998). Extracts from environmental samples for PCN analysis are usually purified using activated alumina, or multilayered silica-gel columns (McGoldrick *et al*., 2018), to prevent interferences from other POPs such as PCBs before instrumental analysis. Silica alumina column was used to purify the concentrates obtained from both aqueous and solid samples from River Chenab in Pakistan. The column was sequentially packed with silica gel, anhydrous Na_2SO_4, and alumina for the purification (Mahmood *et al*., 2014a). In other studies, extracts obtained from sediment samples were cleaned on a glass column containing 50% (w/w) sulphuric acid, and silica gel, followed by purification on a multi-leveled column sequentially filled from uppermost to undermost with dried Na_2SO_4, inactive florisil, neutral silica gel, and neutral alumina, respectively (Li *et al*., 2017; Wang *et al*., 2012). Dat *et al*. (2019) used an acidified multidimensional silica column fastened with a carbon column to purify their sediment extracts.

According to Kucklick and Helm (2006), the first study in the 1970s to have reported the occurrence of PCNs in sediment samples employed packed-column gas chromatograph (GC) fused with electron capture detector (ECD) for the quantification, while the qualitative analysis was performed with packed-column GC-mass spectrometer (MS). The major setbacks with GC-ECD analyses were interferences from PCBs and chlorinated pesticides, and the unavailability of many individual PCN standards. Kucklick and Helm (2006) stated that most of the 75 PCN congeners have been manufactured, but less than half of them are available for sale as standards. Another major problem is the co-elution of certain PCN congeners (UNEP, 2017b). Hence, the use of mass spectrometry has been recommended as a better analytical technique for detection, especially for environmental samples (van de Plassche and Schwegler, 2002). International Organisation for Standardization (ISO) developed a GC method with mass spectrometry for the analysis of PCNs in water samples in 2015 (ISO/TS 16780) (UNEP, 2017b). Determination of PCNs is commonly based on fractionation and carbon clean up followed by GC-MS.

Gas chromatography-mass spectrometry (GC-MS) is an analytical technique that incorporates the components of gas-liquid chromatography (GLC) and mass spectrometry (MS) to analyse various constituents of an analyte (test sample of interest). Conventional GC is able to separate volatile and semi-volatile compounds in the sample with good resolution, but it cannot identify them. MS will furnish comprehensive information on basic structures of compounds in a way that they can be precisely identified and quantified based on their mass-to-charge ratio (m/z) (Hussain and Maqbool, 2014). The two analytical techniques complement each other. GC-MS is a very fast separation technique with many advantages, which include its ability to separate complex mixtures, identification and quantification of analytes at trace levels, although it is only suitable for volatile and/or semi-volatile samples. GC can be operated with different types of detectors depending on sensitivity and types of analysis required (whether qualitative or quantitative analysis). The choices of detectors for PCN analysis among others are electron capture detector (ECD) and mass spectrometer (MS). Routine determinations are now carried out by capillary gas chromatograph and detected by low- or high-resolution mass spectrometer in either electron impact or electron capture negative ion modes (EI-MS, ECNI-MS), after sample clean-up using florisil, alumina, silica, or size exclusion techniques (Fernandes *et al*., 2017; Horii *et al*., 2004).

The 39 PCN congeners determined in water and sediment samples from Pakistan by Mahmood *et al*. (2014a) were quantified by GC/ECNI/MS with Halowax 1014 used as quantification standards.

In order to determine accurately PCNs that occur at very low concentrations and following the US EPA Method 1613 and European Standard method EN 1948-1/2/3, some researchers employed high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC-HRMS). This became necessary to prevent interferences from PCBs, PCDDs, and PCDFs, and because only HRMS has the required sensitivity and specificity. Nevertheless, the main disadvantage with the use of this instrument is the high cost of purchase and maintenance (Céline *et al*., 2002). GC is mostly employed for the separation of PCNs while the identification is usually performed by low-resolution or high-resolution mass spectrometer (GC-MS, GC-HRMS) (Kucklick and Helm, 2006). Following the automated SPE and LLE extraction of groundwater samples of Llobregat aquifer near Barcelona in North East of Spain, PCNs were analysed by high-resolution gas chromatograph coupled with electron capture detector (HRGC-ECD) using Halowax 1013, 1014 and 1099 as reference standards (Marti and Ventura, 1997).

2.4.2.2 Air samples

Atmospheric samples for PCN analysis are usually extracted with a single or combination of reagent(s) such as dichloromethane, hexane, toluene, and acetone. The air samplers as reported by Hu *et al*. (2019) were extracted with a mixture of DCM/hexane (1:1 v/v) using an accelerated solvent extraction (ASE) system, while soxhlet extraction (SE) method was used with acetone in another study (Hogarh *et al.,* 2012). The latter method is widely used because it is cheaper when compared with the more expensive ASE method, which is faster in operation and requires less solvents and time. Sixty-three (63) congeners of PCN were analysed from Ghana atmosphere using HRGC-HRMS (Hogarh *et al*., 2012). The use of gas chromatography negative ion mass spectrometry (GC-NIMS) was also reported for the quantification of PCNs in air samples (Harner *et al*., 1998).

2.4.2.3 Fish, biota and food samples

After homogenizing the biota samples collected from Gdansk Basin, Baltic Sea with anhydrous Na_2SO_4, Falandysz *et al*. (1996) soxhlet-extracted them with a combination of acetone/n-hexane (2.5:1), fat-free extracts were obtained with n-hexane/diethyl ether (9:1). Fish samples from various waters of the Great Lakes in Canada were extracted with DCM/hexane (10/90) using PLE (Gewurtz *et al*., 2018). Kim *et al*. (2018) sonicated their food samples with mixed solvents of hexane/DCM (1:1).

Almost all foods are composed of different mass of lipids, they are extricated from the matrix using either acid hydrolysis (Fernandes *et al*., 2010), or gel permeation column (Domingo *et al*., 2003). Another issue is the cleanup of PCN extracts in order to eliminate related fat-soluble (lipophilic) pollutants, which may coexist and be extracted alongside with the PCNs. Some analytical procedures integrate a fractionation stage using either alumina (Jiang *et al*., 2007), porous graphitic carbon (Jiang *et al*., 2007) or activated carbon (Fernandes *et al*., 2019; Isosaari *et al*., 2006) while other procedures incorporate sample extraction, purification and fractionation in one-step (Fernandes *et al*., 2019, 2010).

Recent studies to determine PCN in foods employed HRGC-HRMS after successive sample treatments; Fernandes *et al.* (2019) determined PCN levels in UK studied food samples by HRGC-HRMS. Eleven groups of food samples from seven cities of Catalonia in Spain were soxhlet extracted with different organic solvents, followed by a multilayer-silica column cleanup process, and quantification by HRGC-HRMS (Domingo *et al*., 2003). Twenty-five (25) PCN congeners determined in Great Lake fish samples by Gewurtz *et al*. (2018) were analysed using gas chromatograph-high resolution mass spectrometer (GC-HRMS).

2.4.2.4 Human samples

Li *et al*. (2020) freeze-dried their human blood samples and extracted with ASE using hexane and dichloromethane (1:1, v/v) mixture as extraction solvent. In another study, blood sample was extracted by LLE method with acetone and hexane (2:1) mixture (Park *et al*., 2010). Fatty tissue samples were milled with dried Na_2SO_4, before extracting on soxhlet-apparatus with dichloromethane and hexane (3:1) mixture for several hours. The extracts were concentrated on rotary-evaporator, followed by fractionation and purification (Schiavone *et al*., 2010; Kunisue *et al*., 2009). Human samples are composed of lipids, this is usually separated from the extracts by gel permeation chromatography (GPC) using a Bio-beads S-X3 packed glass column (Schiavone *et al*., 2010), followed by purification on a multilevel silica gel column (Schiavone *et al*., 2010; Kunisue *et al*., 2009). Other studies on human samples hydrolyzed the lipids in the extracts using acid, separated the possible contaminants on activated carbon, and were purified on alumina column before instrumental analysis (Pratt *et al*., 2013). The extracted human serum samples obtained from Yantai city in Shandong Province of East China were purified with gel permeation chromatography column and basic alumina column (Jin *et al*., 2019).

Published reports on PCN analysis on various human samples employed different models of gas chromatograph coupled with mass spectrometer; HRGC-HRMS, GC-HRMS, GC-MS (Li *et al*., 2020; Jin *et al*., 2019; Fromme *et al*., 2015). Li *et al*. (2020) determined the levels of specific PCN congeners present in human blood samples of China by HRGC-HRMS.

2.5 Human and environmental levels of PCNs

With the commercial availability of many newly synthesized reference standards and development of advanced analytical methods, all CN congeners have been analysed from various environmental matrices around the World including North America (Kannan *et al*., 2000a, b), Europe (Fernandes *et al*., 2019, 2011, 2010; Jarnberg *et al*., 1999; Falandysz *et al*., 2019, 1997, 1996), to mention a few. The percentage of CN congeners in Halowax admixtures were studied by Falandysz *et al*. (2000). PCN occurrences were reported in the atmosphere, biotic and abiotic samples (Dat *et al*., 2018; Hogarh *et al*., 2012; Brack *et al*., 2003; Falandysz *et al*., 1997). They were also detected in adipose tissues, blood and other human fluid samples (Li *et al*., 2020; Fromme *et al*., 2015; Park *et al*., 2010; Schiavone *et al*., 2010; Kunisue *et al*., 2009; Norén and Meironyté, 2000; Weistrand and Noren, 1998), and widely evaluated by Fernandes *et al*. (2017). Humans become exposed to PCNs mainly by ingestion of foods (Fernandes *et al*., 2017). CNs bioaccumulate largely in fish and other fatty foods, but not as much in other biota (shrimp and algae). Their level of bioaccumulation rises with the extent of CNs chlorination, but octachloronaphthalene, which is the most chlorinated naphthalenes, show little or no bioaccumulation due to its poor water retention capacity (CICAD, 2001).

2.5.1 Aquatic environment

Groundwater samples collected from Llobregat aquifer close to Barcelona in North East of Spain was analysed for PCNs by Marti and Ventura (1997). The concentrations of the total PCNs were between 0.0005-79.1 µg/L, while tetra-CN was the dominant congeners. The authors reported that the study site previously served as waste dumping ground (landfills), and higher PCN levels (2.5-79.1 µg/L) were recorded in four borehole samples. They concluded that the previous unlawful use of the site as refuse heap was the source of PCN pollution (Marti and Ventura, 1997). Kannan *et al*. (1998) also determined PCN congeners in biotic and abiotic specimens gathered from a chloralkali plant located in Atlanta Georgia, USA. The total PCNs concentration in the sediments was 23 μg/g dry weight (dw), hexa-CN (CN-71, 72) and hepta-CN (CN-74) were the prevalent congeners. They concluded that the congeners were likely formed during the chloralkali process, which makes it an important PCNs fountain in their domain. The total PCN concentrations in biota were much less than sediments, which implied that the congeners adsorbed firmly to the sediment samples and were, therefore, not readily available to the fauna and flora (Kannan *et al*., 1998).

The first study on PCN in the water and sediments from Pakistan was carried out by Mahmood *et al.* (2014a). The total levels detected in water and sediments were in the range of 178–489 ng/L and 8.94–14 ng/g dw, respectively. In both matrices, octa-CN (75) was the prevalent congener. Burning of wood, coal and other related products, industrial and thermal processes, radiation from Halowax and PCB mixtures were considered as the sources of PCN in the studied environment, with sampling sites located near the city and manufacturing districts being more polluted with PCNs, followed by downriver, middle and upriver sites (Mahmood *et al.*, 2014a). Dat *et al.* (2019) first reported levels of PCNs in northern Taiwan River (Laojie River) sediment. The Laojie River that flows through manufacturing and urban areas have a total Σ_{73}PCNs that ranged between 0.408–1.47 ng/g dw found in its sediment samples. It was concluded that various sources especially melting (thermic) operations, vapourization from technical mixtures of PCB contributed to high PCNs reported. Penta-CN, tetra-CN and di-CN predominated in the sampled sediments from upriver, midriver and downriver, respectively (Dat *et al.*, 2019).

According to Table 2.5, the PCN levels reported in sediment matrices around the globe ranged from 0.08-23,000 ng/g. The highest concentration (23,000 ng/g) was observed in the sediments collected near an erstwhile chloralkali plant in Atlanta Georgia, USA (Kannan *et al.*, 1998), while the lowest concentration (0.08 ng/g) was recorded from Upper Detroit and lower Rouge Rivers, Michigan, USA (Kannan *et al.*, 2001b), indicating that chloralkali process is a significant route of PCNs to the surroundings. The data obtained from the research showed that target organic compounds in form of effluents from various industrial infrastructures and drainage systems situated along the course of these rivers were the causes of sediments contamination (Kannan *et al.*, 2001b). Elevated PCN levels of 2.77-4,610 ng/g dw were reported for sediment specimens collected in Suzhou, an economically viable city in China with many chemical and metal smelting industries, which are believed to be the origin of emission containing such levels of PCNs (Zhang *et al.*, 2015a).

Table 2. 5 Reported levels of PCN in sediment samples around the world

Locations	Sample matrix	Concentrations (ng/g dw)	Extraction method	Standards	Analysed congeners	Instrument	References
Chlor-alkali plant, Georgia, USA	sediment	23, 000	soxhlet	Halowax 1014,1051 mixtures	63	GC-MS	Kannan *et al.* (1998)
Upper Detroit and lower Rouge Rivers, Michigan, USA	sediment	0.08-187	soxhlet	Halowax 1014,1051 mixtures	63	HRGC-HRMS	Kannan *et al.* (2001b)
River Chenab, Pakistan	sediment	8.94 – 414	soxhlet	Halowax 1014 mixture	39	GC–ECNI-MS	Mahmood *et al*. (2014a)
Wuxi, Yangtze River Delta, China	sediment	0.89–39.8	ASE	$^{13}C_{10}$-labeled standards	63	GC-QMS	Zhang *et al.* (2015a)
Suzhou, Yangtze River Delta, China	sediment	2.77- 4,610	ASE	$^{13}C_{10}$-labeled standards	63	GC-QMS	Zhang *et al.* (2015a)
Nantong, Yangtze River Delta, China	sediment	0.60–34	ASE	$^{13}C_{10}$-labeled standards	63	GC-QMS	Zhang *et al.* (2015a)
Gdansk Basin, Baltic Sea, Poland	sediment	6.7 (mean)	soxhlet	Halowax 1014 mixture	44	GC-MS	Falandysz *et al.* (1996)
Laojie River, Taiwan	sediment	0.408–1.47	soxhlet	Individual congeners	73	HRGC- LRMS	Dat *et al.* (2019)

DCM = Dichloromethane; GC-QMS = Gas Chromatograph coupled with a triple Quadrupole Mass Spectrometer, ASE = Accelerated solvent extraction system, dw = dry weight

The highest levels in the water matrix (79,100 ng/L) as contained in Table 2.6 were recorded in the underground water samples from Llobregat aquifer, Spain (Marti and Ventura, 1997). The high PCN concentration in the aquifer was attributed to contamination from landfill leachates (Marti and Ventura, 1997), whereas the lowest values (0.014-0.41 ng/L) were obtained from Greenland fjords, an industrialized area of Southern Norway which has been grossly polluted by discharges from magnesium production but decreases with time (Ishaq *et al*., 2009).

Table 2. 6 Reported levels of PCN in water samples

Locations	Sample matrix	Concentrations (ng/l)	Extraction solvent	Extraction method	Standards	Analysed congeners	Instrument	References
Greenland fjords, Norway	water	0.014- 0.41	toluene	soxhlet extraction of GFF/PUFs	Halowax 1014 and ^{13}C-labelled non PCBs mixture	47	HRGC-HRMS	Ishaq *et al.* (2009)
River Chenab, Pakistan	water	178–489	DCM	LLE	Halowax 1014 mixture	39	GC–ECNI-MS	Mahmood *et al.* (2014a)
Llobregat Aquifer, Spain	water	0.5-79,100	DCM	SPE, LLE	Halowax 1099 mixture	72	HRGC-ECD	Marti and Ventura (1997)

GFF = Whatman Glass Microfibre Filter; PUFs = Polyurethane Foam, LLE = Liquid-liquid extraction, SPE = Solid phase extraction

Different fish species collected in Michigan waters of the Great Lakes were also reported to contain total PCN levels that ranged from 0.019–31.4 mg/g, with Detroit River fish recording the highest concentration of 31.4 mg/g. Penta-CNs dominated in most of the fish samples. Domestic waste burning, Halowax and PCB technical mixtures were attributed to be the sources of PCN measured in these fishes (Kannan *et al*., 2000b). As shown in Table 2.7, the levels of total PCNs in foods, fish and other biota collected from the different aqueous environments around the world ranged between “Not Detected” (ND) and 31,400,000 ng/g wet weight (ww). The highest values (19,000 – 31,400,000 ng/g ww) were found in fish from Michigan waters and the Great Lakes, which depend on fish species and sampling points (Kannan *et al*., 2000b) while the lowest values (0.00015 – 0.037 ng/g) were obtained in UK food samples (Fernandes *et al*., 2010). According to Kannan *et al*. (2000b), fish species called “Walleye” from Detroit River had the highest value of 31,400,000 ng/g ww PCNs. Fish also had the maximum concentration of 0.037 ng/g among the various groups of UK foods (milk, fish, eggs, poultry, vegetables, fruits, dairy, meat and meat products) studied by Fernandes *et al*. (2010). These findings showed that PCNs are prevalent contaminants in fishes, depending on the contamination sources (Kannan *et al*., 2000b).

2.5.2 Foods

One of the latest investigations into the incidence and human exposure to POPs through food consumption reported PCN levels in major foods and food products among which are; dairy products, eggs, fish, meat/meat products, milk, poultry, oil and fats etc. The PCN concentrations in all the various foods ranged from 0.0001-0.166 ng/g, with oil and fats having the highest levels, followed by fish and eggs (Fernandes *et al*., 2019). This is expected considering the PCN lipophilic nature. The values obtained in this study are lower than previous reports from other nations across the globe; this was attributed to factors such as decline in PCN applications and pollution control put in place by UNEP and other international bodies. The most toxic CN-66/67, CN-73 are the prevalent congeners recorded in this study (Fernandes *et al*., 2019).

Another research that revealed the distribution of PCNs in staple foods in Pakistan (Mahmood *et al*., 2014b) recorded the sum of thirty-nine PCN congeners $\sum_{39}$PCN concentrations in wheat and rice samples as 0.02-0.21 ng/g and 0.02–1.21 ng/g, respectively. Their results for both food samples were dominated by tetra and penta-CNs, and the values compared well with those obtained from UK foods (Fernandes *et al*., 2019, 2010). Domingo *et al*. (2003) were the first investigators to report PCN levels in human diets in Catalonia, Spain. PCN concentrations were measured in certain food classes; vegetables, tubers, fruits, cereals, pulses, oils and fats, fish and shellfish, eggs, milk, dairy products, meat, and meat products. Maximum and minimum total concentrations of PCNs were recorded in oils and fats (447,000 ng/g) and milk (400 ng/g), respectively. In all food sampled, tetra-CNs dominated with the exception of fruits and pulses where hexa-CN was prevalent. Octa-CN was least found in all samples. Since this is the first report on occurrence of PCNs in foods in this region, their results were compared with an earlier study by this same group of researchers on PCB dietary levels among Catalonian population. It was inferred that the total PCNs contribution to the ∑TEQs in their present study is smaller when compared to PCBs (Domingo *et al*., 2003).

Fernandes *et al*. (2010) investigated some ranges of foods: milk, fish, dairy products, poultry, vegetables, fruits, meat and meat products from UK. All the analysed specimens contained PCNs with fish having the highest level (0.037 ng/g wet weights). The most harmful PCN congeners; CNs 66, 67, 73, and 52 were mostly found in all their food samples, while 75 was the least detected congener. PCN TEQ linked with these concentrations was less than the reported values for PCDDs or PCBs in food and it was concluded that these PCN concentrations in foods alone do not pose any toxic threat (Fernandes *et al*., 2010). Kim *et al*. (2018) who also studied PCNs occurrence in samples of seafood comprising fish, mollusks and crustaceans obtained from local mart in five cities of Korea reported the sum of PCNs varying from ND-110,000 ng/g ww. The maximum value of 110,000 ng/g was recorded in fish samples, dominated by penta-CN. Tetra-CN was prevalent among other samples. The authors stated that

PCNs contribution to TEQ values from everyday consumption of seafood was comparatively small when compared to PCDD/Fs and PCBs (Kim *et al.*, 2018).

Table 2. 7 Reported levels of PCN in foods, fish and other biota around the world

Locations	Sample matrix	Concentrations (ng/g)	Extraction method	Standards	Analysed congeners	Instrument	References
Korea	seafood	ND-110,000	sonication	ECN-5178 PCN mixture	37	GC-MS	Kim *et al*. (2018)
Catalonia, Spain	foods	400-447,000	soxhlet	^{13}C-labeled standard	49	HRGC-HRMS	Domingo *et al*. (2003)
Pakistan	foods	0.02-1.21	soxhlet	Halowax 1014	39	GC-MS	Mahmood *et al*. (2014b)
Michigan Waters and Great Lakes, USA	fish	19,000-31,400,000	LLE	Halowax 1001, 1014, and 1051 mixtures	54	HRGC-HRMS	Kannan *et al*. (2000b)
UK	foods	0.00015-0.037	cold solvent	CRM 350	11	HRGC-HRMS	Fernandes *et al*. (2010)
Chlor-alkali plant, USA	biota	1.06-13.3	solvent	Halowax 1014,1051 mixtures	49	GC-MS	Kannan *et al*. (1998)
Gdansk Basin, Poland	biota	6.3-320	solvent	Halowax 1014 mixture	44	GC-MS	Falandysz *et al*. (1996)

ND = Not detected

2.5.3 Human samples

Like every other lipophilic POPs, PCNs get to humans and animals mostly through food consumption pathway (Fernandes *et al*., 2017). The rate at which they and their by-products are eliminated from body fluid is gradual. Some studies reported PCNs incidence in human samples as the amount ingested through diets (Fernandes *et al*., 2019, 2011, 2010). Previous studies carried out in certain countries such as Japan, Canada, Sweden, Russia, and Germany showed that PCNs are found in human fluid samples (blood, breast milk) (Li *et al*., 2020; Jin *et al*., 2019; Fromme *et al*., 2015; Park *et al*., 2010; Norén and Meironyté, 2000; Lunden and Noren, 1998), and adipose tissues (Schiavone *et al*., 2010; Kunisue *et al*., 2009; Witt and Niessen, 2000; Kawano *et al*., 2000; Weistrand and Noren, 1998).

The sum of 75 $\sum_{75}$ PCN congeners measured in human milk samples from 19 Provinces of China varied from 211–2497 pg/g lipid (Li *et al*., 2020). The results were dominated by hexachlorinated naphthalene (Hexa-CN66/67) congeners, the pervasiveness of these harmful congeners in the breast milk samples implied great danger to children being breastfed and people living in that region. The authors argued that industrial discharge of PCN from thermal processes was the major source of PCN found in the milk samples. The values were smaller to that recorded in similar milk samples from Ireland ($\sum_{12}$= 59-168 pg/g lipid, Pratt *et al*., 2013). The values were comparable with those recorded in other human samples from other countries; Germany (101–1406 pg/g lipid, Fromme *et al*., 2015), Korea (2070-2480 pg/g lipid, Park *et al*., 2010), New York, USA (61–2500 pg/g lipid, Kunisue *et al*., 2009), but much higher than that obtained from human seral samples among Yantai populace in Shandong Province of East China (14300–50700 pg/g lipid, Jin *et al*., 2019).

Park *et al*. (2010) determined PCN levels in serum of Korea human population, and reported levels in the fatty tissue varying between 21 and 2,500 pg/g lipid with mean levels of 2,170 pg/g lipid. Hepta-CN-73 was the most abundant congener, which contributed about 17.5% of the total serum PCN concentration. It was concluded that the occurrence of hepta-CN-73 in the human serum samples might be due to contributions from combustion sources (Park *et al*., 2010). Kunisue *et al*. (2009) also reported PCN concentrations between 61–2500 pg/g lipid weight (wt) in males, and 21–910 pg/g lipid wt. in female human adipose tissues from New York, USA. Even though the highest concentration of 2500 pg/g was recorded in males, they argued that the inputs of PCNs to total dioxin-like toxic equivalents (TEQs) were minimal and that the PCN concentrations were lower than that of previous studies obtained in PCB and PBDE concentrations from similar matrix and contributors in the same locality (Johnson-Restrepo *et al*., 2005). This could have resulted from a temporal trend since their study was carried out during the period of 2003-2005, while previous studies were carried out in early 1990s (Kunisue *et al*., 2009). The concentrations detected in the human milk of Sweden population between the periods of 1972–92 showed a decrease from 3,100 to 480 pg/g milk fats and in the same manner the total TEQs also declined from 100 to 39 pg/g milk fat (Lunden and Noren, 1998).

Table 2. 8 Reported levels of PCN in human body samples around the world

Locations	Sample matrix	Concentrations (pg/g lipid)	Extraction solvent	Extraction method	Standards	Analysed congeners	Instrument	References
China	Human breast milk	211–2497	Hexane: DCM (1:1)	ASE	Mixed standard solutions	75	HRGC-HRMS	Li *et al.* (2020)
China	Human serum	14300–50700	HIHM	-	Halowax 1014	75	GC-HRMS	Jin, *et al.* (2019)
Munich, Germany	Human blood (plasma)	101–1406	Acetone: hexane (2:1)	-	ECN-5489	33	GC-HRMS	Fromme *et al.* (2015)
Ireland	Human breast milk	59-168	mixed organic solvents	soxhlet	$^{13}C_{10}$ labeled PCN standards	12	HRGC-HRMS	Pratt *et al.* (2013)
Italy	human adipose tissues	500-14000	DCM/hexane (3:1)	soxhlet	Halowaxes, and PCN–MXB standard mixture	-	GC-HRMS	Schiavone *et al.* (2010)
Korea	human serum	2070-2480	Acetone: hexane (2:1)	LLE	-	46	HRGC-HRMS	Park *et al.* (2010)
New York, USA	human adipose tissue	61–2500 (males) 21–910 (females)	DCM/ hexane (3:1)	soxhlet	PCN–MXB standard mixture	38	GC-HRMS	Kunisue *et al.* (2009)

HRGC-HRMS = High-resolution gas chromatograph/high-resolution mass spectrometr, DCM = Dichloromethane, HIHM = hydrochloric acid, isopropanol, hexane and methyl tert-butyl ether mixture (1:1, v/ v)

2.5.4 Air

Hogarh *et al.* (2012) in a research organized nationwide on Ghana air to monitor PCN atmospheric levels documented high concentrations of the pollutants, with a total of 63 congeners ranging between 27 and 95 pg/m^3 with tri- and tetra-CNs being the prevalent homologues. The southern region of the country seems mostly affected, with waste combustion, and discharges from industries being the major sources of PCN into the environment (Hogarh *et al.,* 2012). PCN characteristics of air samples during sunny and wintertime at three different sites in northern Taiwan were reported by Dat *et al.* (2018). The mean PCN concentration measured at manufacturing, metropolitan, and rural sites were 172 ± 111, 45.2 ± 8.20 and 45.9 ± 24.4 pg/m^3 respectively, the PCN levels at the three sites were greater in summer than in winter. The main fountain of PCNs at manufacturing site was thermic operations, while mixed sources of thermic discharges and vapourization were responsible for PCN occurrence at the metropolitan and rural sites. Tetra-CN was found to dominate in all the air samples of northern Taiwan (Dat *et al.*, 2018).

Some reported PCN levels in air samples around the world are presented in Table 2.9 and vary from 0.38 to 310 pg/m^3. The highest value (310 pg/m^3) was recorded from Hazelrigg, England (Lee *et al*., 2005), while the lowest mean value (0.38 pg/m^3) was found in Tagish, Canada (Helm *et al*., 2004). The study of Lee *et al*. (2005) was aimed at discovering factors controlling PCN occurrences in ambient air. Hazelrigg (HR), one of the studied sites, is a field station owned by Lancaster University, England. Their findings revealed that PCN levels in HR had not reduced since 1990s and 2001. Similarly, PCN levels during summer were majorly controlled by temperature, which indicated that exchange processes in air-surface play a significant role, while advection is more swayful during winter. The work carried out in 2004 to determine PCN levels and seasonal trends of atmosphere samples obtained from three distant monitoring stations at Alert and Tagish, Canada, and Dunai Island, Russia revealed that PCN level at one of the sites, Tagish, was due to irregular air movements across the Pacific Ocean, which impinged the concentration (Helm *et al*., 2004).

Table 2. 9 Reported levels of PCN in air samples

Locations	Sample matrix	PCN levels (pg/m^3)	Quantification standard	Extraction method	Extraction solvent	Congeners	Instrument	References
Ghana	Air	27-95	ECN-5102	soxhlet	acetone	63	HRGC-HRMS	Hogarh *et al.* (2012).
Taoyuan City, Taiwan	Air	18.5-153	Individual congener	soxhlet	DCM	73	HRGC-LRMS	Dat *et al*. (2018)
Alert and Tagish, Canada	Air	0.69, 0.38 (annual mean values at Alert and Tagish respectively)	Halowax 1014 technical PCN mixture	soxhlet	Hexane and DCM	63	GC-ECNIMS	Helm *et al*. (2004)
Dunai Island, Russia	Air	0.82 (mean)	Halowax 1014 technical PCN mixture	soxhlet	Hexane and DCM	63	GC-ECNIMS	Helm *et al*. (2004)
Chilton, Hazelrigg, England	Air	31-180, 31-310 respectively	Halowax 1014 technical PCN mixture	Soxhlet	DCM	44	GC-MS	Lee *et al*. (2005)
Mace Head, Ireland	Air	1.7-55	Halowax 1014 technical PCN mixture	Soxhlet	DCM	44	GC-MS	Lee *et al*. (2005)
industrial park, Tibet–Qinghai Plateau, China	Air	21.9–75.1	$^{13}C_{10}$-isotope-labeled PCNs (isotope dilution method)	ASE	DCM/Hexane	63	GC-MS	Hu *et al.* (2019)
University of Toronto, Canada	Air	31-78	Halowax 1014, RF	Soxhlet	PE and DCM	63	GC-ECNIMS	Helm and Bidleman (2003)
Meteorological Service of Canada	Air	7-84	Halowax 1014, RF	Soxhlet	PE and DCM	63	GC-ECNIMS	Helm and Bidleman (2003)

HRGC-HRMS = High Resolution Gas chromatograph/ High-Resolution Mass Spectrometer. GFF = Glass Fibre Filter, PUF = Polyurethane Foam disk passive air samplers. GC-ECNIMS = Gas Chromatograph-Electron Capture Negative Ion Mass Spectrometer. RF = Response factors. PE = Petroleum ether, DCM = Dichloromethane, ASE= Accelerated solvent extraction system, GC-MS = Gas chromatograph coupled to mass spectrometer

CONCLUSION

PCNs were widely applied in manufactured consumer products because of their good dielectric properties, fire resistance, stability, and compatibility with other materials among other properties. Their universal occurrence in virtually all environmental samples and bioaccumulation in humans and animals have been reported: while studies have indicated fish as the main PCN reservoir. Humans become exposed to PCNs mainly by ingestion of fish and other fatty foods such as milk, oils, and fats. They are released into the various environmental matrices during usage and disposal of the PCN-containing consumer products through evaporation and combustion processes. Most importantly, combustion has been reported as the major source of emitting PCNs into the environment. Some reported harmful health effects in humans after exposure to PCNs include chloracne, cirrhosis of the liver, irritation of the eyes, fatigue, headache, anemia, hematuria, nausea, and the likelihood of all forms of cancers. Proper handling and disposal of our generated wastes can mitigate global occurrence of PCNs. General assessment of the analytical procedures employed by various researchers for the determination of PCNs in all the matrices showed that Halowax technical mixtures were mostly used as quantification standards. There is a need for the production and commercial availability of more specific individual standards for all the available 75 PCN congeners to enhance PCN determinations. The LLE method is frequently used for water analysis than the SPE because of its affordability, while the soxhlet extraction method is mostly considered for determinations in other environmental matrices. Technological advancements in chemical analysis have introduced automated extraction systems, which have been applied for PCN extraction from different samples. However, most laboratories still employ the conventional methods because they are cheaper when compared with these expensive automated systems. The gas chromatograph is generally employed for the separation of PCNs, while the identification or quantification is usually performed by mass spectrometer (MS). The reviewed data revealed that CN 66, 67 and 73, which are the highly toxic congeners were prevalent in most human and food samples. There is need for proper and continuous monitoring of these pollutants in our environment.

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CHAPTER THREE

LITERATURE REVIEW

Incidence of polybrominated diphenyl ethers in South Africa environmental and human samples: A Review

Abstract

Polybrominated diphenyl ethers (PBDEs) have served over the years as flame-retardants (FRs) in household appliances and industrial products to curtail fire-related trauma and accidents. However, their detrimental ecological damage has become of great concern as they are additive FRs and can easily leach out from products in which they have been added into the environment. PBDEs swiftly bioaccumulate in the environment, foods, wildlife, humans and have been discovered in almost all creatures. This chapter describes sources, and routes by which PBDEs enter the environment including human beings, and compares studies relating to occurrence of PBDEs in certain environmental matrices in South Africa (SA) with those obtained from other countries around the world. Humans become exposed to these pollutants through ingestion of contaminated water or foods, inhalation or dermal contact with contaminated air and dust particles. Even though PBDEs were never produced in SA, this study and many others have established their presence in our environment. People living in the studied locations become exposed to these pollutants mostly through dust particles via cars and other electrical appliances they used in the indoor environment, but there is still paucity of data on their occurrence, distribution and toxicity to both humans and environment in major Provinces of the Republic of South Africa. Hence, there is need for more comprehensive studies especially on their levels in foods, water and human samples (breast milk, blood, placenta etc.), and their health implications.

Keywords: Persistent organic pollutants; Polybrominated diphenyl ethers, brominated flame-retardants; congeners; toxicity

3.0 Introduction

Persistent organic pollutants (POPs) are chemical compounds that repel ecological breakdown from chemical, biological, and photolytic procedures. All POPs share four distinctive features; they are environmentally persistent, toxic, experience long-distance movement and bio-accumulate in living organisms (Ashraf, 2017; Ritter *et al*., 1995*)*. These include "Dirty Dozen”, the most harmful compounds, and the “Nasty Nine” (Zacharia, 2019; Haffner and Schecter, 2014). The dirty dozen is made up of eight pesticides, two industrial chemicals and two inadvertent industrial by-products that are utilized in farming and industrial manufacturing of certain consumer goods (Zacharia, 2019). On the contrary, the nasty nine include alpha- and beta hexachlorocyclohexane, chlordecone, lindane, pentachlorobenzene, perfluorocotane sulfonic acid, (used as insecticides, fungicides, pesticides) and brominated flame-retardants (BFRs), of which polybrominated diphenyl ethers (PBDEs) are key components (Haffner and Schecter, 2014).

PBDE distributions in various environmental matrices have become a major concern among environmental scientists around the world because of their toxicity to human, wildlife and the environment. High volumes of these compounds are employed as flame-retardants (FRs) in different consumer goods. They make up reasonable proportion (5–30%) of the consumer goods and are intentionally blended in order to intercept fire hazards while using the products (Segev *et al*., 2009). FRs have been widely applied in electrical, construction, transportation, textile industries, among others. According to the 6th market survey report on FRs in 2019 by Ceresana (one of the leading global market research institutes which specializes in analysing industrial market development), it was predicted that the construction sector will be the leading users of FRs until 2026 with about 30% global demand, followed by electrical and electronics industries which will claim about 534,000 tons global demand of FRs (Flame Retardants Market Report, 2019).

About 175 FRs are industrially manufactured and are available in four groups as: “inorganic, organophosphorus, nitrogen-containing and halogenated-organic FRs”. Halogenated-organic FRs comprise brominated flame-retardants (BFRs) and chlorinated flame-retardants (Birnbaum and Staskal, 2004; EHC 162, 1994). The most common class of FRs is the “BFRs” due to their **e**fficient action and minimal production cost (Altarawneh and Dlugogorski, 2014). Studies have revealed that BFRs ranked second among the FRs used globally, accounting for almost 20 to 25 percent of overall FRs in use

(Abbasi *et al*., 2015). They are included in many manufactured products; rugs, padded furnishings, electrical appliances and automobiles to impart them with fire resistance property and prevent fire injuries or possibly deaths (Qi *et al*., 2014; Zhou *et al*., 2014; Segev *et al*., 2009).

BFRs as a major subgroup of halogenated organic FRs are generally categorized as “reactive or additive”. Reactive BFRs, for example tetrabromobisphenol A (TBBPA) and its by-products, are chemically bound (covalent bond) with the copolymers, while additive BFRs are blended with the synthetic resin but not chemically bound and are able to disperse out of the products into the surroundings; these include hexabromocyclododecane (HBCD), and PBDEs. All these chemicals have been discovered in diverse environmental sources (de Wit *et al*., 2010).

PBDEs occurrence have been reported across the globe in different environmental samples, including surface water, air, soil, sediment, sewage sludge, indoor dust, landfill leachates, fish and other marine organisms, to mention a few (Sun *et al*., 2020, 2018, 2016, 2015; Liu *et al*., 2015; He *et al*., 2014; Zhu *et al*., 2014; Moon *et al*., 2012a; Clarke *et al*., 2010). They were also determined in human hair, milk, blood and adipose tissues (Matovu *et al*., 2019; Chen *et al*., 2018; Kucharska *et al*., 2015; Abdallah and Harrad, 2014; Moon *et al*., 2012b; Kim *et al*., 2005).

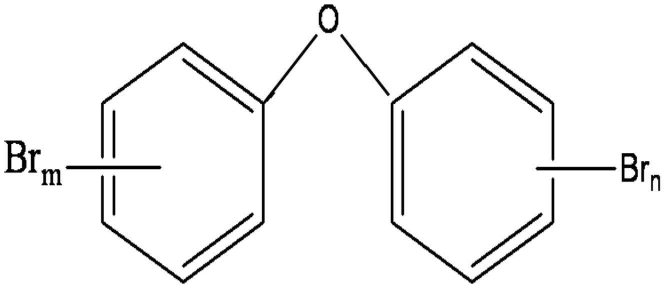
This review chapter is aimed at providing an overview of the sources and pathways through which PBDEs get into the environment or humans, and most importantly at comparing reported concentrations of PBDEs in certain environmental matrices of South Africa (SA) with other countries around the world.

3.1 Polybrominated Diphenyl Ethers (PBDEs)

PBDEs are toxic organobromine chemicals, which can persist, and bio-accumulate in the environment. They were grouped as POPs on the SC list in May 2009 (Birnbaum and Bergman, 2010). They belong to a group of “additive BFRs” that were previously included in many manufactured materials including impact-resistant polystyrene, rug, varnish, clothing materials (textiles), construction materials, motor vehicles, flexible polyurethane foams (employed in house furnishings, beddings, cushions), and as plastic casing in electrical appliances to reduce fire risk (Ali *et al*., 2015; Abbasi *et al*., 2014). They were included in these manufactured products as FRs because of their obvious fire retarding properties and constitute 5% to 30% (w/w) of these materials (de Wit, 2002; Hooper and McDonald, 2000). The commercial mixture comprises of penta-, octa-, and deca- BDE mixtures and the penta- BDE mixtures are often included in polyurethane foams employed in home furnishings and fabrics, while octa- and deca-BDE mixtures are utilized in plastics and plastic casings in electronics (ATSDR, 2017).

PBDEs have one to ten bromine atoms attached anywhere on the diphenyl ether molecule. They comprise of 209 congeners that are divided into ten homologues based on position and numbering system of the bromine atoms on the double phenyl rings. Their general molecular formula is $C_{12}H_{(10-n)}Br_nO$; where *n* ranges from 1 to 10. They are grouped as mono- to deca bromodiphenyl ethers; mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and deca-BDEs have 3, 12, 24, 42, 46, 42, 24, 12, 3 and 1 congeners independently (Chen *et al.*, 2012).

As a BFR, the role of PBDEs is to delay the combustion of these products by emitting bromine atoms at elevated temperatures. Bromine atoms act by effectively binding to free radicals and suppressing the chemical reactions responsible for fire ignition. PBDEs being an additive BFR possess the ability to leach out of the polymers to which they have been previously added and evaporate into the environment when subjected to conditions responsible for their leaching (Eljarrat and Barcelo, 2011; Choi *et al.*, 2009).



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Where, m + n = 1 to 10

Figure 3. 1 PBDEs general chemical structure

3.2 Physicochemical and toxicological properties of PBDEs

PBDEs are bicyclic aromatic ethers which are only sparingly soluble in water (ng/L to µg/L) but are highly fat-soluble (lipophilic), they bio-accumulate easily in adipose tissues of humans and animals. They are impervious to acidic, basic and biological decompositions (Allchin *et al*., 1999). They can withstand physical, chemical and biological deteriorations in the environment; hence, PBDEs are persistent in the environment, comparable with PCBs (Bocio *et al*., 2003). Their boiling points range from 310 to 450°C and vapour pressures at room temperature are comparatively low (3×10^{-4} Pa for tetra-BDEs to ~2×10^{-7} Pa for octa-BDEs), octanol-water partition coefficient is relatively high (~10^{6} for tetra-BDEs to ~10^{10} for deca-BDEs) (de Wit, 2002; Darnerud *et al*., 2001). Like every other POPs, PBDEs are toxic, bio-accumulate and can experience long-range atmospheric transport (LRAT) (Moon *et al*., 2007a; Hardy, 2002; McDonald, 2002).

Penta- and octa-BDEs were forbidden in Europe and USA in 2002 and 2003 respectively, because of their neuro-toxicity (Akortia *et al*., 2016); hence, their inclusion as one of the POPs (UNEP, 2009). The inclusion of deca-BDE in manufacturing of electrical appliances was also prohibited in Europe and USA (Ma *et al*., 2013; Stapleton *et al*., 2012). Bioassay studies on rats and mice have experimentally linked PBDEs with endocrine and thyroid disruption (caused by penta and decabromodiphenyl ether), liver toxicity, diabetes and other health issues (ATSDR, 2017; Birnbaum and Staskal, 2004). PBDEs show intense toxicity and are proven endocrine disruptors that interrupt normal thyroid hormone function in human beings, which may cause adverse neurobehavioural defects and cancer (ATSDR, 2017; Birnbaum and Staskal, 2004; Darnerud, 2003; McDonald, 2002). Among the known congeners, penta-BDEs showed the highest toxicity leading to neurodevelopmental problems even at low concentrations of 0.8 mg/kg body weight (Eriksson *et al*., 2001), while octa-BDEs are known to be “teratogens” (Darnerud *et al*., 2001) and deca-BDEs are grouped as human carcinogens by the US Environmental Protection Agency (USEPA, 2010). Worse still, PBDEs have the ability to be transformed to more toxic chemicals such as “polybrominated dibenzodioxins and polybrominated dibenzofurans” in a pyrolysis process which frequently occurs when plastic materials containing PBDE are recycled or during uncontrolled combustion e.g., unintentional or dumpsite fires (Barontinia and Cozzani, 2006; Rupp and Metzge, 2005). Due to their widespread use, lipophilicity, persistence, and inert characteristics, PBDEs are prevalent in our environment and have become of great concern to humans (USEPA, 2010).

Table 3. 1 List of PBDE homologues

Congener group	Acronym	Molecular formula	No. of individual congeners
Monobromodiphenylether	MonoBDE	$C_{12}H_9BrO$	3
Dibromodiphenylether	DiBDE	$C_{12}H_8Br_2O$	12
Tribromodiphenylether	TriBDE	$C_{12}H_7Br_3O$	24
Tetrabromodiphenylether	TetraBDE	$C_{12}H_6Br_4O$	42
Pentabromodiphenyl ether	PentaBDE	$C_{12}H_5Br_5O$	46
Hexabromodiphenyl ether	HexaBDE	$C_{12}H_4Br_6O$	42
Heptabromodiphenyl ether	HeptaBDE	$C_{12}H_3Br_7O$	24
Octabromodiphenyl ether	OctaBDE	$C_{12}H_2Br_8O$	12
Nonabromodiphenyl ether	NonaBDE	$C_{12}HBr_9O$	3
Decabromodiphenyl ether	DecaBDE	$C_{12}Br_{10}O$	1

3.3 Analysis of PBDEs

The methods adopted for PBDEs extraction, purification and instrumental analysis from samples are similar to other POPs' (Fulara and Czaplicka, 2012).

3.3.1 Sample collection and storage

The first step involved in both qualitative and quantitative analysis of organic chemicals present in environmental samples is sample collection and storage (Fulara and Czaplicka, 2012). As an illustration, aqueous specimens from Cape Town, SA were fetched into properly cleaned 1000 mL amber glass bottles with screw covers, kept cool below 4°C until analysis (Daso *et al*., 2013a, 2012). Sediment samples from the Eastern Indian Ocean were collected by stainless steel grab sampler, wrapped with aluminium foil and stored in freezer (Qiu *et al*., 2020). Sediment, soil, and dust samples from Guiyu town, China were packed with cleaned stainless-steel spatula, stored in glass bottles and air-dried prior to analysis (Labunska *et al*., 2013). Dust samples from cars, residential houses and offices in Durban, SA were gathered with dust unit connected to a vacuum cleaner and amber glass bottles was used for its storage (Abafe and Martincigh, 2016, 2015a). Indoor dust samples from certain homes in Canada, New Zealand, United Kingdom (UK), United States of America (USA) were gathered using nylon sample socks attached to vacuum cleaners, and stored in polythene bags at −20°C (Harrad *et al*., 2008a**)**. Indoor air specimens from West Midlands microenvironments were collected on polyurethane foam (PUF), disks passive air samplers were kept inside stainless-steel housings and stored in cleansed aluminium foil in airtight glass jars at 4°C until extraction (Harrad *et al*., 2006**)**. Fish samples from two lagoons located on the western French Mediterranean coast were caught with fish traps and transported to laboratory in well-ventilated water containers (Labadie *et al*., 2010). Liu *et al*. (2018) applied bottom trawling to collect their fish samples, and anesthetized them before transporting to the laboratory.

3.3.2 PBDE extraction methods

PBDEs share analogous physicochemical properties with polybrominated biphenyls (PBBs), polybrominated dibenzodioxins (PBDDs) and polybrominated dibenzofurans (PBDFs), and as a result, their extraction methods are comparable. The commonly applied methods and solvents for their separation from aqueous, air, sediments and other semisolid samples are discussed below.

3.3.2.1 PBDEs extraction from aqueous samples

Following PBDEs affinity for lipids and their insolubility in water, most studies employ the classical liquid–liquid extraction (LLE) method with large water quantity (between 500-1000 mL) for the extraction of these pollutants by agitating both water samples and organic solvents in a separating funnel for satisfactory analyte recovery. Some of the extracting organic solvents used include dichloromethane (DCM), hexane, and isooctane (Daso *et al*., 2013a; Vonderheide, 2009). LLE was also used for PBDEs extraction from storm water (Daso *et al*., 2012).

LLE method routinely employed for extracting PBDEs from water samples was substituted with solid phase extraction (SPE) (Liu *et al*., 2018; Wang *et al*., 2017; Johnson, 2011; Covaci *et al*., 2007) due to SPE reduced extraction time, efforts and solvent consumption. Cartridges such as C_{18} are widely employed in SPE as the adsorbing materials because of their ability to retain both polar and nonpolar compounds on the surface (Wang *et al*., 2017; Barco-Bonilla *et al*., 2015). PBDEs are eluted from the solid phase with organic solvents (ethyl acetate, acetone, acetonitrile, DCM and hexane but higher PBDEs volume was recovered with hexane and dichloromethane mixture, 3:2 v/v) (Liu *et al*., 2009). Liquid samples from Spain were extracted with SPE method using C_{18} cartridges, 70-120% recovery was recorded for all PBDE congeners in the water samples (Barco-Bonilla *et al*., 2015). Microwave-assisted extraction (MAE) is a distinct procedure used for extracting POPs from different environmental samples. MAE employs microwave to boil the whole sample concurrently without heating the vessel. MAE is very fast, consume less solvent, cheap and environment friendly (Chan *et al*., 2011). Solid-phase microextraction (SPME), single drop microextraction (SDME), microwave-assisted solvent extraction (MASE), dispersive liquid–liquid microextraction (DLLME) among other advanced techniques are employed for PBDEs extraction from aqueous samples. The advantages of these new developed extraction methodologies include user-friendliness, high efficiency, low cost, decrease in extraction time and solvents utilization (Santos *et al*., 2015; Vonderheide, 2009). Santos *et al*. (2015) extracted their aqueous samples with DLLME method and 91–107% of BDE-100 was recovered as the targeted congener.

3.3.2.2 PBDEs extraction from dust and air specimens

The respiratory system has been affirmed as another route humans become exposed to PBDEs after food consumption. It was evaluated that an average human ingests 123 ng and 32.9 ng of PBDEs through food and inhaled air consecutively, this is equivalent to 70% and 27% of PBDEs overall daily ingestion (Watanabe and Sakai, 2003).

Dust and air samples are primarily fortified on polyurethane foams, followed by soxhlet extraction with acetone, dichloromethane, hexane, or mixtures of these solvents (Fulara and Czaplicka, 2012). Soxhlet is a conventional solid-liquid extraction method which is simple, cheap, rugged and highly efficient (Shao *et al*., 2016). It was used for PBDEs extraction of indoor air from Birmingham, UK (Harrad *et al*., 2006) and East-Central, United States (Hoh and Hites, 2005). House dust samples from Kuwait were soxhlet extracted with DCM: hexane (1:1 v/v) mixture with over 70% recoveries (Gevao *et al*., 2006). Major limitations with soxhlet extraction include usage of large volume of solvents and lengthy extraction time, which usually transcend 8 hours (Fulara and Czaplicka, 2012).

Pressurized liquid extraction (PLE) is another technique for extracting PBDEs from solid samples (Liu *et al*., 2018), which consumes lesser solvents and uses lesser extraction time; but requires complex sample cleaning (Covaci *et al*., 2007). Martínez *et al*. (2010) employed PLE to extract PBDE from indoor dust specimen; they obtained a more purified extracts and 82%-101% recovery values.

3.3.2.3 PBDEs extraction from solid samples

PBDEs extraction from solid specimens is usually performed using soxhlet extractor with water dispersible solvents; acetone, methanol, or mixture with hexane in diverse ratios (Covaci *et al*., 2007). Qiu *et al*. (2020) extracted their Eastern Indian Ocean sediment samples in a soxhlet extractor with DCM for 36 hours. PLE otherwise called “accelerated solvent extraction”, is an automatic green extraction procedure that uses high temperature and pressure to accomplish comprehensive solid samples extraction, thereby minimizes solvent utilization and increases sample recovery when compared with conventional methods (Liu *et al*., 2018; Vazquez-Roig and Picó, 2015). Another swift and easy method used for PBDEs extraction from solid samples is supercritical fluid extraction (SFE) using supercritical CO_2 as solvent. SFE is simple, faster and has higher analytes recovery when compared with soxhlet (Peng *et al*., 2014; Fulara and Czaplicka, 2012).

3.3.2.4 PBDEs extraction from polymeric materials

Although the application of several PBDEs in electrical components is forbidden, PBDE concentrations in some polymer products (macromolecules) are more when compared with other environmental samples. Thermal desorption (TD) is a very easy process employed for PBDEs extraction from polymers. TD is performed below the polymer's decomposition temperature (300–400C), followed by GC-MS instrumental analysis. PBDEs are extracted from water-soluble polymers by LLE, while soxhlet is used for water-insoluble polymers' extraction with solvents such as toluene, tetrahydrofuran or acetonitrile. The extracts are purified by gel chromatography (Fulara and Czaplicka, 2012). Polymers found in television and computer sheaths were extracted using PLE (Schlummer *et al*., 2005) and ultra-sonication methods with 2-propanol solvent (Pohlein *et al*., 2005).

3.3.2.5 PBDEs extraction from biological samples

Blood is a complex sample because it contains both the compound of interest and other interferences, which can impinge the analysis of results (Covaci *et al*., 2007). The analytical procedures for blood samples involve first denaturing of the protein constituents of the blood samples with formic acid, while the extraction is usually carried out by SPE or LLE, followed by extract clean-up (purification), concentration and instrumental analysis (Stapleton *et al*., 2006). Xiao *et al*. (2007) employed hollow fibre–liquid phase microextraction (HF-LPME) method to extract PBDEs from blood samples. The rate of recovery for the four analysed PBDEs was 84.5-111.7% (Xiao *et al*., 2007).

3.3.2.6 PBDEs extraction from food samples

In the determination of PBDEs from fat-rich foods, the preliminary step is the defatting of the sample with an organic solvent. This is achievable by either boiling the sample at 90^0C followed by nonpolar solvent extraction, or forthright sample extraction with nonpolar solvent, followed by dehydrating the sample with anhydrous sodium sulphate (VI) and column clean up with nonpolar solvents. Tissue and fat-rich food samples are commonly extracted in soxhlet apparatus with various solvent mixtures (Covaci *et al*., 2007). Liu *et al*. (2018) extracted their fish samples with PLE system.

3.3.3 Clean-up of PBDE extracts

Extract clean up or purification step is pivotal to the elimination of interferences and the successful outcome of the whole procedures (Vonderheide, 2009). In view of the low selective characteristics of these extraction methodologies and intricacies of some environmental specimens, purification stage becomes imperative in any chemical methods of analysis. Elemental sulphur, one of the intrusions that affect solid samples (sediments or soil) is removed during the purification process with copper powder, while lipid or fat is the major interference removed before tissue and food analysis. Either extracting the samples with organic solvents or gel/adsorption chromatography removes lipids. The adsorption chromatography purification process is hinged on liquid-solid chromatography using activated silica gel, alumina, florisil or other materials. C_{18} is a nonpolar sorbent used for defatting samples during the MSDP, PLE and SFE extraction methods. Protein constituents in blood samples are first denatured using formic acid, followed by LLE or SPE extractions, purification, and further concentration (Fulara and Czaplicka, 2012; Vonderheide, 2009; Covaci *et al*., 2007).

3.3.4 Instrumental analysis

Determination of halogenated organic compounds (chlorinated or brominated) is usually accomplished with GC-MS. PBDE instrumental analysis is routinely achieved by GC-MS or GC-ECD with varying optimization conditions. Qiu et al. (2020) employed Agilent GC-MS with a DB5-MS column for their sediments PBDE analysis, while Daso *et al*. (2012) employed GC-ECD for measuring PBDEs present in their effluent samples. A recent advancement in PBDE analysis was the construction of a cheap GC-ECD instrument for quantitative analysis of specific PBDE congeners in storm water. The method concurrently determined lower and higher molecular weight PBDEs in one run (Komolafe *et al*., 2019). Another improvement in PBDE measurement was the development of a novel technique, GC-HRMS by Barco-Bonilla *et al*. (2015) for concurrent analysis of two classes of pollutants (polychlorinated biphenyls, PBBs and PBDEs) at very low concentrations in liquid and solid specimens. The levels of recovery for all the compounds were 70-120% (Barco-Bonilla *et al*., 2015).

3.4 Production and emission sources of PBDEs into the environment

Individual PBDE is manufactured industrially in advanced nations of the world by catalytic bromination of the polymer (diphenyl ethers); the products formed are mixtures of penta-, octa-, and deca-BDE, depending on the extent of bromination (Marsh *et al*., 1999)**.** The gross annual global world PBDEs utilization was evaluated in 1992 to be 40,000 metric tons/year; of which 75% were deca-BDE, while 15% and 10% were octa-BDE and penta-BDE products, respectively and by 1999, PBDEs in circulation was estimated to be 67,000 metric tons/year. Worldwide utilization of products containing deca, octa, and penta-BDEs in 1999 was 55,000, 3,800, and 8,500 metric tons, respectively (Environment Canada, 2010).

According to the statistics made available to the POPs Reviewing Committee at Stockholm Convention, the past total PBDEs production from 1970 – 2005 was approximated to 1.3 – 1.5 million tons (UNEP, 2010). The production of commercial penta- and octa-BDE is believed to have stopped in some countries such as USA, Europe, and Japan since 2004, while deca-BDE production continues (Li *et al*., 2015). Apart from PCBs and organochlorine pesticides, the production and application of PBDEs continued worldwide. PBDEs may be discharged into the surroundings by diffusion during their production, vapourization from PBDE-containing materials and disposal or recycling of wastes (ATSDR, 2017). The routes of their escape into the environment are closely related to manufacturing, applications, and disposal of the consumer products in which they have been intentionally added to prevent fire outbreak. After discharge into surroundings, PBDEs can bioaccumulate in human and other environmental matrices (Daso *et al*., 2010). Some of the reported PBDEs emission sources into the environment include waste from electrical and electronic appliances, wastewater treatment plants, landfill sites, importation of used vehicles, and indoor surroundings.

3.4.1 Electrical and Electronic Equipment Waste (EEEW)

The distinct pathway through which PBDEs are emitted into the surroundings is through discharges from companies manufacturing PBDEs, and fire impeded products (including electronic devices) (Watanabe and Sakai, 2003). The collection and sorting of electronic wastes (E-waste) were shown as a significant way of emitting PBDEs into the environment. In Africa, electrical and electronic products remain major sources of PBDEs emission, and this has resulted in elevated levels of EEEW (La Guardia *et al*., 2013). Balde *et al*. (2015) recorded that the sum of EEEW generated in Africa in 2014 was 1.9 megaton (Mt), which happened to be the least when compared to reported values for Asia (16 Mt), USA (11.7 Mt), and Europe (11.6 Mt) (Balde *et al*., 2015). However, La Guardia *et al*. (2013) reported that almost 80% of total EEEW generated in advanced nations is now shipped to developing nations under the false pretense of recycling them.

3.4.2 Wastewater Treatment Plants (WWTPs)

Wastewaters are generally made up of both domestic and industrial liquid wastes generated by human activities (Sanchez-Avila *et al*., 2009). They contain many pollutants, which include “BFRs and non-brominated flame-retardants” (Li *et al*., 2016). Because of PBDEs low water solubility, they have the tendency to accumulate on solid suspensions in wastewater and occur in high concentrations in sludge (Stiborova *et al*., 2017). WWTPs have been recognized as another route the contaminants get into the surroundings (Martellini *et al*., 2012). Daso *et al*. (2012) reported PBDE in liquid wastes and mud taken from a WWTP in Cape Town, SA.

3.4.3 Landfill Sites

Landfill sites were recognized as another route for PBDEs emissions into our environment. Developing countries of the African continent rarely sort wastes before being discarded in landfill sites. Many of these sites are open dumps in Africa without preventive measures against environmental pollution. PBDEs can be found in the atmosphere because of the elusive release of dust particles during waste packing and conveyance from one place to another (Kajiwara *et al*., 2014).

Earnshaw *et al*. (2013) suggested that the waste management sequences primarily carried out in landfill sites remain the main route of discharge to other sections of the environment. Many African countries employ “open dumpsites” for their waste’s disposal rather than well designed “landfill sites”. For instance, in SA, the open dumpsites authorities only manage the waste by burning to prevent vexatious sight that could result from discarded garbage (Remigios, 2010).

3.4.4 Importation of Used Vehicles

Some African countries are in the habit of importing used vehicles from advanced nations such as Japan, UK, USA, China, and others, because of their inability to afford new cars, which are quite expensive when compared with used ones. Many of these used vehicles are approaching their “end of the line” thereby becoming BFRs emission sources (Ajayi and Dosunmu, 2002).

3.4.5 Indoor environment

De Wit (2002) reported that additive BFRs can be easily transmitted from the over side of manufactured materials to the interior surroundings (indoor environment). The interior surrounding is the principal donor to the entire PBDEs in human, because over 90% of people’s times are spent indoors; whether in-house, office, or school. Elevated amount of PBDEs in the interior surroundings are released from electronic gadgets and padded furniture (De Wit, 2002). Melymuk *et al*. (2016) reported elevated PBDE levels in residences containing many electronic gadgets. It was also reported that most electronics used by Africans are shipped from advanced nations; that their desires for these gadgets keep rising, which could lead to elevated PBDE concentrations in our future environment (La Guardia *et al*., 2013). Mandalakis *et al*. (2008) showed that the passenger compartment in vehicles is another main indoor environment where human beings become susceptible to various dangerous materials including PBDEs. Eight PBDE congeners were detected in interior dust collected from some houses, workplace and varsity computer workshops in Durban, SA (Abafe and Martincigh, 2015a). In addition, Abafe and Martincigh (2016) investigated dust samples collected from different personally owned automobiles and automobiles on sale at a dealer shop in Durban city of SA. Kefeni and Okonkwo (2012) measured six PBDE congeners (BDE-47, 66, 85, 99, 153 and 209) in fine soil particles gathered from office environment in Pretoria, SA. High PBDE levels were recorded from USA indoor environment (Batteman *et al*., 2009; Sjodin *et al*., 2008; Harrad *et al*., 2008a) and UK (Harrad *et al*., 2008a, b) where they are extensively applied as FRs in household materials, but lower values were recorded from Pakistan (Ali *et al*., 2013, 2012), Germany (Fromme *et al*., 2014), New Zealand (Harrad *et al*., 2008a), Sweden (Thuresson *et al*., 2012), and Vietnam (Tue *et al*., 2013).

3.4.6 Soil erosion

Soil erosion in combination with run-off water was indicated as a significant way PBDEs are transported from land until seashore (Zou *et al*., 2007); this implies that the pollutants are conveyed through many frontiers (Hale *et al*., 2006), amass in soil, sediments, ground water and marine organisms (Streets *et al*., 2006). Soil is a major ecological reserve for POPs, and serves as a natural medium for transmitting them in various environmental spheres (Cetin, 2014). PBDE levels in the soil and sediment specimens gathered around an electronic waste dumping and reprocessing unit situated in Guiyu, Guangdong, China was 0.34-824 ng/g and 0.26-6.81 ng/g, respectively. Soil specimens were taken from topsoil of two dumpsites used for discarding plastic and electronic waste, while the sediment was collected from Lianjiang River bank that flows through the Guiyu town. The PBDE concentrations in soil samples were more than the concentrations in the sediment samples. It was concluded that the soil was contaminated by e-wastes disposal and recycling operations around the sites, and that the PBDE in the river sediments migrated from the soil erosion (Wang *et al*., 2005).

The sum Σ_7PBDE measured in industrialized area of Dilovasi in Kocaeli, Turkey was 0.70-203 ng/g (dry weight). It was concluded that soil PBDE concentrations were controlled by precipitates and gases discharged from adjoining sources (Cetin, 2014). Wu *et al*. (2015) investigated concentrations of 14 congeners in soil samples collected from Jiading District, Shanghai City, China. The sum $\sum_{14}$PBDEs ranged from 4.31-141.8 ng/g dry weight (dw), with BDE-209 being prevalent.

3.5 Routes of human exposure to PBDEs

PBDEs found in human body can emanate from any of these reported routes of exposure: food consumption (dietary intake), airborne particulates or dust inhalation, and skin (dermal) contact. Similar to every POP, PBDEs dissolve easily in lipids (lipophilic) and as a result, they have a great tendency to amass in adipose or fatty parts of humans. It becomes expedient to describe some possible routes in which these pollutants enter human bodies (Daso *et al*., 2010).

3.5.1 Dietary Intake

Several works have reported PBDEs occurrence in diverse food items all over the world (Babalola and Adeyi, 2018; Cade *et al*., 2018; Trabalon *et al*., 2017; Fromme *et al*., 2016; Zhang *et al*., 2013; Domingo, 2012; Fraser *et al*., 2009; Spliethoff *et al*., 2008; Staskal *et al*., 2008; Meng *et al*., 2007). The work of Babalola and Adeyi (2018) evaluated PBDE concentrations in major local foods (aquatic foods, meats, oil, dairy products, cereals, vegetables, etc.) eaten by adults in Southwest region of Nigeria. Their results revealed that aquatic foods had the greatest PBDE levels while dairy products had the least. They concluded that no health risk was involved with the studied food groups for adults of this region, but recommended more researches into other food groups consumed by the younger and older citizens (Babalola and Adeyi, 2018).

Cade *et al*. (2018) studied PBDE bioaccumulation in seafood (finfish and shellfish) consumed by inhabitants of Puget Sound region, Washington State of USA. Their findings revealed that finfish contained more PBDE concentrations than shellfish with BDE-47 and -99 as the prevalent congeners in the analysed samples. Zhang *et al*. (2013) reported the foremost nationwide inquiry into pollutant levels (PBDEs and PCBs) contained in different Chinese foods. The survey showed that PBDE levels in meats and aquatic foods exceeded other food categories. Trabalon *et al*. (2017) reported the incidence of eight PBDEs in ten groups of fish and shellfish commonly eaten by citizens of Tarragona Province (Catalonia, Spain). PBDEs occurred in all the analysed samples; Salmon, the specie with the greatest lipid content recorded maximum sum of PBDEs concentration (1.3 ng/g wet weight, ww), while squid and shrimp, the species with small lipids, had the least $\sum_8$PBDEs (0.6 ng/g ww). The authors concluded that consumption of fish and shellfish posed no health risks.

Fraser *et al*. (2009) discovered in their study that consumption of spoilt meats adds to PBDE levels in residents of USA. Their findings also revealed that the sum of total PBDEs in serum was more in humans who feed on poultry and red meats when compared with vegetarians (Fraser *et al*., 2009). Frederiksen *et al*. (2009) found out that the comparative contribution from human diets to total PBDE was more in fish and meats than in vegetables. The source of PBDEs in these meats could have been from bioaccumulation of these chemicals in the adipose tissues of the animals.

Domingo *et al*. (2008) recorded elevated PBDE levels in fish, shellfish, oils and fats but very low concentrations in vegetables. Similar observations were reported from Spain (Gomara *et al*., 2006) and in Finland (Kiviranta *et al.*, 2004). Generally, dietary intake of PBDEs by means of fish consumption may be enormous in areas where fish is widely consumed. Their findings showed that eating of fish contributes immensely to PBDEs load in the human body (Kiviranta *et al.*, 2004). Meng *et al*. (2007) studied human's exposure to PBDE in conjunction with inhalation and eating of fish in China. Their work focused on PBDE daily intake through inhalation, fish and human milk consumption in distinct age categories. Although fish is known as a major PBDE donor, the contribution from food intake was discovered to be less than through inhalation (Meng *et al*., 2007). Reports from the USA on human dietary studies was inconsistent; Anderson *et al*. (2008) reported an insignificant input from the eating of fish to PBDE levels in humans; while other studies revealed significant input (Spliethoff *et al*., 2008; Staskal *et al*., 2008). Generally, the comparative impact of eating fish to PBDE ingestion in USA was lower when compared to other nations from Europe and Asia. Fish consumption is the major donor to human body level in Europe while feeding on meat remains the main route humans are exposed to PBDE in the USA (Daso *et al*., 2010).

Human exposure from other food categories: “meat, dairy product, and vegetables” is also important to evaluate the dietary intake of PBDE. For example, fish is rarely consumed as food in North America; the flesh of animals (meat) and fats are the major donors of PBDE in humans in that region. Schecter *et al.* (2008) discovered this pattern in their work where it was documented that PBDE levels in Americans eating animal meat were as high as 60%–70%, but just 10%–20% from fish.

Absorption of PBDEs by plants poses a danger for humans after consuming the edible portion of plants. Because of the low water solubility of these pollutants, it is anticipated that the rate at which they will be absorbed by plants will be inconsequential. Nonetheless, investigations revealed that PBDEs occur particularly in esculent plants such as roots, greens, grains, fodders among others (Zhao *et al*., 2009a; Bocio *et al*., 2003; Ohta *et al*., 2002). Notwithstanding, the routes by which the pollutants are absorbed by the plants remain a mystery, but it could be deduced that absorption by the root system is a likelihood (Daso *et al*., 2010). Amid the various types of eatable plants (spinach, carrot, and potato) studied by Ohta *et al*. (2002), spinach PBDE level was the highest (134 pg/g fresh weight). Their result was greater than the levels reported for meat products in the same study. It was inferred that PBDE absorption from the immediate atmosphere by foliage plants such as spinach could be attributed to the observed pattern (Ohta *et al*., 2002).

3.5.2 Human breast milk

PBDEs have been detected in human liquid samples; their occurrence in milk indicates the past environmental conditions an individual had been exposed. Newborn babies and infants are usually unguarded against the injurious effects of these pollutants via this route; hence it is required that the presence of POPs, especially the PBDEs be efficiently monitored in human milk (Matovu *et al*., 2019; Antignac *et al*., 2016; Hooper and McDonald, 2000). Antignac *et al*. (2016) collated the PBDE levels in breast milk samples from women in selected nations. PBDE concentrations for women from Denmark, Finland and France were 1.22-111.10, 1.47-19.02, and 0.45-15.27 ng/g lipid weight (lw), respectively. Matovu *et al*. (2019) determined PBDE concentrations in breast milk samples from primiparous women of Kampala and Nakaseke community, which represent metropolitan and rural regions of Uganda, respectively. PBDE concentrations in samples from Kampala (0.91-8.11 ng/g lw) exceeded those from Nakaseke (0.59-2.23 ng/g lw), with BDE-209 as the prevalent congener. The calculated risk quotients were less than one in most samples, and the authors concluded that the breast milk of Uganda women was healthy for human consumption.

Despite important benefits of breastfeeding in providing enhanced nourishment and healthful living to young children, it also provides a pathway for these toxic chemicals to get to these infants. Higher PBDE levels were measured in the serum of infants fed with mother breast milk when compared with infants fed with baby foods. The total PBDEs found in children fed with breast milk was 65 ng, while it was 10 ng for children fed with baby foods (Carrizo *et al*., 2007). Thirteen PBDE congeners including BDE 209 were analysed in human breast milk samples taken from voluntary donors from Austin and Dallas, Texas, USA. The average total BDE was 73.9 ng/g lipid weights (Schecter *et al*., 2003). Johnson-Restrepo and Kannan (2009) studied the routes of human contacts with PBDE for various age classes in the USA. The sum of "daily exposure dose (DED)" in youngest children (less than 1 year) that was breastfed was 86.4 ng/kg body weight/d, which was attributed majorly to their being breastfed. The major route of exposure for the youngest children was breast milk, while oral intake (ingestion) and skin contact (dermal absorption) of fine air particles (dust) were the main routes of PBDE contacts identified for the other age classes (Johnson-Restrepo and Kannan, 2009).

PBDE concentrations in breast milk samples collected from North Americans were reported to be higher than anywhere else, with the concentration doubling each 4–6 years (Hites, 2004). In addition, low BDE congeners (especially BDE 47) were discovered to be the prevalent congeners in most of these studies. The repercussion of these results on infants is their propensity for accumulating greater levels of these toxic lower BDE congeners (Hites, 2004).

3.5.3 Inhalation and ingestion of dust

Apart from human contact with PBDEs via consumption of food, ingestion and oral intake of impure fine air particulates (dust) were reported to immensely add to the total human PBDE concentrations (Harrad *et al*., 2016; Olukunle *et al*., 2015a, b; Allen *et al*., 2007; Jones-Otazo *et al*., 2005). This route of human vulnerability was indicated as the main donor to elevated PBDE concentrations in 2 to 5 years old children (Toms *et al*., 2009a). They concluded that this observation should be anticipated because children of this age bracket generally participate in actions (such as putting hands in mouth, eating dusty food items, crawling and so on) that increase their contacts with these pollutants, thereby increasing their levels in the body (Toms *et al*., 2009a).

Human exposure to PBDEs by means of ingestion and oral intake of impure fine air particulates (dust) is not restricted to infants alone; it occurs among all age classes. It was reported that all classes of human beings may come in contact with these pollutants through dust and fine air particulates especially in small environments (like vehicles, rail, airplanes) (Lagalante *et al*., 2009; Mandalakis *et al*., 2008). Nonetheless, the extent of vulnerability depends on duration and the prevalent environmental conditions (Daso *et al*., 2010). PBDE levels were investigated in both indoor and outdoor environments, especially in dust or air particulates near waste disposal and recycling infrastructures (Mandalakis *et al*., 2009; Julander *et al*., 2005). It is worthy to note that studies on indoor environments are mainly carried out to establish pathways for these pollutants in atmospheric samples (Toms *et al*., 2009b; Zhao *et al*., 2009b).

Interior surroundings (such as bedrooms, sitting rooms, offices, vehicles) are relevant origin of human exposure to pollutants because people spend over 80% of their time inside. Consumer products used by humans in residences, workplaces, and schools that are composed of these pollutants have permitted their indoor determination. As a result, studies reporting indoor evaluation of PBDE concentrations are becoming numerous (Takigami *et al*., 2009*a*, b; Sjodin *et al*., 2008; Allen *et al*., 2007; Jones-Otazo *et al*., 2005). Human exposure through occupation has also been reported (Abafe and Martincigh, 2015b).

3.6 PBDEs health risks and risk estimation

3.6.1 PBDEs health risks in humans and wildlife

The health impacts of PBDEs are yet to be fully studied (Chen *et al*., 2018a), most studies on PBDEs toxicity are performed on animals (rats and mice) (ATSDR, 2017). After administering BDE congeners on these animals for several days, weeks or months, certain changes were observed in the pancreas and reproductive systems. Based on animal experiments, exposure to PBDEs is believed to have effects on the neurobehavioural development, liver, thyroid and reproductive systems (ATSDR, 2017; Linares *et al*., 2015). The adverse impacts of PBDEs on neurodevelopment (Martin *et al*., 2017; Ding *et al*., 2015), endocrine and reproductive systems (Lin *et al*., 2011; Gascon *et al*., 2011) have been reported.

Only decaBDE is regarded as a potential carcinogen based on findings from animal studies by EPA. Notwithstanding, decaBDE is not readily absorbed in human body unlike the lower BDEs that dissolve easily in fat and hence build up in breast milk fat and are subsequently transmitted to infants or fetus. Commercial products containing pentaBDE and octaBDE have higher tendencies to cause other health effects in humans compared to decaBDE. Some of those health effects after short-term exposure include impairment of immune system and skin irritation. Even though, the PBDE concentrations that could lead to significant health hazards in animals are most unlikely to be found in the environment, accumulation of PBDEs over a long period (years) poses greater hazards than short-term exposure to low amounts of the contaminants. Liver cancer was noticed in bioassay animals that consumed very high concentration of decaBDE. Children seem to consume more of PBDEs per kilogram of their small body weights through breast-feeding, hand-to-mouth exposure, eating with dirty hands, or eating soil on purpose or by increased interaction with the ground via crawling and/or lying. They are thus, at greater risk than adults, especially those living close to dumpsites (USEPA, 2009; ATSDR, 2004).

A recent study has linked PBDE levels with cancer risks. Ohajinwa *et al*. (2019) analysed soil samples collected from electronic-waste (e-waste) reprocessing stations in three towns (Ibadan, Lagos, and Aba) in Nigeria in an attempt to determine the extent of pollution of these sites with e-waste chemicals (PBDEs inclusive), and associated health risks with e-waste workers. Cancer and non-cancer risks via three exposure routes (dermal contact, ingestion, and inhalation) by which e-waste workers become exposed to e-waste chemicals were calculated using United States Environmental Protection Agency (USEPA) models. The calculated health risks through all the routes of exposure exceeded the set standard limits for both cancer and non-cancer risks at the e-waste sites. The authors concluded that e-waste personnel were exposed to inimical hazards.

Studies have linked PBDE concentrations estimated in human samples (blood, breast milk) with certain health effects (Matovu *et al*., 2019; Chen *et al*., 2018a; Antignac *et al*., 2016), with fetuses (Chen *et al*., 2018a), neonates and toddlers being more vulnerable due to their exposure via breast milk and dust while crawling (Linares *et al*., 2015). Chen *et al*. (2018a) determined eight PBDE levels in cord blood and investigated their relationship with prenatal outcomes. The blood samples were collected from pregnant women living in an area where brominated flame-retardants are mainly produced in China. The authors found out that BDE-47 affects fetal head size. Matovu *et al*. (2019) determined PBDE levels in breast milk samples from primiparous women living in Kampala and Nakaseke communities, which represent metropolitan and rural region of Ugandan, respectively. PBDE concentrations in samples from Kampala exceeded those from Nakaseke, with BDE-209 being the most prevalent congener. The calculated risk quotients were less than one in most samples, and it was concluded that the breast milk of Uganda women was healthy for human consumption.

Antignac *et al*. (2016) analysed the PBDE levels in breast milk samples of women from selected countries. PBDE concentrations for Denmark and Finland women were comparable, but much lower in France women samples.

The occurrence and adverse impacts of PBDEs on biota were also reported (Sun *et al*., 2020, 2018, 2016; Glazer *et al*., 2018; Trabalon *et al*., 2017; Piersanti *et al*., 2015). Sun *et al*. (2020) investigated the occurrence, spatial distribution, and possible health risk of 18 BDE congeners in mollusks samples of northern South China Sea (NSCS). The targeted PBDEs were measured in all the analysed samples. The Σ_{18}PBDEs in all samples ranged between 6.96-55.6 ng/g lipid weight (lw), with BDE-47 and -209 being the prevalent congeners. PBDEs pollution in these samples from NSCS varied from normal to top level when compared with global PBDEs pollution. Assessment of exposure risk for the PBDE congeners showed that health risks due to consumed green mussel were generally lesser than the U.S. EPA set limits. Glazer *et al*. (2018) studied the neurotoxic effects observed in zebrafish during embryonic stage development after exposing them to small levels of two BDE congeners; BDE-99 and BDE-47. The authors found out that introduction of zebrafish embryos to small dosages of the two BDE-congeners resulted in both short- and long-term behavioural disorders. Inhibition of cell division and certain physiological processes (photosynthesis, nutrient uptake, etc.) in plants have been linked with certain PBDE congeners (Zhao *et al*., 2019).

3.6.2 Health risk estimation

The probable health risks of PBDEs are usually estimated as the chances of developing negative health impacts following exposure of an individual to a specific class of pollutant over a certain period. The carcinogenic or non-carcinogenic risks are calculated for each congener of PBDE, as well as for the total concentration (∑PBDEs) of all the congeners. This estimation is usually carried out based on three possible major routes of exposure, which are direct inhalation, incidental ingestion (oral route) and dermal absorption or contact (Capstick *et al*., 2017).

Usually, average daily dose (ADD) is used to express the possible health risks. This assessment requires some vital information; frequency, magnitude, duration of exposure to a specific class of pollutants in the environment, age, height and body weight of individuals exposed to these contaminants. These exposure parameters vary from one route of exposure to another. For instance, ADD for oral route requires information about the ingestion rate (IR_{ing}), while inhalation rate (IR_{inh}), inhalation unit risk

(IUR) and particle emission factor (PEF) are the essential information needed when estimating ADD via inhalation. Similarly, ADD by dermal contact or skin absorption cannot be calculated without some specific factors such as skin surface area (AS), fraction of exposed skin (FA), dermal absorption factor (ABS) and skin adherence factor (AF) (Ohajinwa *et al*., 2019; Kim *et al*., 2011). USEPA has provided some conventional values for some of the factors after some laboratory experiments were carried out, notwithstanding, some researchers still prefer to conduct an *on-site* assessment using questionnaires to determine if those conventional parameters are suitable for an immediate environment under investigation. Some of these exposure factors are also supplied by the Department of Environmental Affairs, South Africa (DEA 2010), the Korean Exposure Factors (Jang *et al*., 2014) and many other international organizations across the world. The available models for probable risk assessment are commonly used to evaluate possible risks posed by PBDEs or any other organic (or inorganic) pollutants to humans from water, soil, sediment, sewage sludge, air and even indoor or outdoor dust (Ferreira-Baptista and De Miguel, 2005; USEPA, 2001).

Fifth (5th) percentile, mean, median (50th percentile), 90th and 95th percentiles of the experimental data (amounts of the contaminants in an environmental medium) have been used for the calculation of ADD in several studies. With these various percentiles, it would be easy to express the lower, medium and upper levels of possible health risks to humans. Non-carcinogenic risk (NRC) is calculated as the ratio of ADD or LADD (lifetime average daily dose) to either the reference dose (RfD) or reference concentration (RfC) of individual pollutant and this is represented as hazard quotient (HQ). Sum of the hazard quotients for a number of congeners of contaminants in the same class or group (e.g. PBDEs) is expressed as hazard index (HI). In the same vein, carcinogenic risk (RC) or incremental lifetime carcinogenic risk (ILCR) is determined as the product of ADD or LADD and slope factor (SF). Sometimes, this product is multiplied by the gastrointestinal absorption factor (GIABS) which is taken to be equalled to one. Risk index (RI) is also estimated as the sum of all cancer risks for a number of congeners of PBDEs under consideration or any other class of pollutants (Ohajinwa *et al*., 2019; Fowles and Morgott, 2013; Kim *et al*., 2011).

For PBDEs, Ohajinwa *et al*. (2019) stated that RfD and RfC values are only available for four PBDE congeners (BDE-47, BDE-99, BDE-153, and BDE-209) from USEPA handbooks (USEPA, 2011, 1989), and so, non-carcinogenic risk was determined for only those congeners. The probable carcinogenic risk was calculated for only the BDE-209, subject to the availability of slope factor.

Whether by ingestion, inhalation or dermal contact, HQ value of less than one suggests that the level of potential non-carcinogenic risk determined is low or acceptable, but it is considered high or unacceptable if it exceeds one. The same interpretation goes for HI (Adeniji *et al*., 2019a, b). Furthermore, cancer risk or risk index higher than 1×10^{-4} is largely regarded as unacceptable, but values below 1×10^{-6} suggests there would be no adverse health effect. Moreover, RC or ILCR values between 1×10^{-4} and 1×10^{-6} fall within acceptable range. A RC value of 1×10^{-6} indicates that a person has a chance of one in 1,000,000 to develop cancer if exposed to the contaminant(s) (Adamu *et al*., 2015; Olujimi *et al*., 2015). Other exposure factors of importance in this assessment are exposure time adjustment for exposure ratio (T_e), exposure frequency (EF), exposure duration (ED) or exposure time (ET), average time (AT), number of product sucking (MN_{prod}), once sucking product (MT_{prod}), contact time (CT), transfer factor from product to the exposed skin (TF), and conversion factor (CF) among many others (Chen *et al*., 2017; Kim *et al*., 2011).

It is noteworthy to state that different equations will not provide the same risk values, but could yield results that fall within the same range, which could offer similar conclusion.

3.7 Occurrence and PBDE levels in environmental matrices in South Africa

The occurrences of PBDEs were first reported in European nations, North and South America, Asia, and now in Africa (Olisah *et al*., 2020; Law *et al*., 2008). Their occurrence in river water, sediment, leachates from landfills, effluents from wastewater treatment plants and other environmental matrices have been reported in SA (Olisah *et al*., 2020; Daso *et al*., 2016, 2015, 2012; Odusanya *et al*., 2009; Polder *et al*., 2008). Some researchers in SA such as Olisah *et al*. (2018), Akortia *et al*. (2016), and Daso *et al*. (2010) have extensively reviewed on PBDEs.

3.7.1 Biota

The first set of figures on the occurrence of BFRs in living organisms in SA was conducted by Polder *et al*. (2008) who determined PBDE concentrations in eggs of eight assorted Aves (bird) samples obtained from four different locations in the country between November 2004 and March 2005. All the egg samples contained PBDEs and the maximum total concentrations of 61–396 ng/g lw were recorded in “African sacred ibis” eggs obtained from Parys towards the Vaal River. The high PBDE levels in the “sacred ibis” eggs in comparison with other bird breeds was attributed to their scavenging feeding pattern on other animals and litters from waste yards. Their results when compared with other studies from Sweden on perigrine falcon (4450 ng/g, Lindberg *et al*., 2004) and Lake Ontario, USA on herring gull (5309 ng/g, Norstrom *et al*., 2002) were found to be relatively lower, and BDE 47 was the prevalent congener. The values obtained in their work were greater than reported values from Romania (7 ng/g, Covaci *et al*., 2006), and Norway (99 ng/g, Knudsen *et al*., 2005).

Daso *et al*. (2015) studied PBDE concentrations in eggshells of two rare animals “Southern Ground Hornbill (SGH) and Wattled Crane (WC)” obtained from various bird nests in Limpopo and KwaZulu-Natal Provinces, respectively. The PBDEs total sum varied from ND (not detected) to 264000 ng/g lw and 5980–7146000 ng/g lw in the SGH and WC samples sequentially and BDE 47 was the prevalent congener. Their study was aimed at unraveling probable causes of these animals’ extinction, while the possible risks these birds are exposed to through PBDEs were determined by calculating the hazard quotients (HQs). HQs values from 0.58 to 0.94 (SGH) and 27.71 to 45.27 (WC) were obtained. They concluded that the SGHs were prone to little or mild dangers, the WC populace were vulnerable to great dangers, and that exposure of these birds to the reported PBDE concentrations could be responsible for their depopulation and reduction in procreation (Daso *et al*., 2015).

Bouwman *et al*. (2013) researched on levels of certain POPs including BFRs in terrestrial and aquatic bird eggs (Cattle Egret, House Sparrow, Grey Heron, and Southern Masked Weavers) from a rural area within Limpopo Province of SA where malaria was being controlled by dichloro diphenyl trichloroethane (DDT). The maximum mean ΣBDE value of 3.1 ng/g wet mass, wm (equal to 61 ng/g lm) was obtained from Grey Heron eggs and when compared with figures reported by Polder *et al*. (2008), this concentration is low. They concluded that very minute BFRs sway to this location because of lack of big manufacturing companies (Bouwman *et al*., 2013).

3.7.2 Indoor environment (dust/air)

Different studies have been carried out on the interior surroundings (indoor environment) of SA; amongst them is the work of Kefeni and Okonkwo (2012) which reported PBDE levels in office environments in Pretoria. Their study was directed at distinguishing and measuring PBDEs available in workplace dust. Total sum $\sum_6$ BDE determined was 21.6 to 578.6 ng/g dw with BDE 209 being the prevailing congener. Their data were lesser when compared to values obtained in the same office environments from advanced nations. Apart from the reported low concentration, very limited numbers of PBDE congeners (six out of proposed sixteen congeners) were discovered in these office dusts. This is because BFRs were never produced in SA, and they concluded that the PBDEs detected might evaporate from office electronics devices and appliances where the samples were collected (Kefeni and Okonkwo, 2012). Abafe and Martincigh (2015a) studied PBDE levels in indoor fine particles collected from various homes, computer laboratories, and offices. The sum Σ_8PBDE decreased in this pattern: homes > offices > computer laboratories, and the values were 818 to 1710 ng/g. BDE 28 had the lowest values in all the samples, BDE 153 was prevalent among the samples from computer laboratories, while homes and offices contained mostly BDE 209. The concentrations reported in their study for homes and computer laboratories compared well with values obtained from Toronto, Canada by Harrad *et al*. (2008a) and Shanghai, China by Yu *et al*. (2012), but recorded concentrations from Germany, New Zealand, and Vietnam were lower than their own. Nonetheless, the concentrations are not as lofty as reports from the USA and UK where PBDEs are widely utilized as FRs. Their results from homes and offices were significantly greater than values recorded for office environment by Kefeni and Okonkwo (2012), and Kefeni *et al*. (2014) for residential apartments in Pretoria, but they argued that Durban is highly developed and civilized than Pretoria (Abafe and Martincigh, 2015a). Thuresson *et al*. (2012) has linked the dominance of BDE 209 in dust samples to its low volatility. The prevalence of BDE 153 in samples from computer laboratories is worrisome because of its longer half-lives, which can consequently lead to high levels in humans and environment (Sjodin *et al*., 2008).

In an effort to understand the importance of occupational exposure to PBDEs, Abafe and Martincigh (2015b), analysed dust samples collected from one University computer rehabilitation unit and two electronic waste (E-waste) reprocessing stations in Durban, SA for PBDEs. The concentrations in the computer laboratory were lower when compared with e-waste samples, with BDE 209 as the dominant congener (about 76%). Their reported PBDE levels surpassed published concentrations in Guiyu, China (Leung *et al*., 2011), and from similar environment in Vietnam (Tue *et al*., 2013), but much lower than values obtained from e-waste reprocessing stations in Southern China (Labunska *et al*., 2013), and Thailand (Muenhor *et al*., 2010). PBDE concentrations of 123–27530 ng/g reported at one of the E-waste stations were found to be greater than 91–7686 ng/g obtained from the same station after proper cleansing and maintenance, suggesting that regular cleansing of workplace environment can drastically curtail the presence of these pollutants (Abafe and Martincigh, 2015b).

The concentrations of PBDE in the interior dust of 19 individual cars and previously used cars on sale at a trader shop in the city of Durban, was determined by Abafe and Martincigh (2016). The sum of eight

PBDE congeners ($\sum_8$) in the 19 car samples varied from 573 to 11833 ng/g, with BDE- 209 being the dominant congener (about 42% of the total). Their results were lower when compared with 33728 ng/g reported in similar studies in the Czech Republic (Kalachova *et al*., 2012), USA (0.1-322000 ng/g, Lagalante *et al*., 2011), and UK (140–2600000 ng/g, Harrad *et al*., 2008b); but similar to those reported for automobile dust from Portugal (193–22955 ng/g, Cunha *et al*., 2010), Kuwait (165–137000 ng/g, Ali *et al*., 2013), and Pakistan (30–260800 ng/g, Ali *et al*., 2013).

3.7.3 Landfills and wastewater-treatment plant (WWTP)

Odusanya *et al*. (2009) determined BDE concentrations in seepages obtained from five dumping grounds (landfill) in Pretoria, SA. Their study was aimed at discovering the efficacy of liquid-liquid extraction (LLE) method with various dissolving liquids for extracting prevalent PBDE congeners (BDE 28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, and 183) from dumping ground filtrates. The calculated average PBDE levels varied from ND to 9793 pg/L for all the congeners except BDE 209. The predominant congeners were BDE-28, 47, 71, and 77. Two of the aged dumping grounds contained all the analysed PBDE congeners. These reported values were greater than the results obtained from studies conducted in Japan and USA on samples from dumping grounds. Their research revealed that LLE is a good method with petroleum ether as a credible and proven chemical liquid for extracting PBDEs from landfills and they envisaged that these pollutants might percolate in due course into the underground water through the unlined dumping grounds, thereby exposing the public who rely on underground water for their daily water requirements to these pollutants (Odusanya *et al*., 2009).

Concentration of eight BDE congeners was determined in liquid samples of the three functioning dumping grounds (landfills) located in Cape Town by Daso *et al*. (2013b). The total average levels of Σ_8PBDEs were between 0.28 and 2240 ng/L, with BDE 209 being the most prevalent. Their elevated concentrations have distinctly revealed leachate from landfills as crucial PBDE emission sources into the environment, this calls for immediate attention to prevent underground water contamination. Their reported values were higher than results obtained from Pretoria by Odusanya *et al*. (2009), Osaka, Japan (Osako *et al*., 2004), and Minnesota, USA (Oliaei *et al*., 2002). It was reported that the BDE concentrations increased as the rainfall frequency increased (Daso *et al*., 2013b).

Olukunle *et al*. (2015a) reported PBDE levels in liquid runoff (leachates) and silt (sediment) samples from six landfills in Gauteng Province. Total sums of Σ_7PBDEs in leachates were 127 to 3,703 pg/L and sediments (0.8-8.4 ng/g dw), while BDE 209 was the major congener. Maximum values of 2,678 and 3,703 pg/L were recorded in two lined landfills while the lining prevented percolation. PBDE concentrations in their landfill leachate samples were smaller when compared with other studies within SA (2,240 ng/L, Daso *et al*., 2012; 4,009-9,793 pg/L, Odusanya *et al*., 2009) and other developed nations like Canada (1,020–21,300 ng/L, Li *et al*., 2012), Japan (4,000 pg/L, Osako *et al*., 2004), and Shanghai, China (4,000–12,000 pg/L, Huang *et al*., 2013). High concentrations of 3.7–133,000 ng/L were also recorded in leachate samples from municipal solid wastes landfill (MSWL) collected in main towns of Asian nations (Kwan *et al*., 2013). Another study on PBDEs in SA was the work of Daso *et al*. (2012) in which liquid wastes (wastewater) and sewer mud (sewage sludge) taken from a WWTP in Cape Town were scrutinized for eight BDE congeners. The total BDE concentrations for raw water (influent) was 369-4370 ng/L, 19.2-2640 ng/L for secondary effluent, and 90.4-15,100 ng/L for final effluents, while the results for sludge samples varied from 13.1 to 652 ng/g dry weight (dw). In both matrices, BDE 47 and 209 were the dominant congeners (Daso *et al*., 2012). Their results on total PBDE concentrations in WWTPs were compared with other studies across the globe and presented in Table 3.2. Except for the work of Cristale and Lacorte (2015) in which PBDEs were not detected in effluents from the studied WWTPs located near Barcelona, North-East of Spain, the presence of PBDEs in the other treated effluents and sewage sludge revealed that most of the WWTPs were inadequate for the removal of these contaminants from these matrices; hence, the application of wastewater and sewage for irrigation and other agricultural or industrial purposes could lead to health hazards in human beings. They attributed the reported low levels to the replacement of PBDEs as flame retardants with other novel brominated flame retardants (NBFRs) which have similar properties as PBDEs (Cristale and Lacorte, 2015).

Table 3. 2 Comparisons of PBDE concentrations in wastewaters (ng/L) and sewage sludge (ng/g dw) with other studies across the globe

Location/Country	Sample type	WWTP Number	∑PBDE (ng/g)	References
Africa				
South Africa	Influent/effluent	1	19.2- 15,100	Daso *et al*. (2012)
	Sludge	1	13.1-652	Daso *et al*. (2012)
North America				
USA	Sludge	3	1071-3730	North (2004)
USA-Mexico border	Influent/effluent	4	ND-342	Rocha-Gutierrez and Lee (2013)
Canada	Influent/effluent	1	36-265	Song *et al*. (2006)
	Sludge	1	1626-2698	Song *et al*. (2006)
Canada	Influent/effluent	20	3-1000	Kim *et al*. (2013)
Europe				
Spain	Sludge	14	790.3-18209.3	Fabrellas *et al*. (2004)
Spain	influent/effluent	5	ND	Cristale and Lacorte (2015)
Sweden	Sludge	22	ND-840	Oberg *et al*. (2002)
Germany	Sludge	11	109.6-2503	Knoth *et al*. (2007)
Asia				
China	influent/effluent	2	0.867-2445.5	Peng *et al*. (2009)
	Sludge	2	158.6-22990.2	Peng *et al*. (2009)
Hong Kong, SAR	influent/effluent	4	1-254	Deng *et al*. (2015)
Kuwait	Sludge	3	8.1-1623	Gevao *et al*. (2008)

WWTP = Wastewater treatment plant, ND = Not detected

3.7.4 Aquatic environment

La Guardia *et al*. (2013) studied PBDE levels in sediments of Durban Bay (DB) and streams along the coast of “eThekwini” urban district in KwaZulu-Natal Province of SA; their work described Σ_{11}PBDE levels (ND to 46300 ng/g) with the most common congener being BDE 209 (about 93% of total concentrations). Their reported levels were greater than levels found in the sediment of Zhujiang and Dongjiang rivers, the two main rivers of the Pearl River Delta (PRD), which flow through China, the world’s leading electronics manufacturer (Mai *et al*., 2005), but when compared with other studies on aquatic environments from another section of the globe, PBDE levels in sediment from DB could be considered to be high. They stated that the factors responsible for these high levels were the Bay’s unique hydromorphology and urban runoff caused by three named streams (Umbilo, Umhlatuzana, and Amanzimnyama) that infiltrate DB from the southern part after passing across densely populated and manufacturing zones of the large city of Durban (La Guardia *et al*., 2013). PBDE concentrations in sediments gathered from six rivers recognized as pollution hotspots due to anthropogenic activities in

Gauteng Province were determined by Olukunle *et al*. (2015). The rivers include “Alberton, Fouriespruit (Meyerton), Clarington, Lowerklip, Jukskei, and Vaal Rivers”. Mean concentrations of 0.82–44 ng/g (dw) were reported in their work on eight $\sum_8$ PBDEs with a total sum of 114 ng/g, which was lower than values obtained from Fuhe River of China (300.7 ng/g dw, Hu *et al*., 2010), industrialized bay of Korea (2.03 – 2253 ng/g dw, Moon *et al*., 2007b), Niagara River of USA (0.72–148 ng/g dw, Samara *et al*., 2006), and Spain (2.7-136 ng/g dw, Eljarrat *et al*., 2005), but greater than values recorded from Da-an Rivers in Taiwan (0.17 ng/g, Chen *et al*., 2013), and Hong Kong SAR, China (1.7 – 53.6 ng/g dw, Liu *et al*., 2005). Maximum concentration (44 ng/g) was observed in Jukskei River (about 50 km long), the third largest river in Johannesburg, which receives effluent from manufacturing companies and large volume of runoff from different sources, while the least value was from Vaal River. The prevalent congeners were BDE-47, 99, 100, and 153 (Olukunle *et al*., 2015a).

Sediments of two river-systems (Diep and Kuils Rivers) in Cape Town City were collected between June 2010 and March 2011 and evaluated for PBDE by Daso *et al*. (2016). The Σ_8PBDEs in “Diep River” ranged from 1.33 to 59.3 ng/g dw and 5.32 to 239 ng/g dw in “Kuils River”. BDE 209 occurred as the prevalent congener in “Diep River” while BDE 47 was the major congener in “Kuils River”. Discharges from WWTP and wastewater encroachment from unofficial housings situated in various areas within Cape Town were the main cause for the upriver pollution (Daso *et al*., 2016). Comparing their results for total PBDE levels in river sediments with previous reports across the globe, it was discovered that their values were lower than results obtained from Zhujiang and Dongjiang Rivers in China (27.12-3624.61 ng/g and 23.51-3018.57 ng/g respectively, Mai *et al*., 2005), Lake Shihwa of Korea (0.98-18743 ng/g, Moon *et al*., 2012a), but greater than reported results from Pangani River Basin, Tanzania (0.038-2.18 ng/g, Hellar-Kihampa *et al*., 2013), and Lake Maggiore, Italy (0.06-27.13 ng/g, Mariani *et al*., 2008). Their concentrations compared well with values recorded from Cinca River, Spain (2.5-74 ng/g, Eljarrat *et al*., 2004).

Table 3. 3 Reported levels of PBDE in sediment samples across the globe

Locations	Sample Matrix	Concentration (ng/g)	Extraction Method	Prevalent Congener	Instrument	References
South Africa						
EThekwini	sediment	ND- 6,300	ASE	BDE 209	UPLC-APPI-MS	La Guardia *et al*. (2013)
Gauteng	river sediment	0.8-114	soxhlet	BDE 47, 99, 100, 153	GC-MS	Olukunle *et al*. (2015a)
Gauteng	landfill sediment	0.8-8.4	soxhlet	BDE 209	GC-MS	Olukunle *et al*. (2015a)
Cape town	sewage sludge	13.1-652	soxhlet	BDE 209	GC-ECD	Daso *et al*. (2012)
Eastern Cape	sediment	0.08-130.21	soxhlet	BDE 17	GC-µECD	Olisah *et al*. (2020)
Indian Ocean	Ocean sediment	62–260	soxhlet	BDE 209	GC-MS	Oiu *et al*. (2020)
Asia						
Korea	sediment	2.03-2253	soxhlet	BDE 209	HRGC-HRMS	Moon *et al*. (2007b)
Japan	sediment	0.06-2.3	solvent	BDE 209	GC-MS	Minh *et al*. (2007)
Taiwan	sediment	0.17-261	soxhlet	BDE 209	HRGC-MS	Chen *et al*. (2013)
West Africa						
Ghana	sediment	0.019-0.07	soxhlet	BDE 47	GC-ECD	Essumang *et al*. (2018)

ND = Not detected, DCM= Dichloromethane; GC-QMS = Gas Chromatograph coupled with a triple Quadrupole Mass Spectrometer. UPLC-APPI-MS= Ultra-performance liquid chromatograph/atmospheric pressure photoionization, tandem mass spectrometer, ASE = Accelerated solvent extraction, HRGC-HRMS = High resolution gas chromatograph- high resolution mass spectrometer

Table 3. 4 Reported levels of PBDE in liquid samples across the globe

Locations	Sample Matrix	Concentration (ng/L)	Extraction Method	Prevalent Congeners	Instrument	References
South Africa						
Gauteng	river water	below detection limit	LLE	-	GC-MS	Olukunle *et al*. (2015a)
Gauteng	landfill leachate	0.127–3.702	LLE	BDE 209	GC-MS	Olukunle *et al*. (2015a)
Pretoria	landfill leachate	ND- 9.793	LLE	BDE 28,47	GC-ECD	Odusanya *et al*. (2009)
Cape town	landfill leachate	0.28- 2,240	LLE	BDE 209	GC-µECD	Daso *et al*. (2012)
Cape town	WWTP effluent	19.2- 15,100	LLE	BDE 209	GC-µECD	Daso *et al*. (2012)
West Africa						
Ghana	river water	0.04-0.17	LLE	BDE 99, 100	GC-ECD	Essumang *et al*. (2018)
Nigeria	stream water	30-450	LLE	BDE 153	GC-MS	Olutona *et al*. (2017)
Asia						
China	seawater	15.4–65.5	SPE	BDE 209	GC-MS	Wang *et al*. (2017)
China	river water	0.11–4.48	SPE	BDE 47, 99	GC-MS	Liu *et al*. (2018)
Japan	raw landfill leachate	ND-4	LLE	-	HRGC-HRMS	Osako *et al*. (2004)
North America						
Canada	WWTP influent	21-1000	LLE	BDE 209	HRGC-HRMS	Kim *et al*. (2013)
Canada	WWTP effluent	3-270	LLE	BDE 209	HRGC-HRMS	Kim *et al*. (2013)

LLE = Liquid-liquid extraction, SPE = Solid phase extraction, ND = Not detected

Table 3. 5 Reported levels of PBDE in egg samples across the globe

Locations	Sample Matrix	Concentration (ng/g)	Extraction Method	Prevalent Congeners	Instrument	References
South Africa						
Gauteng	bird egg	2.3- 396	LLE	BDE-47	GC-MS	Polder *et al*. (2008)
Limpopo Province	eggshell of SGH	ND -0.264	ultrasonic-assisted extraction technique	BDE-47	GC–EI-MS	Daso *et al*. (2015)
KwaZulu-Natal	eggshell of WG	0.00598–7.146	ultrasonic-assisted extraction technique	Lower congeners	GC–EI-MS	Daso *et al*. (2015)
Europe						
Northern Norway	herring gulls eggs	14.4-183	Ultrasonic technique	BDE 47	GC-MS	Knudsen *et al*. (2005)
Northern Norway	Atlantic puffins eggs	6.4-43.6	Ultrasonic technique	BDE 47	GC-MS	Knudsen *et al*. (2005)
Northern Norway	Black-legged Kittiwakes	7.3-112	ultrasonic technique	BDE 47	GC-MS	Knudsen *et al*. (2005)

SGH = Southern Ground-Hornbill, KNP = Kruger National Park, WC = Wattled Crane, DCM = dichloromethane, LLE = Liquid-liquid extraction

Table 3. 6 Reported levels of PBDE in dust samples across the globe

Locations	Sample Matrix	Concentration (ng/g)	Extraction Method	Prevalent Congener	Instrument	References
South Africa						
Pretoria	office dust	21.6-578.6	soxhlet	BDE 209	GC-MS	Kefeni and Okonkwo (2012)
Durban	office dust	1520	ultrasonication	BDE 209	GC-MS	Abafe and Martincigh (2015a)
Durban	house dust	1720	ultrasonication	BDE 209	GC-MS	Abafe and Martincigh (2015a)
Durban	laboratory dust	818	ultrasonication	BDE 153	GC-MS	Abafe and Martincigh (2015a)
Durban	automobiles dust	573-11,833	ultrasonication	BDE 209	GC-MS	Abafe and Martincigh (2016)
West Africa						
Nigeria	indoor dust	bdl-52,000	PLE	BDE 209	GC-MS	Harrad *et al.* (2016)
Nigeria	car dust	159-736	ultrasonication	BDE 209	GC-EIMS	Olukunle *et al.* (2015b)
America						
US	house dust	320-29,000	PLE	BDE 209	GC-MS	Sjodin *et al.* (2008)
Oceania						
Australia	house dust	500-13,000	PLE	BDE 209	GC-MS	Sjodin *et al.* (2008)
Europe						
Germany	house dust	6-3748	PLE	BDE 209	GC-MS	Fromme *et al.* (2014)
Sweden	Indoor dust	6.1-1400	Ultrasonication	BDE 209	GC-MS	Thuresson *et al.* (2012)
Great Britain	house dust	950-54,000	PLE	BDE 209	GC-MS	Sjodin *et al.* (2008)
Germany	house dust	17-550	PLE	BDE 209	GC-MS	Sjodin *et al.* (2008)

PLE = Pressurized liquid extraction

Table 3. 7 Reported levels of PBDE in human breastmilk samples across the globe

Locations	Sample Matrix	Concentration (ng/g) lw	Extraction Method	Prevalent Congener	Instrument	References
South Africa						
Limpopo	breastmilk	0.70-6.3	LLE	BDE 209	GC-ECD	Darnerud *et al*. (2011)
East Africa						
Uganda	breastmilk	0.59-8.11	Vortex	BDE 209	GC-MS	Matovu *et al*. (2019)
West Africa						
Ghana	breastmilk	0.86–18	solvent extractor	BDE 47	GC-MS	Asante *et al*. (2011)
Europe						
Denmark	breastmilk	1.22-111.1	LLE	BDE 47	GC-HRMS	Antignac *et al.* (2016)
Finland	breastmilk	1.47-19.0	LLE	BDE 47	GC-HRMS	Antignac *et al.* (2016)
Sweden	breastmilk	0.56-7.72	liquid-gel partitioning	BDE 47	GC-MS	Guvenius *et al*. (2003)
Norway	breastmilk	0.48-82	LLE	BDE 47	GC-MS	Thomsen *et al*. (2010)
Greece	breastmilk	0.32-13	soxhlet	BDE 47, 153	GC-MS	Dimitriadou *et al*. (2016)
Belgium	breastmilk	2.0-6.4	SPE	BDE 47	GC-MS	Roosens *et al*. (2010)
North America						
USA	breastmilk	6.2-419	LLE	BDE 47	HRGC-HRMS	Schecter *et al*. (2003)
Canada	breastmilk	2.9-10	sonication	BDE 47	GC-MS	Siddique *et al.* (2012)
Asia						
China	breastmilk	8.89–457	soxhlet	BDE 47	HRGC-HRMS	Leung *et al*. (2010)
Taiwan	breastmilk	3.59±1.07 (mean±SD)	sonication	BDE 153	HRGC-HRMS	Chao *et al*. (2010)

3.8 PBDEs debromination and pollution control measures

Studies have validated the pervasiveness of POPs (including PBDEs) in our environment, with potential to cause health problems and change our ecosystem. If this situation continues, our planet Earth will be endangered, and there may be threat to lives in the future (Alharbi *et al*., 2018). In view of the impending danger, individuals, researchers, and government at all levels need to curtail their environmental pollution. This is achievable by adopting proper control methods and remediation techniques. According to Stockholm Convention held on May 22, 2001, the first control measure is reduction and/or elimination of their production and application (UNEP, 2010). Many nations of the world have adopted the Convention; United States of America and other developed nations have barred their manufacturing and application (Alharbi *et al*., 2018).

The next strategy is the development of appropriate remediation techniques for their removal. PBDEs persistence in the environment is due to their low reactivity, and as an organic pollutant cannot be easily degraded. Researchers have developed several processes; zerovalent iron (ZVI) reduction (Zhuang *et al*., 2010; Keum and Li, 2005), photocatalytic reduction (Guo *et al*., 2019; Lei *et al*., 2016; Sun *et al*., 2009), electrochemical reduction (Liu *et al*., 2014), thermal process (Li *et al*., 2017), biodegradation (Chen *et al*., 2018b), and many more for their breakdown and removal from the environment. Soderstrom *et al.* (2004) showed in an experiment that photolytic debromination of decabromodiphenyl ether (BDE 209) leads to the production of more bioactive and stable lower brominated BDEs (tetra- to nona-BDEs). The time evolution experiment for BDE 209 photodegradation was investigated in different matrices using simulated and natural sunlight. BDE 209 was photolytically volatile and formed debromination products in all studied matrices. Studies have reported other PBDEs debromination procedures; Wei *et al*. (2013) investigated photolytic debromination pathways for 13 PBDEs in hexane under the sun for 64 hours. Sum of 180 PBDE congeners were tested and 74 BDE debromination products were measured. Xu *et al*. (2020) recently synthesized a new palladized zero-valent zinc (Pd/ZVZ) material and compared its capacity with zero-valent zinc (ZVZ) in debrominating PBDE congeners. The plated Pd improved the degradation rate of PBDEs which was unaffected by pH and extent of bromination.

In summary, the reductive debromination of high-brominated BDEs (for instance, BDE 209) yield less reactive but more toxic and stable low-brominated BDEs (Granelli *et al*., 2012; Sun *et al*., 2009; Keum and Li, 2005), but a gradual debromination process is preferable (Guo *et al*., 2019).

Conclusion

This review chapter and other related studies have affirmed that PBDEs are pervasive in SA environment. They find their way into the environment through various routes among which have been described as; electrical or electronic equipment waste (EEEW), wastewater treatment plants (WWTP), landfill sites, soil erosion, emissions from used vehicles, and indoor environment. Studies have indicated WWTPs as a major route through which these compounds get into the surroundings, which make the reutilization of effluent and sludge obtained from WWTPs in irrigation practices and other agricultural purposes pose danger to humans and other biota along the food webs. In addition, the occurrence of these emerging pollutants in treated effluent showed that some of the WWTPs are inept in treatment of the wastewater. Humans become exposed to these pollutants through ingestion of contaminated foods, water or dust. PBDE concentrations in certain environmental matrices in SA were compared with global studies. PBDE levels in sediment samples from aquatic environment and liquid samples from WWTPs or landfills were higher than data from other nations. PBDE concentrations in dust samples from homes, automobiles, computer laboratories, and offices were more than reported values from other SA environmental matrices, but lower when compared with dust samples from other countries. This revealed that inhabitants of SA become exposed to these pollutants mostly through dust particles via cars and other electrical appliances they used in the indoor environment. BDE-209 (2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether), which can be photodegraded into lower brominated congeners under certain conditions is the prevalent BDE congener in most of the studied matrices. Not much research has been published on foods and biological samples from humans in SA; the only reported data on human was below those obtained from other regions. Hence, the student suggested that more comprehensive studies relating to PBDE concentrations in human samples (breast milk, blood, placenta, etc.), drinking water, and foods should be carried out to elucidate properly their distribution in SA environment.

Since environmental pollution is a global issue, there is need for scientists all over the world to develop efficient, fast, ecologically friendly, and economically cheap remediation techniques for removing organic pollutants (PBDEs inclusive) from our environment. Governments at all levels should prohibit their manufacturing and application in consumer products and provide financial support for projects related to remediation processes.

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CHAPTER FOUR

Methods validation for polychlorinated naphthalenes and polybrominated diphenyl ethers analysis in water and sediment samples

Abstract

Chemical analysts have employed different methods for determining polychlorinated naphthalenes (PCNs), and polybrominated diphenyl ethers (PBDEs) in various environmental samples, using gas chromatograph (GC) coupled with various types of detectors such as micro electron capture detector (μECD), mass spectrometer (MS), among others. The use of SPE method for the determination of these two pollutants (PCNs and PBDEs) in water samples and the application of soxhlet extraction method for their investigation in sediment samples are verified in this chapter. The extraction methods competencies were appraised by spiking each sample with mixed calibration standard solutions. Dichloromethane (DCM), and hexane/acetone (3:1) mixture were utilized for extracting PCNs and PBDEs respectively from the pure sand samples, while ethyl acetate, hexane and acetone (4:1, v/v) mixtures were used to elute PCNs and PBDEs respectively from water samples. Average PCNs recoveries were 66-95% and 70-88% from water and pure sand. The mean recoveries of PBDEs from water was 73-87%, and 78-96% from sand. Surrogate standards recoveries in water and pure sand varied from 63-84% and 61-92% respectively. The linearity of the two methods fell within the acceptable range of ≥ 0.990. These validated methods can be applied in the evaluation of these selected organic pollutants in water and sediment samples.

Keywords: Surface water, pure sand, surrogate standards, validation, calibration, recoveries

4.1 Introduction

Validation of an analytical technique is imperative in monitoring chemical assays. Method validation is an approved procedure that shows that an analytical technique is adequate for its predetermined objective (Tavazzi *et al.*, 2016). Several studies have applied traditional liquid-liquid extraction (LLE) method using separatory funnel with different organic solvents including acetone, hexane, dichloromethane (Pei *et al.*, 2018; Olutona *et al.*, 2017; Mahmood *et al.*, 2014; Marti and Ventura, 1997) and solid-phase extraction (SPE) method (Olisah *et al.*, 2020a; Yang *et al.*, 2015; Marti and Ventura, 1997) to extract persistent organic pollutants (POPs) from water samples. The LLE method has some drawbacks; strenuous, requires excess use of solvents and time for extraction when contrasted with SPE which requires less attention, time and solvents, but the SPE is occasionally used because it is costlier than LLE (Adeniji *et al.*, 2017; Johnson, 2011). Solid environmental matrices including sediment samples are commonly extracted using soxhlet extractor following its high recovery and cheap cost, but long experimental time and usage of toxic solvents are required to accomplish extraction (Olisah *et al.*, 2020b; Dat *et al.*, 2019; Mahmood *et al.*, 2014). The excessive use of these extraction solvents (most organic solvents are toxic) could lead to high exposure risk and liquid waste generation (Cabaleiro *et al.*, 2013).

To overcome some of the setbacks arising from the use of these traditional extraction methods, researchers have developed and employed eco-friendly and automated techniques; microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), ultrasonication, accelerated solvent extraction (ASE) (Sibiya *et al.*, 2019; Shao *et al.*, 2018; Xiong *et al.*, 2016; Zhang *et al.*, 2015; Horii *et al.*, 2004), among other techniques for extracting these pollutants from environmental samples.

The pollution of our environment by POPs has raised global issues due to their persistency, volatility, and toxicity. They may occur at trace levels in water because of their excellent lipophilic nature; hence, the analytical procedures employed for their evaluation should be sensitive enough to measure at trace-levels (CICAD, 2001).

This chapter is aimed at validating existing analytical methods for PCNs and PBDEs extraction from water and sediment samples using SPE and soxhlet extractor respectively followed by instrumental analysis with GC-µECD.

4.2 Materials and methods

4.2.1 Solvents, standards and other consumables

GC grade solvents; acetone, dichloromethane (DCM), ethyl acetate, n-hexane, and isooctane were bought from Sigma-Aldrich (Merck Pty Ltd, SA). Anhydrous sodium sulphate (AR grade), pure sand (silicon dioxide, 50-70 mesh particle size), silica gel (70–230 mesh), copper fine powder, and alumina were also bought from Sigma-Aldrich, while C_{18} cartridges were purchased from Promolab Pty Ltd (Separations, SA). Surrogate standards (2, 4, 5, 6-tetrachloro-m- Xylene, TCMX and decachlorobiphenyl, PCB 209) were procured from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). PCN standard mixture (PCN-MXA) containing eight congeners (2, 6, 13, 28, 52, 66, 73 and 75) and PBDE standard containing six BDE congeners (BDE 17, 47, 66, 100, 153, and 183) at concentrations of 5000 µg/L were bought from Wellington's laboratory, Inc. (Guelph, Ontario, Canada). The PCN mixture contained the following PCN congeners: 2-monoCN (CN 2), 1,5-diCN (CN 6), 1,2,3-triCN (CN 13), 1,2,3,5-tetraCN (CN 28), 1,2,3,5,7-pentaCN (CN 52), 1,2,3,4,6,7-hexaCN (CN 66), 1,2,3,4,5,6,7-heptaCN (CN 73) and octachloronaphthalene (CN 75). The congener represents each of PCN homologue groups. The PBDE standard solutions contained 2, 2´, 4-triBDE (BDE 17), 2, 2´, 4, 4´- tetraBDE (BDE 47), 2, 3´, 4, 4´-tetraBDE (BDE 66), 2, 2´, 4, 4´, 6 - PentaBDE (BDE 100), 2, 2´, 4, 4´, 5, 5´ - HexaBDE (BDE 153), and 2, 2´, 3, 4, 4´, 5´, 6 - HeptaBDE (BDE 183).

4.2.2 Calibration of equipment

Standard PCN and PBDE solutions required for equipment calibration (external) were prepared at concentrations between 5-120 µg/L by diluting stock solution in isooctane (Castells *et al*., 2008) to obtain eight calibration points for both pollutants (PCN and PBDE).

4.2.3 Extraction and recovery of PCN congeners from deionized water

Deionised water collected into properly cleaned 1 Litre amber bottles and pure sand (silicon dioxide) were used for the method validation. The extraction and recovery of PCN from spiked deionised water was achieved by the method of Marti and Ventura (1997). Solid phase (Phenomenex—Strata C_{18}, 55 µm, 70A; 500 mg/6 mL tubes) cartridges were preconditioned with 10 mL of methanol and 10 mL of deionized water. About 500 mL of deionized water in duplicate was spiked with 4 mL of 100 µg/L mixed working standards solution. The water samples were passed through the cartridges under a vacuum. Cartridges were set aside for few hours and later dried with nitrogen gas (99.9% purity) to remove any drops of water. The extract was eluted with 20 mL ethyl acetate in the cartridges; the eluate was evaporated and reconstituted with 1.5 mL of isooctane before instrumental analysis. Another 500 mL deionized water was extracted in like manner without the working standards solution to serve as blank (Marti and Ventura, 1997).

4.2.4 Extraction and recovery of PCNs from pure sand (PS)

Ten grams (10 g) of the PS was soxhlet-extracted in duplicate with 200 mL DCM after adding 4 mL of 100 µg/L mixed working standards solution and fine copper powder to prevent interference from elemental sulphur. The extract was evaporated with rotary evaporator, purified on silica alumina column, eluted with hexane, evaporated to dryness, redisolved with isooctane before instrumental analysis. Another 10 g of the PS was extracted the same way without the working standards solution as blank (Mahmood *et al.*, 2014).

4.2.5 Extraction and analysis of PBDE in water

Deionized water (500 mL) was accurately measured in duplicate, spiked with known concentration and volume (4 mL of 100 µg/L) of the working standards solution. C_{18} cartridges were preconditioned with 5 mL each of n-hexane, acetone and deionised water in succession. The water sample was passed through the cartridges under vacuum with a flux speed of 10 mL/min. Thereafter, cartridges were set aside for few hours and later dried with nitrogen gas to remove any traces of water. The extract was eluted with 10 mL hexane and acetone (4:1, v/v) mixture. Another 500 mL deionised water was extracted the same way without the working standards solution as blank. The extract was concentrated with nitrogen gas and the residue was reconstituted with 1.5 mL of ethyl acetate before instrumental analysis on GC-µECD (Barco-Bonilla *et al.*, 2015; USEPA, 2010).

4.2.6 Extraction and analysis of PBDE in PS

Exactly 10 g of the PS was soxhlet-extracted in duplicate with 200 mL hexane/acetone mixture (3:1 v/v) after adding working standards solution and fine copper powder to prevent interference from elemental sulphur. Another 10 g of the PS was extracted the same way without the working standards solution. After the expiration of the extraction time, the extract was evaporated with rotary evaporator, purified in glass column filled with glass wool, acidified silica gel (40% concentrated sulphuric acid, w/w), anhydrous sodium sulphate, copper powder and conditioned with hexane. The extract was eluted with 15 mL hexane and 10 mL DCM, the eluate was concentrated to near dryness with a rotary evaporator and further by a gentle nitrogen stream. The final extract was re-solubilized with 1.5 mL isooctane before GC-µECD analysis (Covaci *et al.*, 2005).

4.2.7 Instrumental analysis

The quantification of eight PCN congeners and six PBDE congeners contained in the mixed standards was determined with an Agilent 7820A gas chromatograph GC (Agilent technologies, Santa Clara, CA, USA) coupled with micro-electron capture detector (μ-ECD) (model—G2397AE, Santa Clara, CA, USA), and fitted with an Agilent HP-5 column (30 m long × 0.32 mm ID × 0.25 µm film thickness), while the identification of the PBDE and PCN congeners was performed using GC-MS (Daso *et al*., 2016; Mahmood *et al.*, 2014). Compounds were identified by measuring retention times of the individual congeners in the standards. The chromatographic conditions are as shown in Table 4.1.

Table 4. 1 Gas chromatograph conditions

	PBDE	**PCN**
Gas chromatograph	7820A Agilent Technology	7820A Agilent Technology
Injection volume (µL)	1	1
Injection mode	Splitless	Splitless
Inlet temperature (ºC)	300	300
Oven		
Initial oven temperature (ºC)	100	80
Initial oven hold (min)	1	0,5
Final hold (min)	10	10
Final temperature (º C)	310	270
Total ramp rate (º C/min)	17	24
Run time (min)	61	47.5
Column		
Type	Agilent HP-5	Agilent HP-5
Length (m)	30	30
Diameter (mm)	0.320	0.320
Film thickness (µm)	0.25	0.25
Carrier gas	Helium	Helium
Column flow rate (mL/min)	3	2
µECD		
Temperature (º C)	325	325
Makeup gas	Nitrogen	Nitrogen
Makeup flow (mL/min)	20	10

Data were generated and processed by the Agilent Chemstation software incorporated into the instrument. For both PCNs and PBDEs, the carrier and makeup gas were helium and nitrogen respectively, while the injection volume was 1 µL. For PCNs analysis, initial oven temperature was fixed at 80°C for 0.5 min, increased to 160°C at a rate of 15°C/min, then raised to 240°C at a rate of 3°C/min and finally increased to 270°C at a rate of 6°C/min for 10 min, the total runtime was 47.5 min. The carrier gas flow rate was set at 2 mL/min (Mahmood *et al.,* 2014). For PBDEs analysis, the oven temperature commenced at 100°C for 1 min, increased to 190°C at a rate of 10°C/min, then increased to 255°C for 0.5 min at a rate of 5°C/min and finally raised to 310^{o}C for 10 min at a rate of 2^{o}C/min. The total runtime was 61 min, while the flow rate of the carrier gas was set at 3 mL/min (Wang et al., 2016).

4.2.8 Quality assurance and quality control (QA/QC)

The quality of analytical data was ascertained by adopting various laboratory QA and QC methods; procedural blanks, surrogate standards, limits of detection, calibration curves, and quantification. Working standard solutions for both pollutants were prepared from their stock solutions in the range of 5–120 µg/L using isooctane as diluting solvent. Instrument was routinely calibrated with different concentrations of prepared calibration standard solutions. Glasswares were properly washed with liquid washing soap, rinsed with tap water, deionized water, methanol, acetone and finally oven dried. All the solvents used for analysis were of GC or analytical grade. The reported data were not corrected with the blanks (Barhoumi *et al*., 2019).

4.3 Results and discussion

4.3.1 Calibration curves

Linear calibration curves were obtained for the two pollutants with their correlation coefficients varying from 0.9984-0.9993 for PCNs (Table 4.2) and from 0.9967-0.9989 for PBDEs (Table 4.3). The overall linearity recorded was within the acceptable range of $R^2 \geq 0.990$ (Rubirola *et al*., 2019). The chromatograms are found in Figures 4.1 and 4.2, while the individual calibration curves are found in Appendix 1.

Table 4. 2 Linearity of the PCNs and surrogate standards

PCNs	Mean retention time (min)	Regression equations	R^2	LOD (µg/L)	LOQ (µg/L)	RSD (%)
CN 2	6.4126±0.0005	y = 18.907x + 60.798	0.9993	0.214	0.647	2.91
CN 6	8.5024±0.0005	y = 82.938x + 260.7	0.9995	0.052	0.157	3.19
CN 13	11.9518±0.0007	y= 1168.1x-985.2	0.9989	0.013	0.040	3.37
CN 28	14.9366±1.2060	y= 355.91x-62.993	0.9989	0.013	0.039	3.94
CN 52	18.6169±0.0010	y= 431.22x+238.71	0.9982	0.009	0.028	4.10
CN 66	24.1184±0.0022	y= 628.96x-164.05	0.9986	0.007	0.020	4.32
CN 73	30.4943±0.0018	y= 908.28x-738.88	0.9988	0.007	0.020	4.57
CN 75	35.3656±0.0022	y= 996.02x-1198.5	0.9984	0.007	0.020	4.23
*TCMX	9.2659±0.0006	y= 928.06x-1046.7	0.9991	0.003	0.010	2.93
*PCB 209	36.6289±0.0012	y= 1169.4x-434.85	0.9989	0.002	0.006	1.56

*Surrogate standards, min = minutes, R^2 = correlation coefficients

Table 4. 3 Linearity of the PBDEs and surrogate standards

PBDEs	Mean retention time (min)	Regression equations	R^2	LOD (µg/L)	LOQ (µg/L)	RSD (%)
BDE 17	15.399±0.008	y= 738.75x-820.2	0.9989	0.004	0.011	1.92
BDE 47	19.444±0.009	y= 850.01x-1709.3	0.9979	0.004	0.013	2.54
BDE 66	19.940±0.010	y= 792.07x-1679.4	0.9976	0.005	0.015	2.82
BDE 100	22.209±0.009	y= 908.61x-1863.5	0.9979	0.005	0.015	3.04
BDE 153	26.945±0.013	y= 431.22x+238.71	0.997	0.008	0.024	4.90
BDE 183	31.802±0.015	y= 881.77x-1953.6	0.9967	0.013	0.040	6.33
*TCMX	8.384±0.004	y= 693.72x-1609.2	0.9982	0.004	0.012	3.64
*PCB 209	24.501±0.010	y= 1196.1x+1866	0.9969	0.002	0.007	1.86

*Surrogate standards, min = minutes, R^2 = correlation coefficients, ARt = Average retention time (min = minutes)

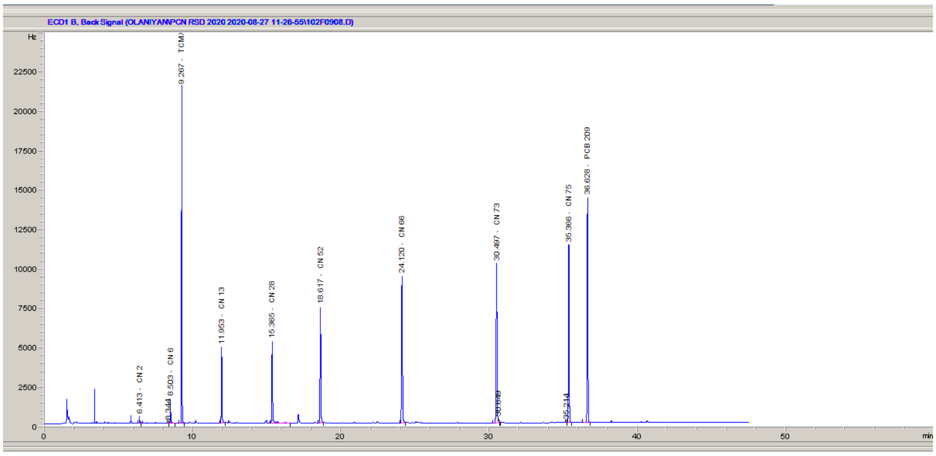

Figure 4. 1 Calibration peaks for PCNs and surrogate standards (TCMX and PCB 209)

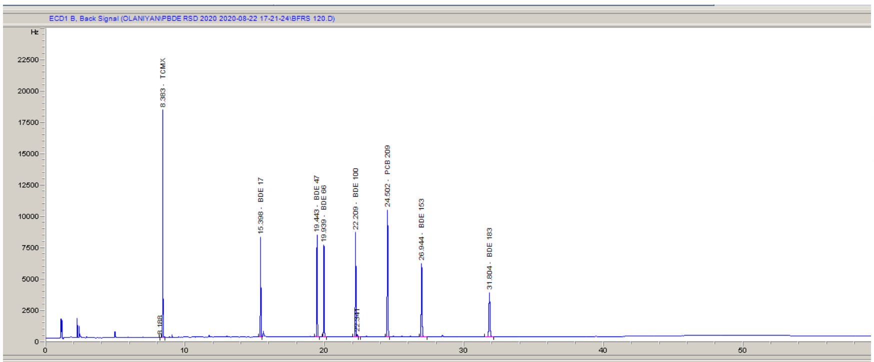

Figure 4. 2 Calibration peaks for PBDE congeners and surrogate standards (TCMX and PCB 209)

4.3.2 Limit of detection, limit of quantification and relative standard deviation

The instrument sensitivity and precision were determined in terms of limit of detection (LOD), limit of quantitation (LOQ), and relative standard deviation (RSD). These were measured after eight-repeated running (injections) of a selected concentration (40 µg/L, median value) of the calibration standard solution on the instrument. LOD and LOQ were calculated using:

$$\text{LOD} = 3.3*(\text{SD}/\text{S})$$

$$\text{LOQ} = 10*(\text{SD}/\text{S})$$

Where, SD is the standard deviation of the instrument responses, S is the slope of the calibration graph (curve) for each congener and surrogate. RSD was estimated from the relation:

$$\text{RSD} = 100*(\text{SD}/\text{M})$$

Where, M is the mean of the instrument responses (Babalola and Adeyi, 2018; Swartz and Krull, 2012).

The results in Tables 4.2 and 4.3 showed that LOD values varied from 0.007 to 0.214 µg/L for PCNs and 0.004-0.013 µg/L for PBDEs. LOQ values were 0.020–0.647 µg/L and 0.011–0.040 µg/L for PCNs and PBDEs, respectively. RSD was 2.91-4.57% for PCNs and 1.92-6.33% for PBDEs.

4.3.3 Recovery of PCNs and PBDEs from spiked water and PS samples

The recovery of PCN congeners and surrogate standards from deionised water and PS samples spiked with mixed calibration standards solution are depicted in Table 4.4. Recovery of the eight PCN congeners in water and PS varied from 66.7-95.4% and 70.2-88.8% respectively. Castells *et al*. (2008) recorded similar average percentage recoveries (76%-98%) for individual PCN congeners in sediment samples. Surrogate standard recovery for PCN ranged between 65.4-84.4% and 61.5-77.7% in water and PS samples, respectively.

% Recovery = (B – A)/C×100

Where, A = Concentration in unspiked samples

B = Concentration in spiked samples

C = Concentration of added standard

The recovery of PBDE congeners and surrogate standards from deionised water and pure sand samples spiked with mixed calibration solution are displayed in Table 4.5. Based on the results, the percentage recovery of PBDE congeners varied from 73.8 to 87.5% and 78.2 to 96.2% in water and PS specimens. The surrogate standards recovery for PBDEs in water and PS varied from 63.7-70.9% and 61.2-92.4%. The PBDEs percentage recovery in a study by Olisah *et al*. (2020a) recorded 79-88%.

Table 4. 4 Percentage recoveries of PCN congeners and surrogates in water and sand

PCN congeners	% Mean recovery ±SD in water	% Mean recovery ±SD in pure sand
2-Monochloronaphthalene (CN 2)	66.69±0.07	72.82±0.51
1, 5- Dichloronaphthalene (CN 6)	75.73±1.56	70.16±0.35
1, 2, 3- Trichloronaphthalene (CN 13)	66.85±0.06	77.53±0.40
1, 2, 3, 5- Tetrachloronaphthalene (CN 28)	95.40±6.02	71.59±0.02
1, 2, 3, 5, 7- Pentachloronaphthalene (CN 52)	93.75±0.24	70.39±0.06
1, 2, 3, 4, 6, 7- Hexachloronaphthalene (CN 66)	79.48±0.41	81.07±0.06
1, 2, 3, 4, 5, 6, 7- Heptachloronaphthalene (CN 73)	79.21±0.79	88.75±0.21
1, 2, 3, 4, 5, 6, 7, 8- Octachloronaphthalene (CN 75)	89.23±3.29	86.96±0.17
*2, 4, 5, 6- Tetrachloro-m-xylene (TCMX)	84.43±0.25	77.69±0.02
*Decachlorobiphenyl (PCB 209)	65.40±1.29	61.50±0.07

*Surrogate standards, SD = Standard deviation

Table 4. 5 Percentage recoveries of PBDE congeners and surrogates in water and sand

PBDE congeners	% Mean recovery ±SD in water	% Mean recovery ±SD in pure sand
2, 2´, 4-Tribromodiphenyl ether (BDE 17)	73.79±0.30	78.19±0.03
2, 2´,4, 4´-Tetrabromodiphenyl ether (BDE 47)	80.90±0.04	80.90±0.23
2, 3´, 4, 4´-Tetrabromodiphenyl ether (BDE 66)	84.13±0.09	82.83±0.26
2, 2´, 4, 4´, 6-Pentabromodiphenyl ether (BDE 100)	81.92±0.02	96.17±0.60
2, 2´, 4, 4´, 5,5´-Hexabromodiphenyl ether (BDE 153)	81.12±0.11	86.73±1.94
2, 2´, 3, 4, 4´, 5´, 6-Heptabromodiphenyl ether (BDE 183)	87.50±0.05	78.35±3.91
*2, 4, 5, 6- Tetrachloro-m-xylene (TCMX)	70.90±5.28	92.41±0.33
*Decachlorobiphenyl (PCB 209)	63.68±0.52	61.17±0.42

*Surrogate standards, SD = Standard deviation

Conclusion

The quality of our aquatic systems must be checked regularly in order to guarantee its safety to potential users. It is imperative to carry out method validation for the determination of these organic compounds to establish that the extraction procedures from environmental samples (aqueous and solid samples) are very effective. The methods validation results have affirmed that these methods can be employed for PCNs and PBDEs extraction and measurements in both water and sediments with high accuracy using GC-µECD.

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CHAPTER FIVE

Evaluation of incidence of two emerging pollutants in three Port Elizabeth surface water sources and their associated health risks

Abstract

The occurrence and distribution of two emerging pollutants, polychlorinated naphthalenes (PCNs) and polybrominated diphenyl ethers (PBDEs) in water samples from three waterbodies comprising of North End Lake (NEL), Chatty River (CHA) and Markman Canal (MMC) in Port Elizabeth, Eastern Cape Province of South Africa were determined with validated analytical methods. Forty-seven (47) water samples were collected from these waterbodies between August and December, 2020. The physicochemical parameters of the water samples were measured on the field using portable Hanna multi-parameter instrument. PCNs and PBDEs were extracted from water samples with SPE and analysed using GC-µECD. The range for physicochemical parameters of water samples across the three sites were as follows: temperature (15.3–24.5°C), pH (7.7–10.5), oxidation reduction potential (-339-130 mV), atmospheric pressure (14.52-15.56 PSI), turbidity (1.0–197.6 NTU), electrical conductivity (114–8004 µS/cm), total dissolved solids (55-4002 mg/L), total suspended solids (4–491 mg/L), and salinity (0.05–4.47 PSU). The sum of eight PCN congeners $\sum_8$PCNs in NEL, CHA and MMC water samples varied from 0.164–2.934 µg/L, 0.026–1.054 µg/L and 0.035–0.699 µg/L, independently. Levels of $\sum_6$PBDEs in the water samples ranged between 0.009-1.025 µg/L in NEL and 0.007-0.079 µg/L in CHA. The hazard quotient (HQ) which is equivalent to the non-carcinogenic health risk due to PBDEs in NEL and CHA water samples were 2.0×10^{-3}-1.41×10^{-1} and 1.6×10^{-3}-7.7×10^{-3} respectively. The estimated TEQ values due to PCNs for NEL, CHA, and MMC water samples varied from 6.10×10^{-7}-3.12×10^{-3} µg/L, 1.0×10^{-7}-6.62×10^{-5} µg/L and 1.19×10^{-7}-1.47×10^{-4} µg/L in that order. The calculated health risks in NEL were higher than the remaining two waterbodies. The pollutants' levels recorded in this study especially in NEL is believed to emanate from effluents discharged into these waterbodies. There is urgent need for construction of good drainage system to channel environmental waste from their place of production to final destination of disposal, and the general populace must adhere strictly to proper waste disposal techniques to safeguard our ecosystems.

Keywords: Polychlorinated naphthalenes, polybrominated diphenyl ethers, non-carcinogenic health risks, GC-ECD, water samples.

5.1 Introduction

Some countries including South Africa agreed to eradicate manufacturing and application of persistent organic pollutants (POPs), among which are polychlorinated naphthalenes (PCNs) and polybrominated diphenyl ethers (PBDEs). The agreement was under the international treaty of Stockholm Convention (SC). PCNs are organochlorine chemicals listed as POPs in May 2015 at the SC following their satisfaction of POPs features (UNEP, 2015). This followed the initial prohibition of PBDEs and other eight chemicals (referred to as nasty nine) at the fourth gathering of the Conference of the Parties (COP) to the SC in May, 2009 (Li *et al.*, 2016). Pollutants are transmitted from their manufacturing spots into distant locations globally and amassed with time in our surroundings (UNEP, 2017).

PCNs are composed of naphthalene ring structures where the hydrogen atoms are displaced with chlorine atoms producing 75 congeners (Agunbiade *et al.*, 2020; UNEP, 2017). PCNs are industrial chemicals historically produced to be used in electrical industries as insulators and dielectric liquids in electrical components. They also serve as supplement in wood preservation, dye and plastic products manufacturing. PCNs diffused into the environment during their industrial manufacturing and as impurities during polychlorinated biphenyls (PCBs) manufacturing (Brack *et al.*, 2003; Yamashita *et al.*, 2003). The percentage of PCNs in PCB formulations could be up to 1% (UNEP, 2017). PCNs can accidentally be discharged into the surroundings through evaporation from PCN-containing consumer products (de Wit *et al.*, 2010), metallurgical processes (Jiang *et al.*, 2019; Liu *et al.*, 2012), municipal waste incineration, and other combustion operations (Liu *et al.*, 2014). PCNs get to humans majorly through food consumption (Fernandes *et al.*, 2017); CNs bioaccumulate more in fish and other fatty foods (CICAD, 2001).

PBDEs are toxic organobromine chemicals that consist of one to ten bromine atoms attached anywhere on the diphenyl ether molecule with the formation of 209 congeners which are divided into ten homologues (Chen *et al.*, 2012). PBDEs were manufactured to be applied as fire-resistants in the production of various consumer and industrial materials among other applications. They account for reasonable percentage in these materials in order to avert fire-hazards while handling (Stiborova *et al.*, 2015; Birnbaum and Staskal, 2004). As an additive brominated flame-retardants (BFRs), PBDEs are blended with the manufactured products but not covalently bond. As a result, they are able to diffuse out of the products and travel into the surroundings during products manufacturing, application, reprocessing and disposal (de Wit *et al.*, 2010). PBDEs are harmful to the environment and human wellness; their levels in humans could be from food ingestion (dietary intake), dust inhalation, or dermal contact (Babalola and Adeyi, 2018; Harrad *et al*., 2016; Daso *et al*., 2010).

The methodology for sampling, extraction, purification and instrumental analysis for both PBDEs and PCNs are analogous to PCBs, PCDDs, and PCDFs. They are isolated from liquid matrices using traditional liquid–liquid extraction (LLE) (Pei *et al*., 2018; Mahmood *et al*., 2014) and solid phase extraction methods (Olisah *et al*., 2020; Marti and Ventura, 1997).

The extraction is accompanied by other treatment (including purification, concentration etc.) and analysis on varying instrument (gas chromatograph coupled with mass spectrometer is now preferred for its different advantages) (Shao *et al*., 2018; Fernandes *et al*., 2017). Other studies have employed gas chromatograph incorporated with microelectron capture detector (Olisah *et al*., 2020; Daso *et al*., 2016).

Past studies from across different regions of the world, including Norway (Ishaq *et al*., 2009), Spain (Marti and Ventura, 1997), Pakistan (Mahmood *et al*., 2014), among others, have reported PCN occurrences in water. These investigations evaluated the concentrations, congener profile, and ecological risk of the contaminants in their respective environments. However, studies relating to PCN levels in South African environment, especially in the aquatic systems are still lacking. PBDEs have been universally detected in water samples around the globe; China (Liu *et al*., 2018; Pei *et al*., 2018; Ju *et al*., 2016; Xiong *et al*., 2016), America (Kim *et al*., 2013; Streets *et al*., 2006; Oros *et al*., 2005), Japan (Osako *et al*., 2004), Turkey (Cetin and Odabasi, 2007), UK (Komolafe *et al*., 2019), Korea (Moon *et al*., 2012), Nigeria (Olutona *et al*., 2017), Ghana (Essumang *et al*., 2018), among other locations. Some researchers have reported PBDEs occurrence and distribution in certain Provinces of South Africa (Sibiya *et al*., 2017; Daso *et al*., 2013, 2012; Olukunle *et al*., 2012; Odusanya *et al*., 2009) to mention a few. Except for the works of Olisah *et al*. (2020) on two estuaries, reports on PBDE levels in Eastern Cape Province (ECP) is still minimal.

North End Lake (NEL), Chatty River (CHA), and Markman Canal (MMC) are located in Port Elizabeth (PE), ECP of South Africa. NEL is an urban surface water located between a residential and industrial part of North End. The CHA is the biggest tributaries of Swartkorps River, flowing across several informal settlements. The MMC is an artificial drainage developed for the discharge of industrial waste. NEL serves recreational purposes (swimming, power boating, canoeing, and fishing) and had been treated for irrigation purpose (Kampire *et al*., 2017). CHA and MMC harbours residential and industrial waste respectively, both serve important pastoral and irrigation purposes

(EFA, 2011, 2009). CHA and MMC were indicated as main tributaries emptying into the Swartkops Estuary (SWE) (Adams *et al.*, 2019). While some studies have reported the pollution status of SWE caused by communal and industrial wastes originating from these water sources (Olisah *et al.*, 2020, 2019; EFA, 2009), there is no published reports on the pollution states of the river and canal. Previous regional studies carried out on NEL include the works of Kampire *et al.* (2015, 2017) in which PCB residues were discovered in several tissues of fish and surface sediment samples collected from the lake. Their reported concentrations were lower when compared to other studies in literature, but they concluded that the presence of PCBs in the studied fishes and sediments was an indicator that effluents coming from nearby homes and industries pollute the lake (Kampire *et al.*, 2015; 2017). Hence, this study was embarked upon to appraise the pollution status of these water bodies.

This research is one of the first to report PCN levels in South Africa and was undertaken to estimate the occurrence and distribution of these pollutants in aquatic environment. This was achieved by measuring the physicochemical parameters, levels of PCNs and PBDEs in the water samples and examining their relationships with physicochemical parameters of water to identify their potential risks. Physicochemical results were compared with set standards, while concentrations of the pollutants were related with other studies around the globe. Findings from this research will provide benchmark data for subsequent investigations of these pollutants in South African environment.

5.2 Materials and methods

5.2.1 Solvents, standards and other consumables

GC grade acetone, ethyl acetate, n-hexane, and isooctane were procured from Sigma-Aldrich (Merck Pty Ltd, South Africa). The surrogate standard TCMX (Dr. Ehrenstorfer Laboratories, Augsburg, Germany), PBDE and PCN calibration standards (Wellington laboratories, Canada), and C_{18} cartridges from Promolab Pty Ltd (Separations), South Africa were also procured. The working standard solutions were prepared from stock solutions (5000 µg/L) by dilution with GC grade isooctane solvent. The working solutions were prepared in the range of 5-120 µg/L to obtain eight external calibration points for both pollutants.

5.2.2 Site description

The study was conducted in Port Elizabeth (PE), ECP of South Africa using three different surface waters; North End Lake (latitude 33°55´53.3"S-33°56´19.1"S and 25°35´27.8"E-25°35´48.0"E longitude), Chatty River (latitude 33°51´02.5"S-33°51´15.2"S and 25°31´32.1"E-25°32´54.9"E longitude), and Markman Canal (latitude 33°47´57.7"S-33°50´35.7"S and 25°36´02.5"E-25°38´38.9" E longitude) (Figure 5.1).

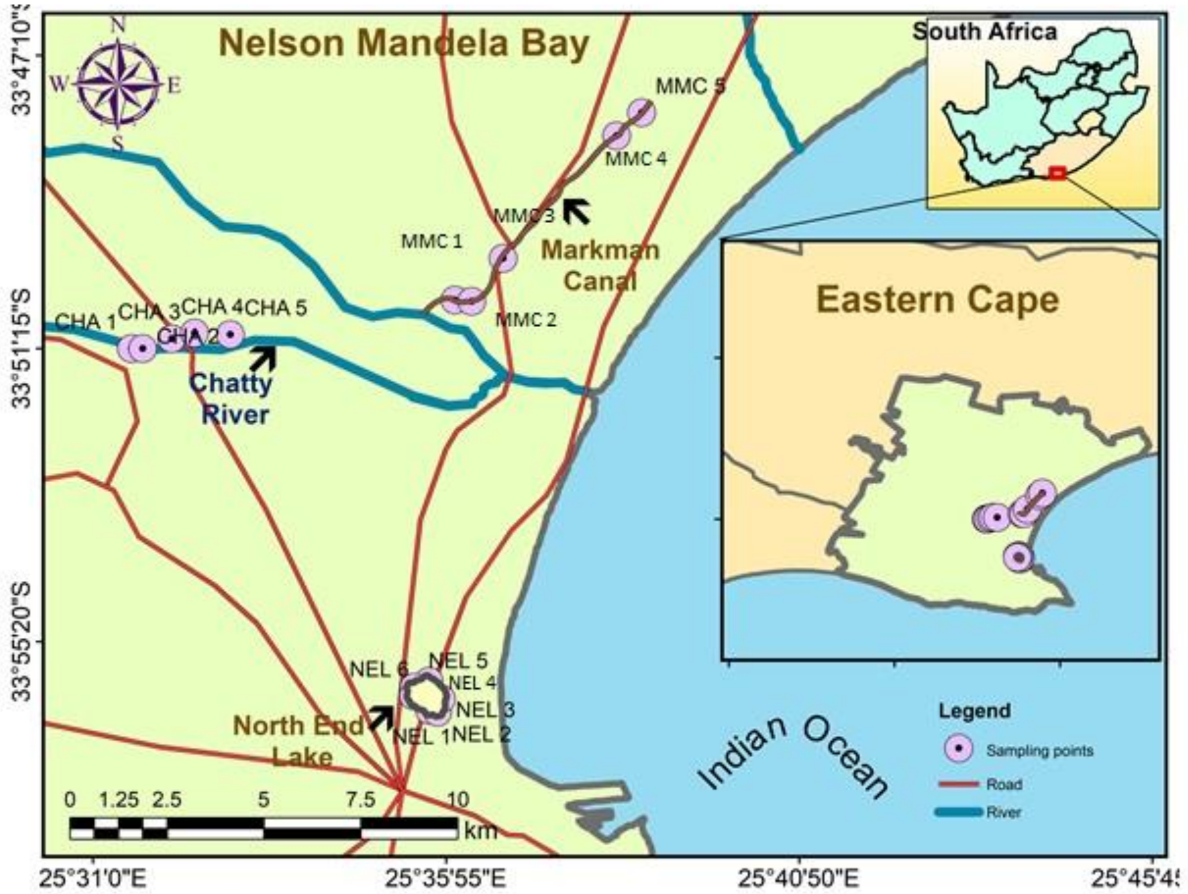

Figure 5. 1 The study area map showing the sampling points at the North End Lake, Chatty River, and Markman Canal

Sampling points coordinates were measured with a global positioning system and selected based on literature survey, proximity to pollution sources detected on the sites, and ease of sample collection. Six sampling points were chosen on NEL and identified as NEL 1, 2, 3, 4, 5, 6. Five points were selected on CHA and MMC, coded as CHA 1, 2, 3, 4, 5, and MMC 1, 2, 3, 4, 5 consecutively. The points are at least 200 m far apart from one another at each sampling site.

Table 5. 1 Description of the study sites

Site Codes	Latitudes	Longitudes	Site Description
NEL 1	33°56´17.5" S	25°35´41.1" E	Located within a recreation centre, and few metres away from a manufacturing company.
NEL 2	33°56´19.1" S	25°35´48.0"E	Located within a recreation centre, near a relaxation spot and point of lowering canoe into the lake for power boating, and fishing.
NEL 3	33°55´53.3" S	25°35´40.9" E	Opposite a residential area, few metres from main road
NEL 4	33° 56´00.0"S	25°35´47.4" E	Opposite a residential area, few metres from main road and residential buildings.
NEL 5	33°56´05.3"S	25°35´27.8" E	Located opposite an industrial area, few metres from an effluent discharging point into the lake.
NEL 6	33°56´05.5" S	25°35´28.2" E	Located opposite an industrial area, about 200 m from manufacturing companies.
CHA 1	33°51´15,2" S	25°31´32,1" E	Located within a residential area, few metres from an informal settlement
CHA 2	33°51´15,1" S	25°31´41,6"E	Located within a residential area, near an informal settlement
CHA 3	33°51´06,6" S	25°32´05,7" E	Located under the bridge on a busy road
CHA 4	33° 51´02,5"S	25°32´25,1" E	Located under the bridge on a busy road, few metres from residential buildings.
CHA 5	33°51´03,4"S	25°32´54,8" E	Located under the bridge on a busy road, few metres from residential buildings and an open field used for animal grazing
MMC 1	33°50´34.8" S	25°36´02.5" E	Entry point into SWE
MMC 2	33°50´35.7" S	25°36´16.6" E	Located in a residential area (Aloes community, an informal settlement)
MMC 3	33°49´59.7" S	25°36´42.9" E	Located between residential area (Aloes community) and industrial area (Markman community)
MMC 4	33°48´09.5" S	25°38´25.9" E	Located within Markman industrial area, near an effluent discharging point
MMC 5	33°47´57.7" S	25°38´38.9" E	Located within Markman industrial area, near an effluent discharging point which empties directly into the canal

5.2.3 Sample collection and preservation

Samples were collected in duplicate from each sampling point. The sampling period was from August to December, 2020. Surface water samples were fetched into properly cleaned 1 Litre amber bottles with screw caps. Hanna multi-parameter instrument (HI 98195) was used to measure on the field certain physicochemical parameters of the water samples; atmospheric pressure (AP), electrical conductivity (EC), pH, oxidation-reduction potential (ORP), salinity, temperature, total dissolved solids (TDS), and turbidity of the water samples. The samples were conveyed to the laboratory in an ice pack. Total suspended solids (TSS) in the water were determined by HACH DR 900 portable meter. The water samples were filtered and extracted on arrival in the laboratory. The remaining specimens were stored inside the fridge.

5.2.4 Extraction of PCNs and PBDEs from water samples

Liquid specimens were filtered with a 120 mm Whatman filter paper for removal of suspended solids. PCN congeners were extracted from water samples using the method of Marti and Ventura (1997). Details of the extraction procedures are provided in previous chapter. Two hundred microliter (200 µ/L) of 5000 µg/L TCmX was added as recovery surrogate standard to a sample in every batch of 10 samples (Liu *et al*., 2018). The procedure of Barco-Bonilla *et al*. (2015) was employed for PBDEs extraction from liquid specimens, the details have been described in previous chapter. A selected sample was spiked with 200 µ/L of 5000 µg/L TCmX surrogate standard in every batch of 10 samples (Olisah *et al*., 2019).

5.2.5 Health risk evaluation of pollutants

5.2.5.1 Health risk estimation due to PCNs in water samples

There are no set guidelines for PCNs risk evaluation in environmental matrices due to insufficient pharmacology and endemic information for the congeners. Since PCN congeners showed comparable toxicities with dioxins, possible health risk due to these congeners are calculated by converting their concentrations to toxic equivalent factor corresponding to 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) using Equation (1) below (Li *et al*., 2020). TCDD has a reference value of one (van den Berg *et al*., 2013**).** The REPs for the studied PCN congeners are listed in Table 5.2.

$$TEQ\sum_{PCN} = \sum (C \times REPs) \qquad (1)$$

Where,

TEQ = Toxic equivalency

C = Concentration of the PCN congener (µg/L)

REPs = Relative potencies for each congener.

Table 5. 2 Reported relative potencies (REPs) for individual CNs

PCN congeners	ID NO	REPs
2-MonoCN	CN 2	0.000018
1,5-DiCN	CN 6	0.0000012
1,2,3-TriCN	CN 13	0.0000044
1,2,3,5-TetraCN	CN 28	No data
1,2,3,5,7-PentaCN	CN 52	0.0000042
1,2,3,4,6,7-HexaCN	CN 66	0.0039
1,2,3,4,5,6,7- HeptaCN	CN 73	0.003
1,2,3,4,5,6,7,8- Octa CN	CN 75	0.00001

Source: Falandysz *et al.*, 2014

5.2.5.2 *Human health risk estimation due to PBDEs in water samples*

PBDEs get to humans via ingestion, inhalation, and dermal contact with polluted foods, water or dust (Daso *et al.*, 2010). Carcinogenic and non-carcinogenic health risks due to POPs are usually estimated using USEPA models (USEPA, 2011). However, there are insufficient data for the variables involved in the determination of PBDE health risks using these models. In order to estimate the health hazards connected with this analysed water, the average calculated PBDE concentrations were employed in this research (Olisah *et al.*, 2020). The estimated daily intake (EDI), hazard quotients (HQ), and hazard index (HI) were calculated using equations (2 – 4):

$$\text{EDI} = (\text{C x IV}) \div \text{Bw} \qquad (2)$$

$$\text{HQ} = \text{EDI} \div \text{RfD} \qquad (3)$$

$$\text{HI} = \Sigma\text{HQs} \qquad (4)$$

Where, C = Average pollutants concentrations (µg/L)

IV= ingestion volume (2L/day)

Bw = Average human body weight (60 kg) (WHO, 2010).

RfD is USEPA reference dose value for each congener (0.1 µg/kg/day for BDEs 47 and 0.2 µg/kg/day for BDE 153). The hazard quotient (HQ) is equivalent to the non-carcinogenic health risk. A value above one (1) signifies a potential adverse effect while a value below 1 signifies no probability of adverse effect of water consumption (USEPA, 2010).

5.2.6 Instrumental analysis

The quantification of eight PCN congeners (CN 2, 6, 13, 28, 52, 66, 73, 75), and six PBDE congeners (BDE 17, 47, 66, 100, 153, and 183) present in the purified extracts were determined with an Agilent 7820A gas chromatograph GC (Agilent technologies, Santa Clara, CA, USA) coupled with microelectron capture detector (µ-ECD) (model—G2397AE, Santa Clara, CA, USA). This is equipped with an Agilent HP-5 column (30 m × 0.32 mm ID × 0.25 µm film thickness) while the identification of the PCN/PBDE congeners was performed using Agilent 7890B gas chromatograph GC (Agilent technologies, Santa Clara, CA, USA) coupled with mass spectrometry detector (Agilent technologies 5977A, Santa Clara, CA, USA). Samples (1µL) were injected in splitless mode at inlet temperature of 300°C. The carrier gas was helium at flow rate of 3 mL/min (for PBDEs, Wang *et al*., 2016) and 2 mL/min (for PCNs, Mahmood *et al*., 2014). Operating conditions for the equipment was enumerated in chapter 4. PCNs and PBDEs were quantified using Agilent Chemstation software incorporated into the instrument.

5.2.7 Quality assurance and quality control (QA/QC)

Glasswares were properly cleaned with liquid soap, rinsed out with tap water and deionised water before and after each use. Rinsing with methanol and acetone followed before they were finally rinsed and oven dried. All the solvents used for analysis were either GC or analytical grade. The analytical procedures were carefully monitored by analysing the surrogate standard and procedural blank alongside each batch of 10 samples. A specific volume of surrogate standard was added to selected sample before extraction to determine the reproducibility and accuracy of the analytical method. Procedural blank sample was simultaneously analysed with each batch of 10 samples to monitor possible contamination during the analysis, but the data obtained were not corrected with blank values since the pollutants concentrations in the procedural blank were insignificant (Barhoumi *et al*., 2019).

External calibration was used for the quantification of analyte. Eight standard solutions of concentrations between 5 and 120 µg/L were run to prepare calibration curve. Linear calibration curves were obtained with the correlation coefficients varying from 0.9984-0.9993 for PCNs (Table 4.2 and Appendix 1) and from 0.9967-0.9989 for PBDEs (Table 4.3 and Appendix 1). Recalibration of the instrument was performed at intervals. The sensitivity of the instrument was evaluated in terms of limit of detection (LOD) and limit of quantification (LOQ). LOD and LOQ were determined by running a known concentration of standard mixture on the instrument eight times.

Liquid and solid wastes generated in the course of this research were emptied into well-labelled plastic bottles with lids and kept in a storeroom designated solely for organic wastes by UFH Chemistry Department.

5.2.8 Data analysis

The instrumental data were processed with Chemstation version B.05.00 software (Agilent Technologies) incorporated into the instrument. Mean, maximum, and the deviation of the parameters were calculated for their descriptive statistics using Microsoft Excel 2016. The Pearson correlation of the parameters was deduced using SPSS 21 version and the significance was defined at $p < 0.01-0.05$ (Liu *et al*., 2017).

5.3 Results and discussion

5.3.1 The surface water physicochemical parameters

Studies have revealed that aside some important physicochemical properties such as octanol/water partition coefficient, octanol/air partition coefficients, vapour pressure, Henry's constant, polarity, aqueous solubility, boiling and melting points; environmental fate of POPs are also impacted by their physicochemical parameters including pH, TDS, EC, temperature, salinity, and turbidity (Barhoumi *et al*., 2019). The values for the physicochemical parameters of water samples across the three seasons and sites are summarised in Figure 5.2 and Appendix 2.

The water temperature at the different seasons in North End Lake (NEL) ranged between 15.3-16°C (winter), 19.1-20.6°C (spring), and 21.5-23°C (summer). The temperature was high during summer but least in winter. This is expected as winter and summer are characterised with low and high temperature, respectively. Interestingly, the temperature values increased from NEL 1 to NEL 6 during summer. The temperature range for Chatty River (CHA) water samples in winter was 15.4-16.9°C, spring (20.2-22°C) and summer (18.8-22.9°C). The temperature ranged between 15.6-16.4°C during winter, 22.8-24.5°C (spring) and 20.4-22.5°C (summer) in Markman Canal (MMC). The temperature was least in winter at all the study sites; this is expected as winter is the coldest season of the year (Awe *et al*., 2020). The temperature values are all within South African Water Quality Guidelines (SAWQG, 15–35°C) for potable waters (DEA, 2012). The recorded values were lesser than 25°C permissible value for aquatic ecosystems (DWAF, 1996). The mean temperature from this study compares well with 14.0-24.2°C recorded from Diep River water by Awe *et al*. (2020). Olisah *et al*. (2019) recorded similar temperature range of 14-26.1°C in Sundays Estuary (SDE) of ECP, South Africa. Variations in water temperature was influenced by seasons of the year, period of the day, latitude, air movement, water flow direction and depth (Chapman and Kimstach, 1996). Some physical and chemical properties of water such as solvability of certain gases (e.g., oxygen), chemical reaction rate, and toxicity are greatly impacted by temperature (Dallas, 2008).

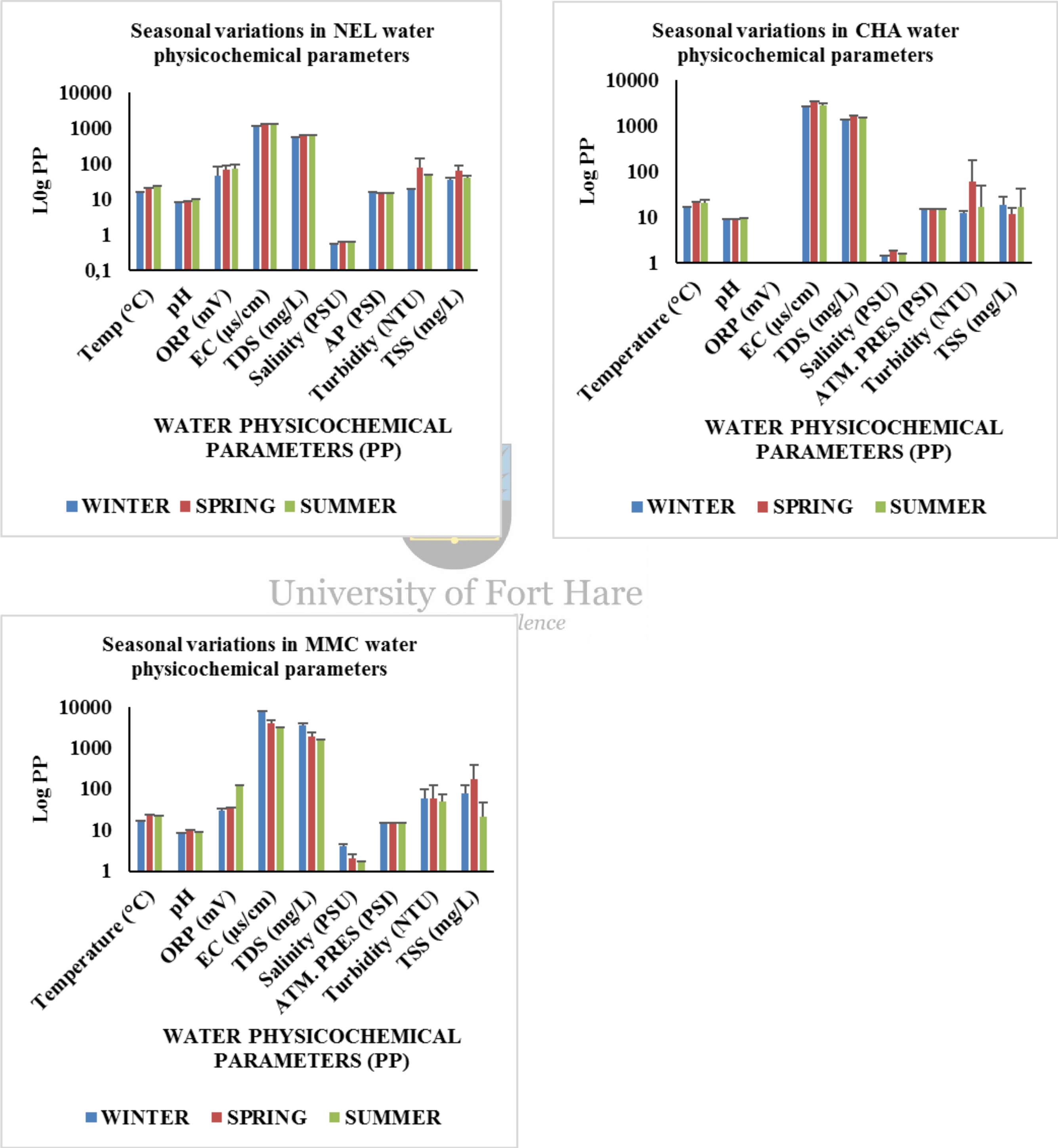

Figure 5. 2 Seasonal variations in NEL, CHA and MMC water physicochemical parameters

The pH values for NEL were 7.9-8.4 during winter, 8.1-9.1 (spring), and 9.2-10.3 (summer). The pH exceeded the 5.0-9.7 set standards for recreational water use by SAWQG (DEA, 2012) at some points (NEL 1-3) on the lake during summer. The values recorded in winter and spring agreed with the 6–9 set limits of the Department of Water Affairs and Forestry (DWAF), South Africa for domestic water use (DWAF, 1996) except at NEL 6. All the summer readings at all points exceeded 6.5-8.5 set limits for potable water by the World Health Organisation (WHO, 2008). The pH values obtained from all the CHA sampling points varied from 8.4-9.3 for winter, 8.6-8.9 (spring), and 7.7-10.5 (summer). These values exceeded the 6–9 set limits by the DWAF for domestic water use at some points (DWAF, 1996). The pH for MMC water samples ranged from 8.4-8.8 in winter, 9.0-10.2 (spring), and 8.6-9.1 (summer). A few of the values obtained during spring exceeded the 6-9 set limits of the DWAF (DWAF, 1996). The values in this study are above the pH values reported from Diep River in South Africa, which varied from 7.16-7.98 (Awe *et al*., 2020). Measurement of pH is consequential in any water analysis as it controls both biological and chemical reactions occurring in the water and provide substantial information on the extent of environmental pollution (Carr and Neary, 2008). Conversely, lower pH accounts for toxicity and bioconcentration of ionizing organic compounds (Rendal *et al*., 2011). As a result, the findings on the relationship of the congeners with pH suggest that PCNs are likely to be more acidic, potent, and consequently more toxic than PBDEs. This discovery aligns with the stance of Falandysz (1998) on the high acnegenic potency of PCN among other anthropogenic organo-halogens.

The ORP for NEL water samples varied as follows: 24.6-97.2 mV in winter, 43.7-92.9 mV (spring) and 23.4-109.5 mV (summer). ORP for CHA water ranged from -339.1 to -0.2 mV in winter, -185.6 to 7.5 mV (spring), and -244.2 to 51.3 mV (summer). The ORP in CHA had negative values at some points; the implication of this is that ORP values in water have strong significance for animal's immunity response, cell homeostasis, energy metabolism and resistance to diseases due to the dependence of aqueous systems on the ORP values (Goncharuk *et al*., 2010). MMC had 7.8-49.2 mV ORP in winter, 9.0-50.7 mV (spring) and 103.1-130 mV (summer). The ORP was highest in summer at the three sampling sites. ORP measurements are equally important as pH in evaluating water quality and extent of water pollution. ORP measures the oxidising or reducing capacity of an aqueous system. It is an oxidising system when electrons are not available, which is denoted by positive ORP values and a reducing system when electrons are easily accessible, indicated by negative values (Copeland and Lytle, 2014). ORP evaluation is essential for purification of drinking water, swimming pools, and wastewaters with chlorine, chlorine dioxide or other oxidants employed during water disinfection processes. High ORP value indicates that many oxygen molecules are dissolved in the water, which in turn reflect the healthy status of the waterbody for the survival of living things (Suslow, 2004).

The measured EC values for NEL water samples were in the range of 114 to 1291 µS/cm in winter, 1220-1256 µS/cm (spring), and 1237-1266 µS/cm (summer). The values at all points for the reported three seasons were lower than the acceptable limit of 1500 µS/cm specified by DWAF, South Africa (DWAF, 1996). EC values for CHA water samples measured 1981-2907 µS/cm in winter, 2837-3542 µS/cm (spring), and 2623-3138 µS/cm (summer). All the EC values from CHA exceeded the safe water set guideline of 1700 µS/cm by the South African National Standards (SANS 241:2015). This is explainable by the magnitude of municipal wastes entering the river from nearby informal communities (EFA, 2011, 2009). The EC of MMC water samples across the 3 seasons ranged from 6755-8004 µS/cm in winter, 3043-4815 µS/cm (spring), and 1885-4025 µS/cm (summer). The reported values at this site for the three seasons were greater than 1700 µS/cm permissible limit for potable water by the South African National Standards (SANS 241:2015). EC was reported to have a direct relationship with salinity, considering its capacity to allow electrical current to flow through at 25^{o}C (Al Dahaan *et al*., 2016). Few of the sampling points are associated with exceedingly high EC beyond the water safety standard of the South African National Standards (SANS 241:2015). This is possibly due to the discharge from the municipal and industrial wastes into the waterbodies (EFA, 2011, 2009). All the EC results in this study from the three sampling sites are below 2200–51300 µS/cm obtained by Olisah *et al*. (2019) in their study on two estuaries in ECP, South Africa. The high EC recorded at the two estuaries was due to dissolved sodium chloride ions in the water caused by seawater intrusion, which in turn could increase their salinity levels. The high EC values at CHA and MMC sites could be attributed to the dissolved ions present in the waterbodies (Edokpayi *et al*., 2015). Human-induced activities and liquid-waste inflow into aquatic system may also increase water EC, thereby making the water unacceptable for household use and farm watering (Korkanç *et al*., 2017).

The TDS of NEL water samples ranged from 55-645 mg/L (winter), 610-628 mg/L (spring), and 618-633 mg/L (summer). All the results at this site are below 1200 mg/L baseline value promulgated for potable water by the South African National Standards (SANS 241:2015). The measured TDS for CHA water samples were 991-1454 mg/L (winter), 1419-1771 mg/L (spring), and 1311-1576 mg/L (summer). All the results except the minimum value of 991 mg/L at CHA 1 during winter exceeded the SANS benchmark of 1200 mg/L (SANS 241:2015). This observation can still be linked to the levels of dissolved solid wastes in the waterbody (EFA, 2011, 2009). The TDS of MMC water samples ranged from 3378-4002 mg/L in winter, 1522-2407 mg/L (spring), and 943-2012 mg/L (summer). The minimum and maximum values were measured at the same point MMC 5 but at different seasons. MMC 5 had the least value during summer, but TDS was at its maximum at the same point (MMC 5) in winter. All the values except at MMC 5 during summer exceeded 1200 mg/L set standard specified for clean water by the South African National Standards (SANS 241:2015). The TDS values in this work share similar trend with the EC such that extremely high TDS values are maintained at the same points with high EC values. Olisah *et al.* (2019) recorded higher TDS 1100-25600 mg/L from their study. The elevated TDS recorded by this group of authors in both estuaries can still be linked to the high dissolved NaCl ions. TDS measurement serves as a water quality indicator, with acceptable limits spanning between 600-1000 mg/L (Kut *et al.*, 2019). Water with a TDS of 600 mg/L or less is viewed as having a satisfactory taste, while water with a TDS above 1000 mg/L are viewed as distasteful. Elevated TDS values could cause unpleasant smell and colour in water, and stunted growth in animals (Sharma *et al.*, 2017).

NEL turbidity values for the three seasons are 15.1-19.4 NTU (winter), 15.4-167 NTU (spring), and 33.4-52.3 NTU (summer). The highest level of 167 NTU was recorded during spring at point 4. Turbidity was generally high at virtually all points during spring season. This could be attributed to impingements caused by incessant runoff and effluents discharged into the lake, which is more at this season. TSS in the lake varied from 20-46 mg/L (winter), 38-107 mg/L (spring), and 31-48 mg/L (summer). The maximum value of 107 mg/L was measured in spring at point 5, which is one of the sampling points located adjacent an industrial area. It is very close to an effluent discharging point, which empties directly into the lake. TSS was observed to be higher in spring than the remaining two seasons. Elevated TSS may be due to industrial effluents from nearby manufacturing companies, municipal wastes and runoff from residential homes surrounding the lake (Kampire *et al.*, 2017). Turbidity values at CHA for the three seasons varied from 2-17.5 NTU for winter, 2.5-197.6 NTU (spring) and 1-47.6 NTU (summer). Turbidity was very high at almost all sampling points on the river in spring; this could be ascribed to the frequent rainfall that characterised wet season resulting in excess runoff and effluent discharges (Shi *et al.*, 2016). TSS measured in the river varied from 6-35 mg/L (winter), 9-15 mg/L (spring), and 9-41 mg/L (summer). The maximum value of 41 mg/L was measured in summer at point 4. Turbidity measurements in MMC were 2.9-142 NTU for winter, 15-154.2 NTU (spring), and 12.2-118.1 NTU (summer). Turbidity was higher at all points during spring than the other two seasons. TSS measurement in the canal water samples varied from 7-168 mg/L (winter), 26-491 mg/L (spring), and 4-54 mg/L (summer). The TSS value was also highest in spring. The runoff from heavy rainfall during spring season conveys more wastes from various sources into the canal, thereby resulting in the elevated turbidity and TSS levels. There is a strong relationship between TSS and turbidity; suspended solids can inhibit light conduction in water samples (Daphne *et al*., 2011). Turbidity in potable water results from atmospheric fine particles found in water, which are caused by improper filtration, suspended solids in the pipework or the occurrence of inorganic particulate matter in underground waters (Daphne *et al*., 2011). Water with a turbidity of less than five (5) NTU is considered satisfactory for consumption (WHO, 2008), while high turbidity in waters is associated with microbial poisoning (Fatoki *et al*., 2003). Turbidity was generally very high at almost all sampling points, and this could be influenced by seasonal hydrological variation (Shi *et al*., 2016). The frequent cases of elevated TSS may be due to industrial effluents from nearby manufacturing companies, municipal wastes and runoff from residential homes.

The measured salinity level of the NEL water ranged from 0.05-0.65 PSU during winter, 0.61-0.63 PSU (spring), and 0.62-0.63 PSU (summer). The least and highest values were both recorded in winter. The recorded salinity in CHA varied from 1.02-1.52 PSU (winter), 1.48-1.87 PSU (spring), 1.36-1.65 PSU (summer). MMC had salinity in the range of 3.73-4.47 PSU (winter), 1.58–2.58 PSU (spring), 0.96–2.14 PSU (summer). The reported salinity values in CHA and MMC exceeded one PSU permissible value for aquatic life protection (Kaushal *et al*., 2005). Salinity is the measurement of total soluble salts (NaCl, KCl and $MgCl_2$) in water (Hussain *et al*., 2017). Salinity level beyond the standard range may alter dissolved oxygen levels and osmosis control (Abou Anni *et al*., 2016; Bœuf and Payan, 2001), which can lead to death of living organisms (Hussain *et al*., 2017). It enables the identification of saline water encroachment in any conventional water purification factory. The deduction on the salinity is in accordance with the findings of Olisah *et al*. (2020, 2019) and compared well with the study of Awe *et al*. (2020) on Diep River, South Africa. The salinity ranges in this study area were possibly influenced by incessant release of wastewaters from various homes and industries surrounding these catchment canal and river (Olisah *et al*., 2020, 2019).

5.3.2 PCN concentrations in water samples

The sum of individual PCN congeners and the spatial distributions of $\sum_8$PCNs recorded in NEL, CHA, and MMC water samples across the three seasons are shown in Figures 5.3 and 5.4.

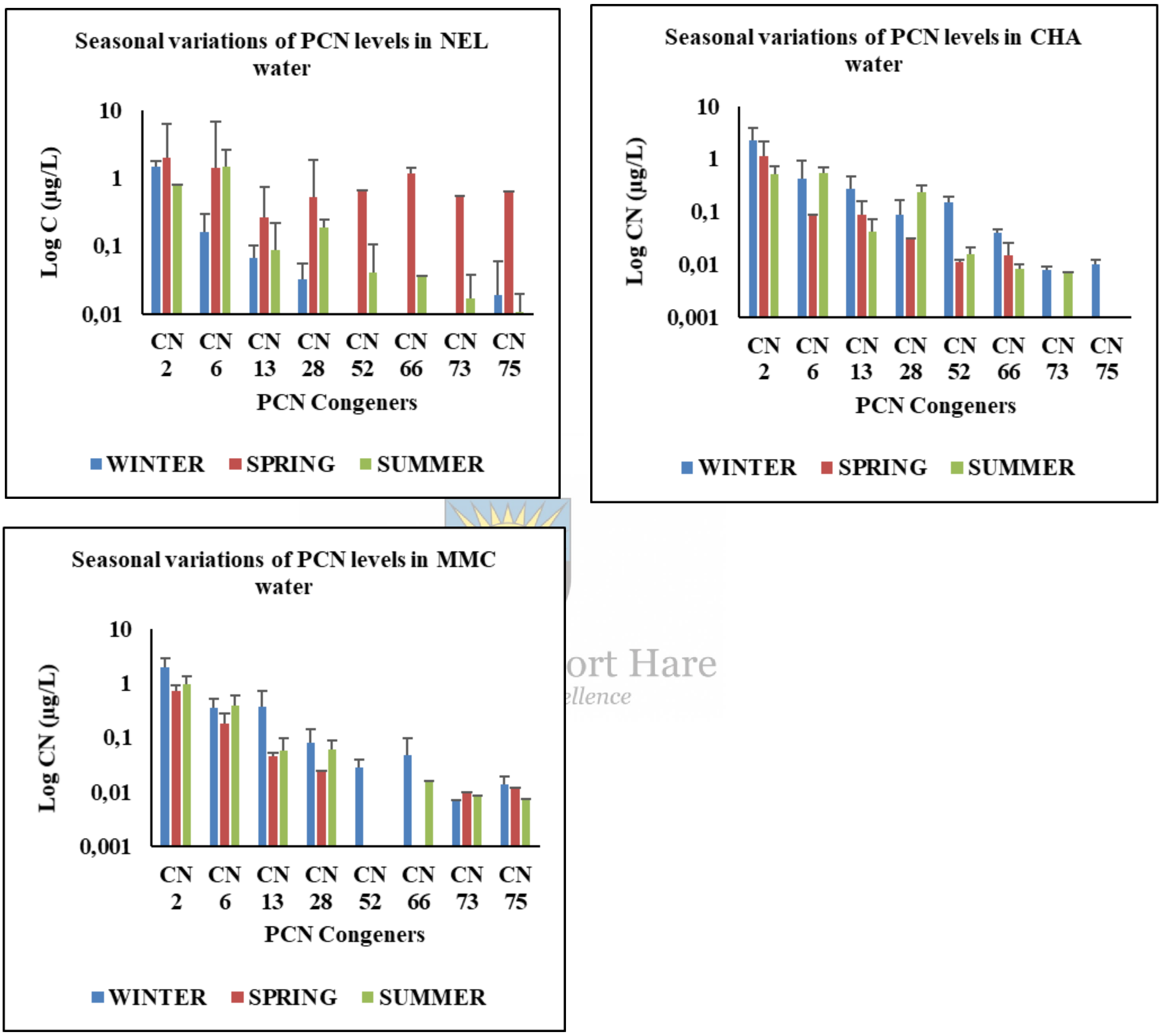

Figure 5. 3 Seasonal variations of PCN levels in NEL, CHA and MMC water samples

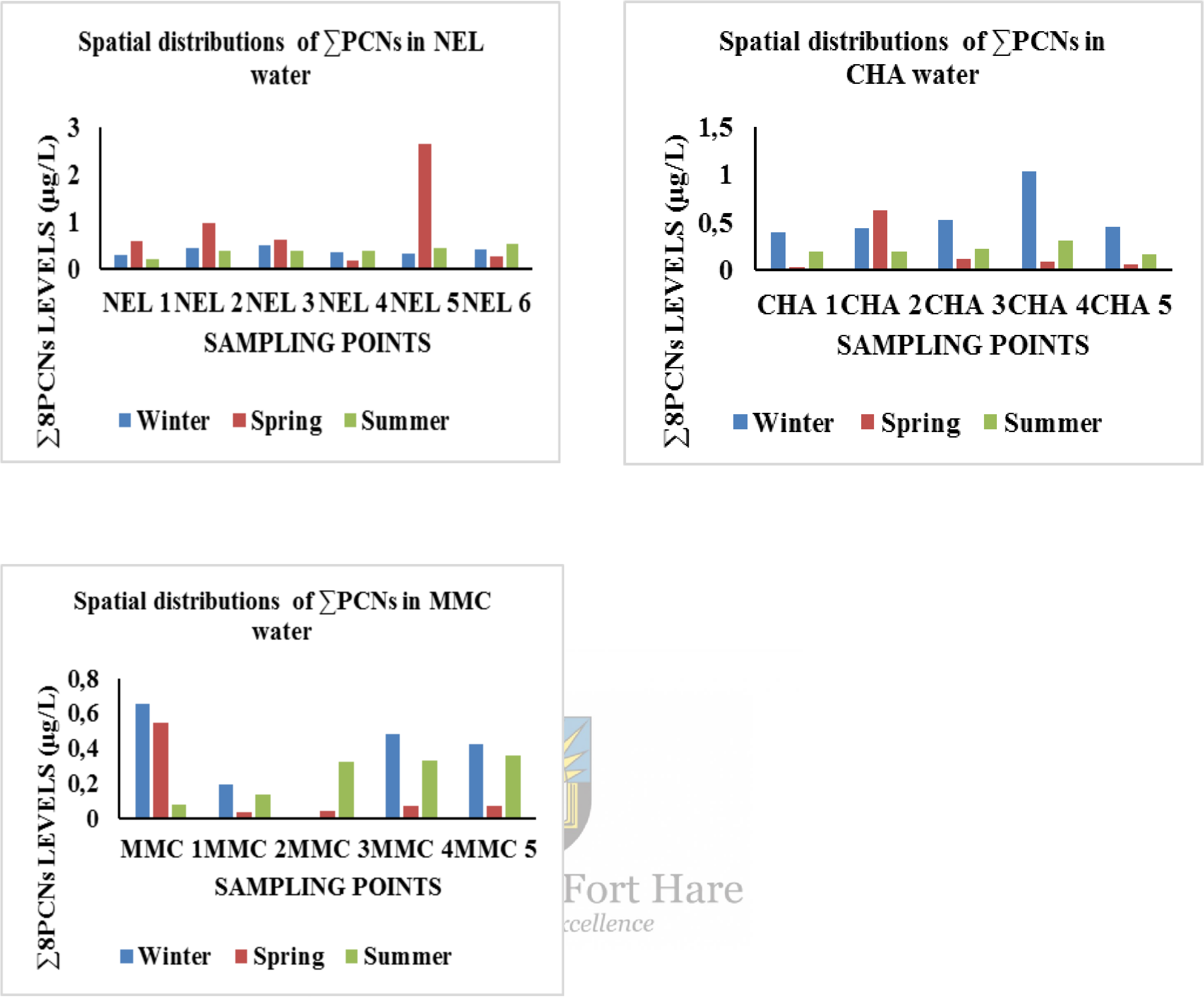

Figure 5. 4 Spatial distributions of $\sum_8$PCNs in NEL, CHA and MMC water

The sum of eight PCN congeners $\sum_8$PCNs in NEL water was 0.284 to 0.490 µg/L in winter, 0.164-2.934 µg/L (spring), and 0.209-0.543 µg/L (summer). The concentration followed the trend: spring > summer > winter. Based on the hydrological reports from South Africa Weather Service (www.weathersa.co.za/) and Owolabi *et al*. (2020), abundant rainfall is usually experienced from October to March by South Africans. The wet seasons (spring and summer) falls within this period of abundant rainfall. The higher PCNs levels in spring could be because of heavy rainfalls peculiar to wet seasons that brought more surface runoffs, culminating in high concentration of POPs than in dry season (Olisah *et al*., 2020). CNs 52, 66 and 73 were below detection limits in the water samples at all points on this site during winter, while other congeners were below detection limits at one point or another across the three seasons. CN 2 recorded highest concentration in spring at NEL 5. All the sampling points on the lake contained some levels of the congeners with highest $\sum_8$PCNs recorded at NEL 5; this sampling point was located across an industrial area and near a drainage system, which discharged domestic and industrial effluents into the lake. NEL becomes polluted by these runoffs and wastes (Kampire *et al*., 2017), and as a result, the high concentrations recorded at this point could be ascribed to these effluent inflows. The percentage distribution of other congeners follows this trend: CN 2 (44.6%) > CN 6 (33.9%) > CN 28 (6.2%) > CN 13 (4.7%) > CN 66 (4.5%) > CN 75 (2.6%) > CN 73 (2.1%) > CN 52 (1.5%).

PCN levels in CHA water samples ranged from 0.391-1.054 µg/L, 0.026-0.885 µg/L and 0.155-0.317 µg/L during winter, spring and summer, sequentially. The decreasing trend followed: winter > spring > summer. The average PCN levels in this study was highest during winter when compared with other two seasons. This is in disparity with the usual occurrence of more POP levels during wet season than dry season due to surplus surface flow caused by rainwater (Li *et al*., 2017). During winter, there is usually no rainfall; the pollutants are accumulated more on the surface soil (Li *et al*., 2012). Point source pollution, suspended particulate matters (SPM), distance travelled or flow rate among other factors might be responsible for the high PCN levels in CHA during winter (Li *et al*., 2017). CN 2 recorded highest level at CHA 4 during winter, while CN 73 and 75 were below detection limits at all points in spring. The sum $\sum_8$PCNs at all points during winter was significant with maximum value also at CHA 4. CHA 4 is located under a bridge on a busy road, few metres from residential buildings. CN 2 was the prevalent congener (65.7%) in CHA water samples across the three seasons, followed by CN 6 (18.7%) > CN 13 (8.6%) > CN 28 (5.0%) > CN 52 (1.0%) > CN 66 (0.5%) > CN 75 (0.2%) > CN 73 (0.1%).

The PCN concentrations in MMC water samples for winter, spring and summer were 0.192-0.699 µg/L, 0.0350.553 µg/L and 0.076-0.368 µg/L, respectively. PCN levels in MMC water samples decreased across the three seasons as follows: winter > spring > summer. The CN 2 had the highest concentration in winter at MMC; CN 52 was below LOD during spring and summer while CN 66 was below detection limit only in spring. CN 73 had the least concentrations across the three seasons. CN 2 (64.9%) predominated in MMC water samples, after which were CN 6 (20.5%) > CN 13 (10.1%) > CN 28 (2.9%) > CN 66 (0.7%) > CN 52 (0.4%) > CN 75 (0.3%) > CN 73 (0.2%). The $\sum_8$PCNs was appreciable at all points in MMC, but elevated levels were recorded at MMC 1 during winter and spring. MMC 1 is the point where Markman Canal connected with Swartkops Estuary. MMC 4 and 5 are two other notable points with higher CNs; they are located within an industrial zone from where raw industrial effluents are discharged into the canal (Adams *et al*., 2019).

CN 2, the least chlorinated congener in this study, was the prevalent congener in the water samples across the three seasons and sites. This is different from the findings of Mahmood *et al*. (2014) on River Chenab in Pakistan where CN 75 and other lower PCN congeners (tri and tetra-CNs) predominated in the river water samples. The predominance of these lower PCN congeners in this study could have resulted from the degradation of higher chlorinated homologues in this locality (Mahmood *et al*., 2014). Similar to other POPs; PCN resist environmental decomposition, but higher molecular weight CNs can be degraded into lower congeners under certain conditions, thereby making them abundant in the ecosystem (Gu *et al*., 2019).

Generally, the average PCN concentrations in spring were above the remaining two seasons. Not much research has been reported on the seasonal variations of PCNs, but Li *et al*. (2017) reported higher PCN concentrations during wet season than dry season in their study on Yellow River, north China. This corresponds with the results obtained in this study. PCN values from NEL were above those from the other two sites. The higher PCN concentrations in NEL could be because of the still nature of lakes, which restricts water movement outside the lake thereby concentrating the pollutants in them (Thomas *et al*., 1996).

Some studies have reiterated the dominance of the PCN congeners in sediments than in water. To this end, the assessment of PCN in water is quite uncommon. However, CICAD (2001) noted the discovery of a huge level of 5.5 µg/L PCN in the 1970s. An extreme PCN concentration documented in water sample remains the discovery of Marti and Ventura (1997) which was 0.0005–79.1 µg/L within Llobregat groundwater in Spain. The findings on the average PCN range in this study (0.026–2.934 µg/L) is fairly within safe margin, though it is higher than the findings of Ishaq *et al*. (2009) in Norway (1.4 x 10^{-5}–4.1 x10^{-4} µg/L), and Mahmood *et al*. (2014) in Pakistan (0.178–0.489 µg/L).

5.3.3 PBDE concentrations in water samples

The seasonal and spatial changes in the PBDE levels of NEL and CHA water samples are displayed in Figures 5.5 and 5.6.

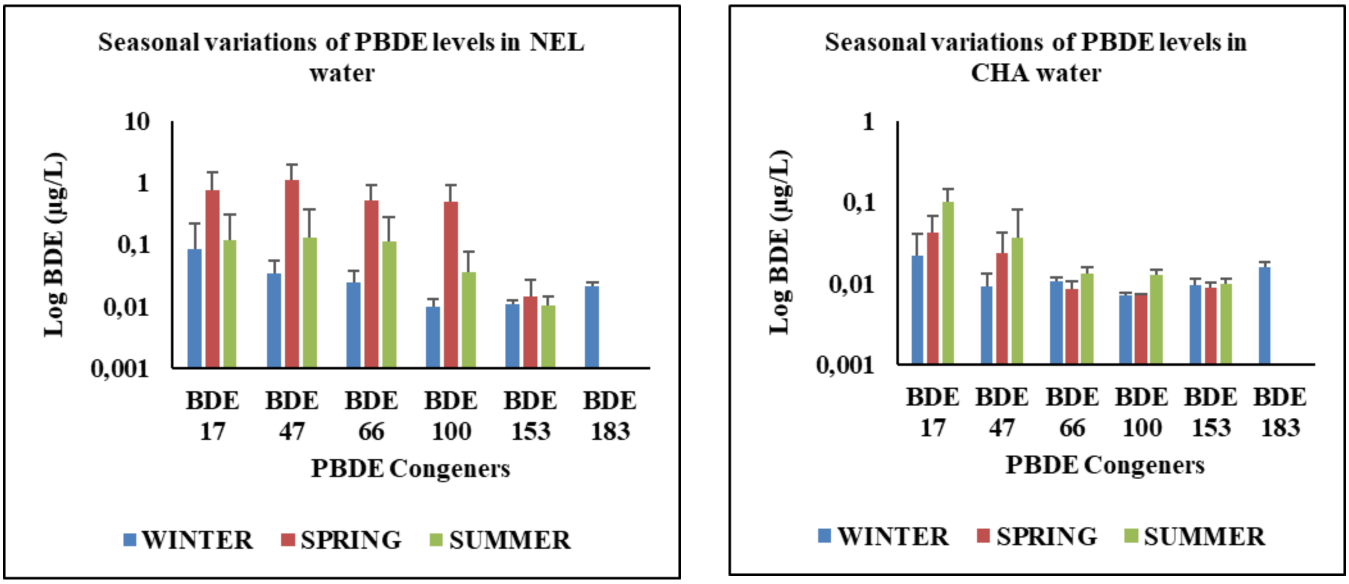

Figure 5. 5 Seasonal variations of PBDE levels in NEL and CHA water samples

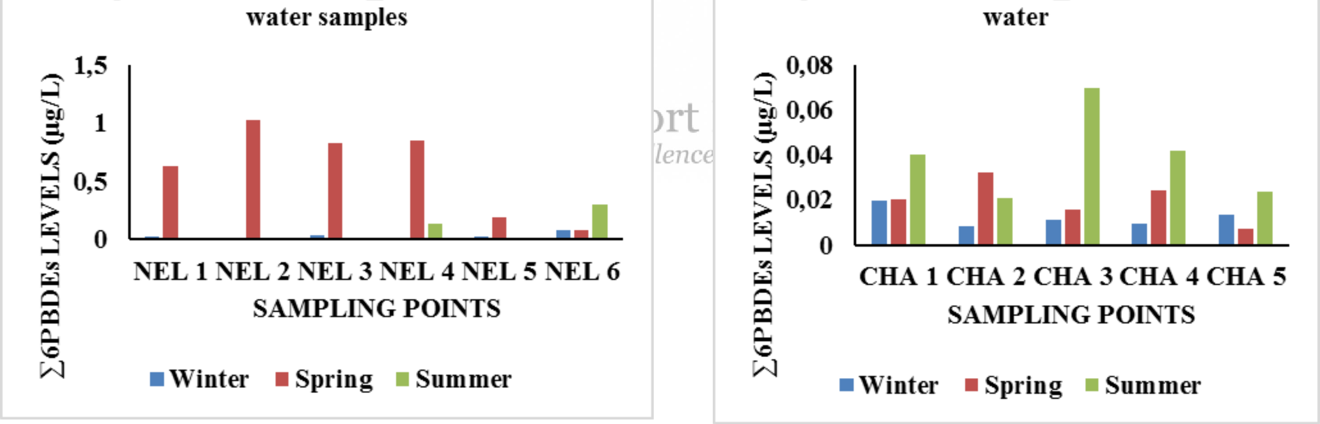

Figure 5. 6 Spatial distributions of $\sum_6$PBDEs in NEL and CHA water

The sum of $\sum_6$PBDE levels in NEL water samples across the three seasons varied from 0.010-0.086 µg/L in winter, 0.079-1.025 µg/L (spring), 0.009-0.298 µg/L (summer). The distribution was in the decreasing order spring > summer > winter, with BDE 47 having the maximum value at NEL 4 in spring. BDE 183 was below LOD at all points in spring, summer and at NEL 3, 4, 5 during winter. BDE 47 (38.5%) and BDE 17 (29.1%) were the dominating congeners across the three seasons; BDE 100 (16.4%) > 66 (14.7%) > 153 (1.0%) > 183 (0.3%) followed. When compared with other reports on water globally, NEL PBDE concentrations in this present determination especially in spring generally exceeded other reported data around the world. This shows that PBDE levels in the liquid phase of NEL is somewhat high. The high levels in NEL water samples could be linked to the fact that the lake lacks much sediment because of the rocky nature of the underneath layer; this might be the reason why the PBDEs remain more in the aqueous phase of the lake. The PBDE levels in this aqueous matrix depend largely on the extent of pollution of the waterbody (Xiong *et al.*, 2015). In contrast, NEL PBDE levels in winter and summer are below those measured in Diep River, Cape Town, South Africa (0.32-0.485 µg/L, Daso *et al*., 2013), Asunle stream, Ile-Ife, Nigeria (0.03-0.45 µg/L, Olutona *et al.*, 2017), and electronic waste dismantling region, southern China (3.1×10^{-4} - 0.89 ug/L, Xiong *et al*., 2015). The $\sum_6$PBDEs at NEL 2 was highest; this point is located within a recreational joint near the point of lowering canoe into the lake for power boating, and fishing. Considering the $\sum_8$PCNs and $\sum_6$PBDEs levels in the lake at these points, NEL 2 and 5 contained more of these two pollutants.

The $\sum_6$PBDE concentrations in CHA water samples during winter, spring and summer ranged from 0.008-0.020 µg/L, 0.007-0.033 µg/L, and 0.020-0.079 µg/L, individually. It followed the order: summer > spring > winter, BDE 17 was the prevalent congener in CHA water samples and had the highest concentrations at CHA 1 during summer. BDE 183 was below LOD at all sampling points during spring and summer, but below LOD at only CHA 1 and 5 during winter. The high PBDE concentrations during the wet season could have emanated from existing PBDE residues in the soil being drained into the waterbodies by the rainfall (Lv *et al*., 2015), or precipitation of airborne PBDEs (Pei *et al*., 2018). Point source pollutions, changes in water influx or condensation could also be responsible for the seasonal changes in the pollutants' concentrations (Lv *et al*., 2015). Pei *et al*. (2018) reported higher PBDEs' concentrations during wet season than dry season in a related study on Yellow River, China. BDE 17 (51.3%) and BDE 47 (21.6%) were prevalent at the three seasons in CHA water, while other percentage distributions were: BDE 66 (9.7%) > 100 (8.5%) > 153 (5.9%) > 183 (3%). CHA 3 contained the highest $\sum_6$PBDEs; CHA 3 is located under an overhead bridge on a busy road, CHA 3 and 4 are regarded as being most polluted with these pollutants at this site.

Studies have revealed BDE 17, 47 and other lower brominated congeners as the most prevalent in our surroundings (Olisah *et al*., 2020; Daso *et al*., 2016). The dominance of lower bromodiphenyl ethers could be linked to the biodegradation (Chen *et al*., 2018) or photodegradation of higher bromodiphenyl ethers (Wei *et al*., 2013; Soderstrom *et al.*, 2004). As in the case of PCNs, PBDE levels in NEL is above that of CHA. This could be because of various surface runoffs discharging into the lake from different sources without an exit route for their flow outside the lake (Thomas *et al*., 1996).

The deduction on the average PBDE levels of 0.007 – 0.079 µg/L in CHA aligns with the result of Olisah *et al*. (2020) on Swartkops Estuary, Port Elizabeth, ECP, South Africa (0.0025-0.1688 ug/L), but are above the mean PBDE level discovered by Daso *et al*. (2013) in Diep River, Cape Town (0.0026–0.00483 µg/L). Globally, the findings here are lower than the average brominated diphenyl ether concentrations in water deduced by Olutona *et al*. (2017) in Nigeria (0.03–0.45 µg/L) and Xiong *et al*. (2015) in the Southern China (0.00031-0.89 µg/L). Other lower deductions compared to the result obtained here include, 0.00005–0.00012 µg/L in North China (Ju *et al*., 2016), 0.00004–0.0017 µg/L in South Korea (Moon *et al*., 2012), and 0.000003–0.000513 µg/L in San Francisco, USA (Oros *et al*., 2005).

5.3.4 Correlation of PCNs and PBDEs with water physicochemical parameters

The relationship of the two pollutants with the water physicochemical parameters were examined using Pearson correlation matrix analysis and validated using Kendall-tau and Spearman rho non-parametric analyses in SPSS 21 as shown in Table 5.3.

Table 5. 3 Correlation of the CNs and BDEs with the physicochemical parameters

	Pearson Correlation				Kendall-tau				Spearman rho			
	PCN	**CN13**	**PBDE**	**BDE17**	**PCN**	**CN13**	**PBDE**	**BDE17**	**PCN**	**CN13**	**PBDE**	**BDE17**
PCN	**1.000**	**0.678**	0.245	0.223	**1.000**	**0.413**	0.122	0.055	**1.000**	**0.513**	0.170	0.077
		0.000	*0.017*	*0.031*	*0.000*	*0.000*	*0.081*	*0.435*	.	*0.000*	*0.102*	*0.460*
PBDE	0.245	0.046	**1.000**	**0.861**	0.122	0.060	**1.000**	**0.766**	0.170	0.078	**1.000**	**0.927**
	0.017	*0.679*		*0.000*	*0.081*	*0.417*	*0.000*	*0.000*	*0.102*	*0.479*	*0.000*	*0.000*
CN13	**0.678**	**1.000**	0.046	0.049	**0.413**	**1.000**	0.060	0.095	**0.513**	**1.000**	0.078	0.136
	0.000		*0.679*	*0.657*	*0.000*	*0.000*	*0.417*	*0.202*	*0.000*	*0.000*	*0.479*	*0.216*
BDE17	0.223	0.049	**0.861**	**1.000**	0.055	0.095	**0.766**	**1.000**	0.077	0.136	0.927	1.000
	0.031	*0.657*	*0.000*		*0.435*	*0.202*	*0.000*	*0.000*	*0.460*	*0.216*	*0.000*	*0.000*
Temperature	-0.189	**-0.284**	0.026	0.014	**-0.271**	**-0.163**	-0.047	0.018	**-0.395**	**-0.298**	-0.073	-0.008
	0.068	*0.009*	*0.805*	*0.896*	*0.000*	*0.028*	*0.503*	*0.796*	*0.000*	*0.006*	*0.487*	*0.937*
pH	-0.123	-0.190	-0.181	-0.182	**-0.138**	**-0.182**	-0.113	-0.099	**-0.210**	**-0.291**	-0.154	-0.135
	0.238	*0.083*	*0.080*	*0.079*	*0.050*	*0.015*	*0.109*	*0.157*	*0.043*	*0.007*	*0.138*	*0.195*
ORP	0.024	-0.036	0.202	0.177	0.027	**-0.174**	0.126	0.082	0.053	**-0.252**	0.185	0.124
	0.816	*0.747*	*0.051*	*0.087*	*0.697*	*0.019*	*0.073*	*0.244*	*0.611*	*0.021*	*0.074*	*0.233*
EC	-0.153	**0.214**	**-0.325**	**-0.291**	**-0.212**	0.020	**-0.327**	**-0.232**	**-0.294**	0.022	**-0.466**	**-0.347**
	0.140	*0.050*	*0.001*	*0.004*	*0.003*	*0.784*	*0.000*	*0.001*	*0.004*	*0.844*	*0.000*	*0.001*
TDS	-0.153	**0.214**	**-0.325**	**-0.291**	**-0.210**	0.023	**-0.326**	**-0.233**	**-0.294**	0.024	**-0.466**	**-0.347**
	0.140	*0.050*	*0.001*	*0.004*	*0.003*	*0.760*	*0.000*	*0.001*	*0.004*	*0.828*	*0.000*	*0.001*
Salinity	-0.147	**0.220**	**-0.320**	**-0.286**	**-0.226**	0.020	**-0.328**	**-0.237**	**-0.310**	0.023	**-0.461**	**-0.347**
	0.158	*0.045*	*0.002*	*0.005*	*0.002*	*0.792*	*0.000*	*0.001*	*0.002*	*0.834*	*0.000*	*0.001*
AP	0.065	0.088	**0.250**	**0.270**	-0.006	-0.043	**0.294**	**0.266**	-0.012	-0.060	**0.435**	**0.404**
	0.535	*0.428*	*0.015*	*0.008*	*0.932*	*0.562*	*0.000*	*0.000*	*0.906*	*0.589*	*0.000*	*0.000*
Turbidity	-0.008	**0.236**	**0.206**	0.020	-0.080	0.082	0.091	0.069	-0.108	0.116	0.125	0.095
	0.936	*0.031*	*0.046*	*0.850*	*0.258*	*0.275*	*0.198*	*0.330*	*0.299*	*0.292*	*0.229*	*0.360*
TSS	-0.028	0.108	0.011	0.011	0.099	0.035	0.105	0.063	0.135	0.054	0.166	0.096
	0.792	*0.329*	*0.920*	*0.916*	*0.162*	*0.637*	*0.138*	*0.374*	*0.193*	*0.624*	*0.110*	*0.359*

Correlation coefficients in bold are statistically significant at p<0.01 and 0.05

Table 5.3 summarises the correlation coefficients of PCNs and PBDEs against the physicochemical parameters of water while the p-values are in italics. PCN (average of the CNs), CN 13, PBDE (average of the BDEs), and BDE 17 were selected to represent PCN and PBDE homologues among others and correlated with the physicochemical parameters. The applicability of average CN and BDE for the representation of PCNs and PBDEs was validated by the strong significant correlation of

PCN and PBDE with CN 13 and BDE 17, respectively. The assessment shows that both the PCNs and PBDEs have strong substantial and negative relationship with water salinity, total dissolved solids and electrical conductivity, although, this may vary with the molecular mass of the PCN. The strong significant relationship of the two pollutants with salinity, TDS, and electrical conductivity corroborate the association of PCN and PBDE with waste as posited by numerous researchers (Jiang *et al*., 2019; Liu *et al*., 2014; Liu *et al*., 2012; de Wit *et al*., 2010). The strong substantial relationship between salinity, TDS, PCN and PBDE provides considerable information on the potential health risk of high concentration of the congeners in water.

Only the PCNs showed significantly negative correlation with temperature and pH (p-value < 0.01). No significant relationship was exhibited between the PBDEs and either temperature or pH (p-value > 0.05). Similarly, atmospheric pressure exhibited a strong significant and positive relationship with PBDEs (p-value < 0.01) while its relationship with PCN was not significant (p-value > 0.05). Turbidity showed no significant relationship with either PCN or PBDE while the nature of the relationship of oxidation-reduction-potential with PCN and PBDE are dependent on molecular mass. The deduction on PCN relationship with ORP suggests that potency of chlorinated congeners vary with the degree of chlorination. The findings also have important implication on their biodegradability and sorptivity (CICAD, 2001). Hence, at certain concentration threshold, trichloronaphthalene can exhibit the degradability attributes of highly chlorinated PCN (CICAD, 2001).

5.3.5 Correlation analysis across the sites and seasons

The correlation matrix across the three sampling sites and seasons were determined using XlStat engine of Microsoft Excel and the results are displayed in Table 5.4. The means of $\sum_8$PCNs in water samples of NEL, CHA, and MMC during winter and spring were designated as NwintWCN, CwintWCN, MwintWCN and NsprWCN, CsprWCN, MsprWCN, respectively. The mean $\sum_8$PCNs during summer across the three sites is coded as NsumWCN, CsumWCN and MsumWCN. The The highest correlation coefficient of 0.787 in Table 5.4c showed that there is a strong linear relationship between NsumWCN and MsumWCN, while the correlation between NsumWCN and CsumWCN is extremely weak (0.017). The average $\sum_6$PBDEs values during winter, spring and summer in NEL water samples were designated as NwintWBDE, NsprWBDE, NsumWBDE and CHA (CwintWBDE, CsprWBDE, CsumWBDE). The correlation coefficients of 0.871 during spring between NSprWBDE and CSprWBDE is an indication that strongly linear correlation existed between water samples from these two sites and PBDE during summer, but the relationship existing between NsumWBDE and CsumWBDE is extremely weak (0.032).

Table 5. 4 Correlation of PCNs and PBDEs in water samples across sites

(A)

	NwintWCN	CwintWCN	MwintWCN
NwintWCN	1	-0.081	-0.567
CwintWCN	-0.081	1	-0.083
MwintWCN	-0.567	-0.083	1

The values in the table represent the correlation coefficeients.

(B)

	NsprWCN	CsprWCN	MsprWCN
NsprWCN	1	-0.066	-0.217
CsprWCN	-0.066	1	-0.363
MsprWCN	-0.217	-0.363	1

The values in the table represent the correlation coefficeients.

(C)

	NsumWCN	CsumWCN	MsumWCN
NsumWCN	1	0.017*	0.787
CsumWCN	0.017*	1	0.284
MsumWCN	0.787	0.284	1

The values in the table represent the correlation coefficeients.

(D)

	NwintWBDE	CwintWBDE
NwintWBDE	1	0.556
CwintWBDE	0.556	1

The values in the table represent the correlation coefficeients.

(E)

	NSprWBDE	CSprWBDE
NSprWBDE	1	0.871
CSprWBDE	0.871	1

The values in the table represent the correlation coefficeients.

(F)

	NsumWBDE	CsumWBDE
NsumWBDE	1	0.032*
CsumWBDE	0.032*	1

The values in the table represent the correlation coefficeients.

5.3.6 Estimated risks due to PCNs and PBDEs

5.3.6.1 Estimated risks due to PCNs

With the application of relative potencies of each PCN congener, the estimated TEQs for NEL, CHA and MMC water are listed in Table 5.5.

Table 5. 5 Estimated TEQs for PCNs in NEL, CHA and MMC water samples

PCNs congeners	TEQ (µg/L) NEL	TEQ (µg/L) CHA	TEQ (µg/L) MMC
CN 2	2.69×10^{-5}	2.94×10^{-5}	2.39×10^{-5}
CN 6	1.28×10^{-6}	5.04×10^{-7}	4.10×10^{-7}
CN 13	6.10×10^{-7}	6.50×10^{-7}	7.39×10^{-7}
CN 52	6.67×10^{-7}	1.45×10^{-7}	1.19×10^{-7}
CN 66	3.12×10^{-3}	6.62×10^{-5}	1.47×10^{-4}
CN 73	5.62×10^{-4}	2.19×10^{-5}	2.56×10^{-5}
CN 75	1.18×10^{-6}	1.0×10^{-7}	1.24×10^{-7}

According to the results, TEQ values for NEL, CHA, and MMC water samples varied from 6.10×10^{-7}-3.12×10^{-3} µg/L, 1.0×10^{-7}-6.62×10^{-5} µg/L and 1.19×10^{-7}-1.47×10^{-4} µg/L, respectively. The highest TEQ value of 0.0031 µg/L was due to CN 6 at NEL. All the results obtained from this study are below 0.0001-0.211 µg/L TEQ values recorded from River Chenab, Pakistan (Mahmood *et al.*, 2014), which is the only available TEQ data on water samples. CNs 66, 73 and 2 were the major donors to the TEQ values recorded in this study. The results are all less than one, and this implies that the selected waters are safe.

5.3.6.2 Estimated risks due to PBDEs

PBDE levels recorded in this study were compared with the Federal Environmental Quality Guidelines (FEQG) for PBDEs in Canada: tri-BDEs (0.046 µg/L), tetra-BDEs (0.024 µg/L), penta-BDEs (0.0002 µg), hexa-BDEs (0.12 µg/L), and hepta-BDEs (0.017 µg/L) (Environment Canada, 2013). The average values recorded in this study at NEL for BDE 17 (tri-BDEs) across the three seasons were 0.319±0.522 µg/L, BDE 47 and 66 (tetra-BDEs, 0.422±0.689 and 0.181±0.295 µg/L respectively), BDE 100 (penta-BDEs, 0.179±0.327 µg/L), BDE 153 (hexa-BDEs, 0.012±0.008

µg/L), and BDE 183 (hepta-BDEs, 0.022±0.003 µg/L). The concentrations at NEL were above the set FEQG except for BDE 153. In CHA, BDE 17 measured 0.055±0.046 µg/L, BDE 47 and BDE 66 (0.023±0.029 and 0.011±0.003 µg/L) individually, BDE 100 (0.009±0.003 µg/L), BDE 153 (0.009±0.002 µg/L), and BDE 183 (0.016±0.002 µg/L). BDEs 47, 66 and 153 in CHA were below the FEQG set limits for water.

Associated health risks due to PBDEs in the water were further determined by calculating the noncarcinogenic risk using the available reference doses for BDE-47 and BDE-153. According to Table 5.6, the estimated daily intakes (EDIs) of Σ_2PBDEs were 3.0×10^{-4}-1.41×10^{-2} µg /kg/day for adults through drinking of water. Following the EDIs, hazard quotients (HQs) corresponding to the theoretical noncarcinogenic risk were 1.6×10^{-3}-1.41×10^{-1}. The HQ values were lower than one, suggesting that usage of the water would not cause a noncarcinogenic health risk. Nevertheless, their oral consumption would only be possible after strict compliance with other microbiological, physical and chemical qualities of water.

Table 5. 6 Estimated daily intake (EDI) and hazard quotient due to PBDEs in water

	NEL		**CHA**	
PBDEs	**EDI (µg/kg/day)**	**HQ**	**EDI (µg/kg/day)**	**HQ**
BDE 17	1.06×10^{-2}	-	1.83×10^{-3}	-
BDE 47	1.41×10^{-2}	1.41×10^{-1}	7.7×10^{-4}	7.7×10^{-3}
BDE 66	6.04×10^{-3}	-	3.7×10^{-4}	-
BDE 100	5.98×10^{-3}	-	3.0×10^{-4}	-
BDE 153	4.0×10^{-4}	2.0×10^{-3}	3.1×10^{-4}	1.6×10^{-3}
BDE 183	7.2×10^{-4}	-	5.3×10^{-4}	-

Conclusions

In this study, PCN concentrations were assessed in water samples collected from three different bodies of surface water, while PBDE concentrations were evaluated from two sites (NEL and CHA). The results have established the ubiquitous nature of both pollutants (PCNs and PBDEs) in Port Elizabeth, ECP, South Africa. This study has presented the pollution state of the water sources in relation to the PCN TEQ values and the Hazard Quotient for BDE 47 and BDE 153. Information on the possible fate and contamination risk of the waterbodies by PCNs and PBDEs were drawn from their interrelationship with physicochemical parameters. The following conclusions were drawn from the assessments:

- The prevalence and concentration of the chlorinated and brominated congeners decrease with increase in the degree of halogenation.
- The seasonal levels of these two pollutants are a function of the topography of the sites; NEL had higher concentrations of both chemicals during wet season, believed to have emanated from heavy deluge that discharged wastes into the lake, while PCN concentrations in CHA and MMC followed the same trend during winter and summer due to their similar nature as a flowing water.
- The concentrations of PCN in NEL water exceeded those of the remaining two waterbodies, while PBDE levels in NEL are above that of CHA.
- The molecular mass plays a relevant role in the correlation of PCN with salinity.
- Mono- and tri-CNs, tri- and penta-bromodiphenyl ethers constitute the most predominant halogenated pollutants in the Port Elizabeth surface water within permissible limits.

All the pollution sources into these surface waterbodies should be controlled considering the elevation of TDS concentration above the standard limit in CHA and MMC. Further studies on PCN levels in other environmental matrices and human samples are required globally.

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CHAPTER SIX

Determination of environmental levels of polychlorinated naphthalenes and polybrominated diphenyl ethers in sediments from lake, river and canal

Abstract

This study reports concentration of polychlorinated naphthalenes, PCNs in sediments from three waterbodies in Port Elizabeth, ECP of South Africa and polybrominated diphenyl ethers, PBDE levels at two of these sites. Soxhlet was used for samples extraction, and analysed using GC-µECD. Moisture content, organic matter and organic carbon of the sediment samples were in the range of 0.01–18.92%, 0.08–4.47% and 0.05–2.59% respectively across the three sites. The $\sum_8$PCNs in NEL, CHA and MMC sediment samples were 0.991–237 µg/kg dw, 0.429–1889 µg/kg dw and 0.260–6744 µg/kg dw, independently. The results revealed that MMC sediments were more polluted with PCNs. Levels of $\sum_6$PBDEs varied as 0.354-28.85 µg/kg dw in NEL and 0.347-6.468 µg/kg dw in CHA sediments. The calculated TEQ due to PCNs in NEL, CHA, and MMC sediment samples varied from 3.70×10^{-5}-1.96×10^{-2} ug/kg, 1.10×10^{-5}-6.40×10^{-2} µg/kg and 4.43×10^{-5}- 4.19×10^{-1} µg/kg, respectively. MMC had the highest TEQ values, while CNs 66, 73 and 2 were the main contributors to the TEQ. The running of Pearson's correlation matrix on the data revealed that all the selected PCN and PBDE congeners have strong positive correlation with the organic matter and carbon. Studies have linked high POP levels in aqueous systems with inflows of industrial and municipal wastes, thus, the elevated levels of these pollutants especially PCNs could result from effluents discharged from surrounding industries and residences. Hence, there is need for government to sensitize the citizens on pollution control measures.

Keywords: persistent organic pollutants, congeners, bioaccumulation, lipophilic, toxic equivalency

6.1 Introduction

Organo-halogens such as polychlorinated naphthalenes (PCNs) and polybrominated diphenyl ethers (PBDEs) were industrially manufactured since 1900s in several countries for their huge contribution to livelihood and improvement of technologies (Falandysz *et al*., 2008). PCNs make up a valuable component of polymerics for production of engine oil, wood coatings, cable insulators, capacitors, raw materials for dyes, among other applications (Gewurtz *et al*., 2018; CICAD, 2001). Meanwhile, PBDEs find application in production of plastic fire retardants for electronics, construction materials, furniture materials, textiles, and automobiles (Ji *et al*., 2017). About 75 PCN congeners distributed into eight homologues (Agunbiade *et al*., 2020; UNEP, 2017) and 209 PBDE congeners have been reported (Ji *et al*., 2017). In the recent time, scientists are becoming worried about the environmental and medical health challenges of leachates from PCNs and PBDEs due to their ubiquitous distribution, bioaccumulation potential and toxicity (Jiang *et al*., 2018; Daso *et al*., 2013; de Wit, 2002). Health concerns and toxicity cases such as feto-toxins, embryo-toxins, and teratogenic effects were related to PCNs (Dat *et al*., 2019; Klimczak *et al*., 2018). PBDEs were noted for the disruption of thyroid hormone balance and have been responsible for neurological defects (Alharbi *et al*., 2018).

PCNs and PBDEs were reported to leach into the environment during their production, usage and disposals, reservoir and river have played substantial role in the leaching. Both PCN and PBDE have been detected in water (Liu *et al*., 2018; Mahmood *et al*., 2014), fish (Gewurtz *et al*., 2018; Sun *et al*., 2016), air (Hu *et al*., 2019; Harrad *et al*., 2006), and human samples (Li *et al*., 2020; Matovu *et al*., 2019). Sediments are regarded as natural reservoir and conveyor medium for POPs where they are rapidly adsorbed on suspended solids existing in the aquatic sediments (Qiu *et al*., 2020; Olukunle *et al*., 2015). The hydrophobic nature of POPs also supports their accumulation in sediments (Malik *et al*., 2014; Binelli *et al*., 2007). Organic carbon (OC) contents in sediment are a key determinant in the absorption and distribution of POPs in environmental matrices. A strong positive correlation between OC and POP concentrations indicates that organic matter influences POPs movement and partitioning in sediment (Xiong *et al*., 2015). These chemicals enter the aquatic environment via direct or indirect discharge, deluge or as deposits in the atmosphere (Kannan *et al*., 2001). Li *et al*. (2019) pointed out that lakes are major reservoir for POPs; residual POPs in the soil and atmosphere are washed into the lake by rain and thereafter, the chemicals settle on the sediments. As a result, investigation of their occurrence in sediment would unravel the extent of pollution of the selected area. Past studies from across different regions of the world, including Taiwan (Dat *et al*., 2019), East China (Liu *et al*., 2018), Czech Republic (Kukucka *et al*., 2015), Pakistan (Mahmood *et* *al*., 2014), North China (Pan *et al*., 2011) among others, have reported PCN occurrences in sediment. These investigations evaluated the concentrations, congener profile, and ecological risk of the contaminants in their respective environment. However, reports on PCN occurrence in South African environment are still limited.

PBDEs have been universally detected in sediment samples around the globe; China (Pei *et al*., 2018; Ju *et al*., 2016), USA (Samara *et al*., 2006; Oros *et al*., 2005), Japan (Minh *et al*., 2007), Belgium (Covaci *et al*., 2005), Czech Republic (Kukucka *et al*., 2015), Korea (Moon *et al*., 2012, 2007), Nigeria (Ohajinwa *et al*., 2019), Ghana (Essumang *et al*., 2018) among other studies. Some researchers have reported PBDEs occurrence and distribution in sediment samples from certain Provinces of South Africa (Sibiya *et al*., 2019, 2017; Daso *et al*., 2016) to mention a few. Except for the reports of Olisah *et al*. (2020) on Sunday and Swartkops Estuaries, published data on PBDE levels in ECP, South Africa is still insufficient. Hence, the justification for embarking on this study.

This chapter describes the environmental levels of PCNs in sediments of three Port Elizabeth waterbodies, while PBDEs was reported at two sites. The waterbodies include Chatty River, North End Lake and Markman Canal. The sites have been described in the previous chapters. Samples were collected from August to December, 2020. Certain physicochemical parameters (such as moisture content, organic matter and carbon), levels of PCNs and PBDEs in the sediment samples were evaluated. PCN concentrations obtained from this study were compared with previous studies from other nations. Measured PBDE levels in this study were collated in relation to reports from South Africa and other parts of the world. The reported data will serve as a reference for subsequent studies on these pollutants in South Africa and globally.

6.2 Materials and methods

6.2.1 Solvents and standards

GC grade solvents: acetone, dichloromethane (DCM), ethyl acetate, n-hexane, and isooctane were bought from Sigma-Aldrich (Merck Pty Ltd, SA); dehydrated sodium sulphate (AR grade), silica gel (70–230 mesh), copper fine powder (> 230 mesh ASTM), and alumina (70-290 mesh) were also bought from Merck Pty Ltd SA. PBDEs (BDE-MXD) and PCNs (PCN-MXA) standard mixtures were bought from Wellington’s laboratory, Canada. Surrogate standard, TCMX (CAS Number 877-09-8) was procured from LGC Limited (Dr. Ehrenstorfer Laboratories, Augsburg, Germany).

6.2.2 Site description

The description of the studied sites was given in previous chapters.

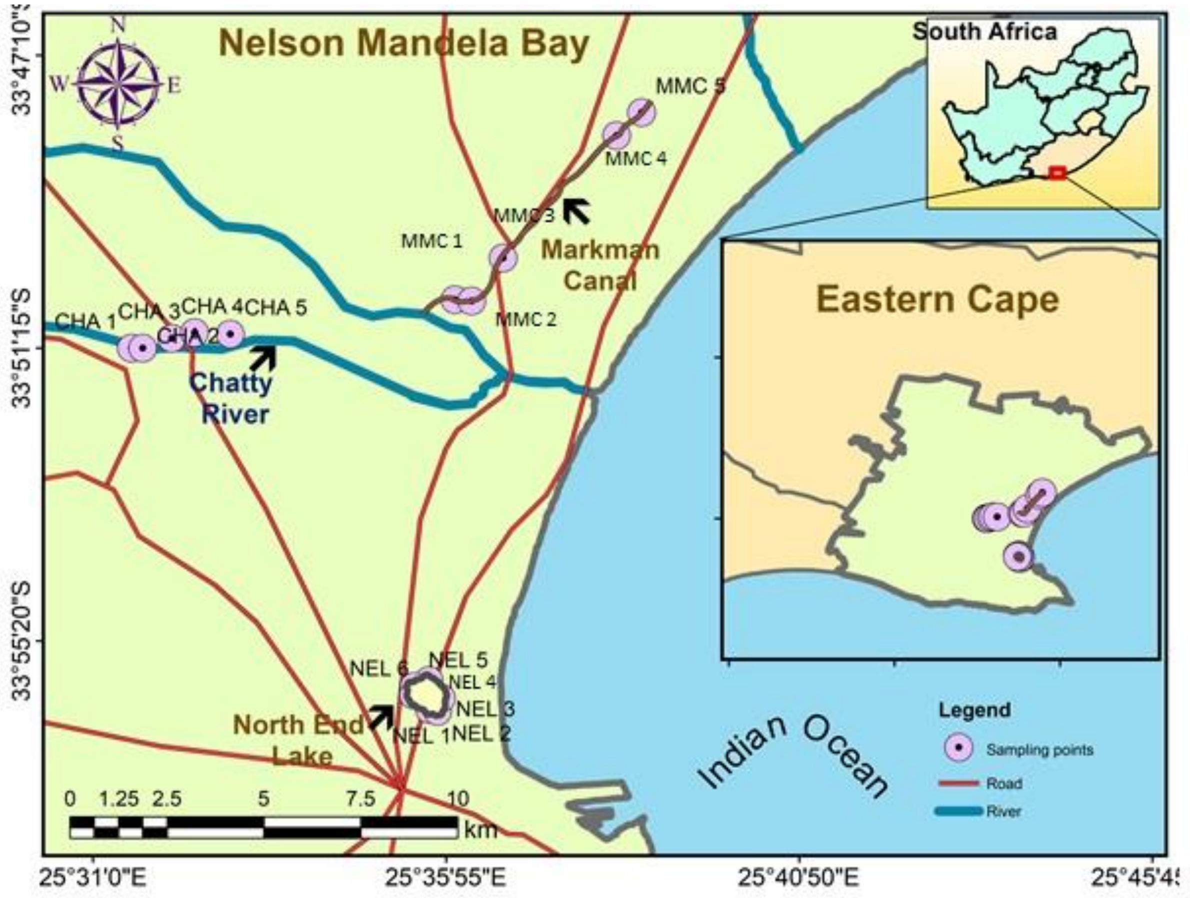

Figure 6. 1 The study area map

6.2.3 Sample collection and preservation

Forty-four sediments were collected with grab sampler across three sampling sites between August and December, 2020. The samples were stored in aluminium foil and preserved with ice packs. They were air-dried for several days in a well-ventilated drying room, and sieved with 500-µm mesh sized sieve to remove foreign matters. Moisture, organic carbon (OC) and organic matter (OM) contents were evaluated with gravimetric procedures (Heiri *et al*., 2001).

6.2.4 Extraction of PCNs and PBDEs from sediment samples

Chlorinated naphthalenes in sediment samples were extracted by the method of Mahmood *et al.* (2014), while the method of Covaci *et al*. (2005) was employed for PBDE extraction. Full details of the extractions are described in chapter 4. A control specimen was analysed following the same procedure to ensure quality control.

6.2.5 Instrumental analysis

The quantification of eight PCN congeners (CNs 2, 6, 13, 28, 52, 66, 73, 75) and six PBDE congeners (BDEs 17, 47, 66, 100, 153, 183) in the purified extracts were determined with an Agilent 7820A gas chromatograph GC (Agilent technologies, Santa Clara, CA, USA) coupled with microelectron capture detector (µ-ECD) fitted with an Agilent HP-5 column, while the identification of the PCN/PBDE congeners was performed using GC-MS. The operating conditions for both pollutants were already stated in previous chapters; in brief, one µL sample was injected in splitless mode at inlet temperature of 300°C. Helium was the carrier gas used at a flow rate of 3 mL/min (for PBDEs) and 2 mL/min (for PCNs). The detector temperature was 325°C for both pollutants. The initial and final oven temperature was fixed at 100°C and 310°C for PBDEs quantification (Wang *et al*., 2016a), while it was 80°C and 270°C respectively for PCNs (Mahmood *et al*., 2014**)**. PCNs and PBDEs in the samples were quantified using Agilent Chemstation chromatographic software integrated into the equipment.

6.2.6 Data analysis

Descriptive analysis of data was achieved by Microsoft excel 16 packages. Regression analysis, Kendal-tau, and Spearman rho correlations were performed to measure the association between the PCN, PBDE and the sediment physicochemical parameters in IBM SPSS 21 version (Pei *et al*., 2018).

6.2.7 Quality Control

Glasswares were properly cleaned with liquid soap, tap water and deionized water before and after each use. Rinsing with methanol and acetone followed that of deionised water, and they were finally oven dried at 105°C. All the solvents used for analysis were GC or analytical grade. The analytical procedures were monitored by analysing the surrogate standard and procedural blank alongside each batch of samples. Selected samples were spiked with known volume of surrogate standard to ascertain extraction method efficiency. Procedural blanks were simultaneously analysed with samples to monitor possible contamination during the analysis (Barhoumi *et al.*, 2019). Results replicability were established after eight-repeated running (injections) on the instrument of 40 μg/L calibration standard solution. The instrument was automatically operated and part of the coding instructions was for the GC syringe to wash itself several times before and after each injection with specific organic solvents.

6.3 Results and discussion

6.3.1 Seasonal levels of physicochemical parameters of sediments

The average moisture content (MC), organic matter (OM), and organic carbon (OC) contents of the sediment samples are displayed in Figure 6.2 and Appendix 3.

The MC for NEL sediment samples during winter, spring and summer were in the range of 0.04-0.20%, 1.3-6.1% and 4.3-8.0% respectively. The OM and OC followed the same trend as 0.4-1.6%, 0.2-0.9%, 0.1-2.2% and 0.1-1.3%, 0.14-1.8%, 0.1-1.0%. CHA had MC in the range of 0.01-0.2%, 1.2-2.4% and 4.2-10.2% in winter, spring and summer. The OM were 0.4-1.2%, 0.2-0.3% and 0.2-1.3% during winter, spring and summer. OC on the other hand was 0.3-0.7%, 0.1-0.2%, 0.1-0.8% in winter, spring and summer. The MC for MMC sediments during winter, spring and summer were 0.4-2.6%, 3.2-9.5%, and 4.3-18.9% sequentially, while the OM and OC followed the same trend as 0.4-4.5%, 0.2-1.1%, 0.4-2.0% and 0.2-2.6%, 0.1-0.6%, 0.2-1.2% in winter, spring and summer, respectively. It was observed that the MC was highest in summer but least in winter across the three sampling sites. This can be linked with the drought peculiar to dry (winter) seasons in South Africa (Archer *et al.*, 2019). Organic carbon composition is an important feature that regulates POPs' partitioning in sediment (Wang *et al.*, 2016b). The maximum OC value (2.6%) from this study was recorded at point 4 on Markman Canal (MMC); this value was greater than those recorded in sediment from Yellow River, China (0.61 ± 0.19%, Pei *et al.*, 2018), seven major river basins in China (2.03 ± 1.00%, Wang *et al.*, 2016b), and Beijiang River, China (1.29 ± 0.82%, Chen *et al.*, 2009). However, it was below that from Lake Shihwa, Korea (4.5 ± 5.1%, Moon *et al.*, 2012).

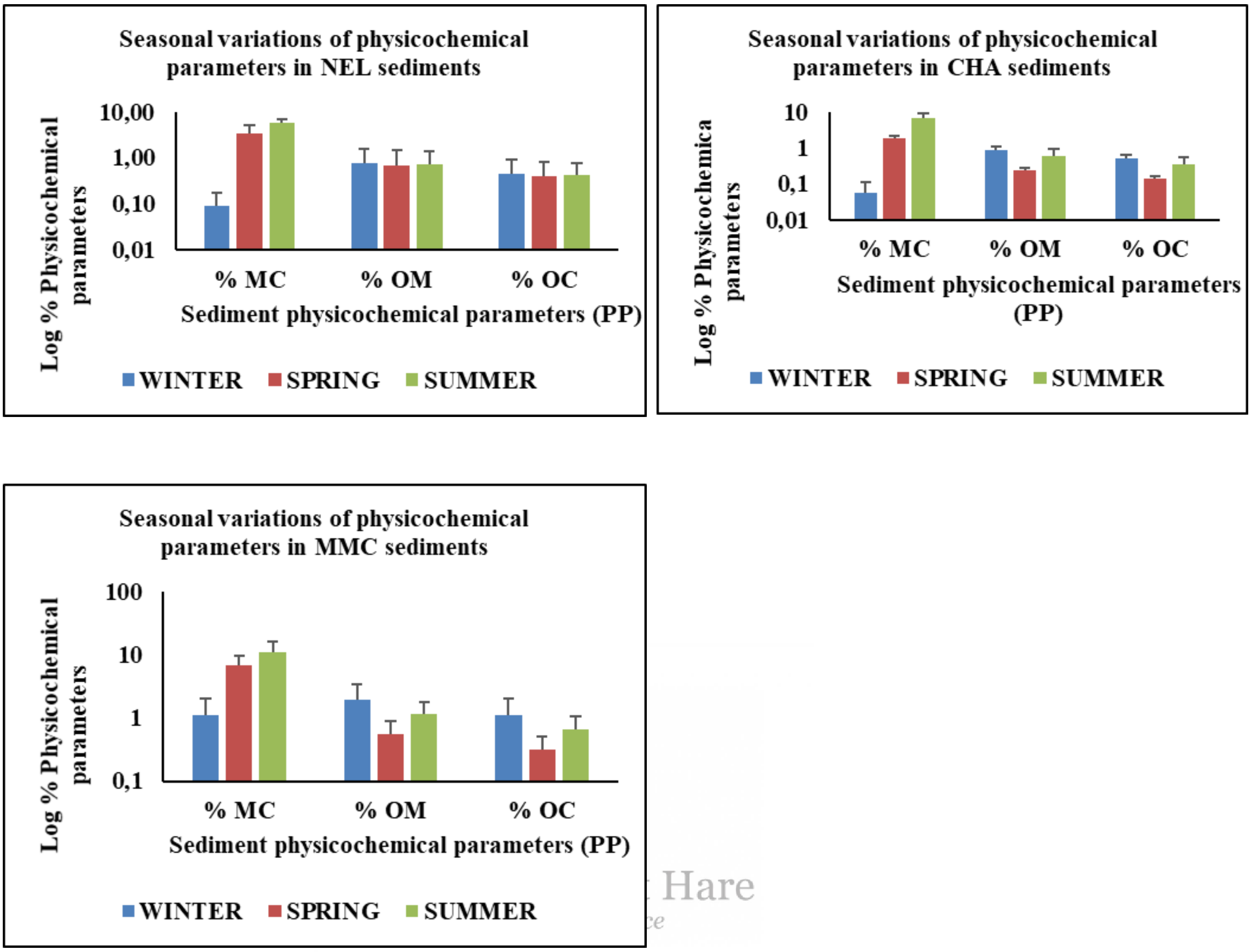

Figure 6. 2 Seasonal variations of physicochemical parameters in NEL, CHA and MMC sediments

6.3.2 Seasonal variations of PCN levels in sediment samples

The changes in PCN concentrations in sediment samples across the seasons and sampling locations are depicted in Figures 6.3 and 6.4.

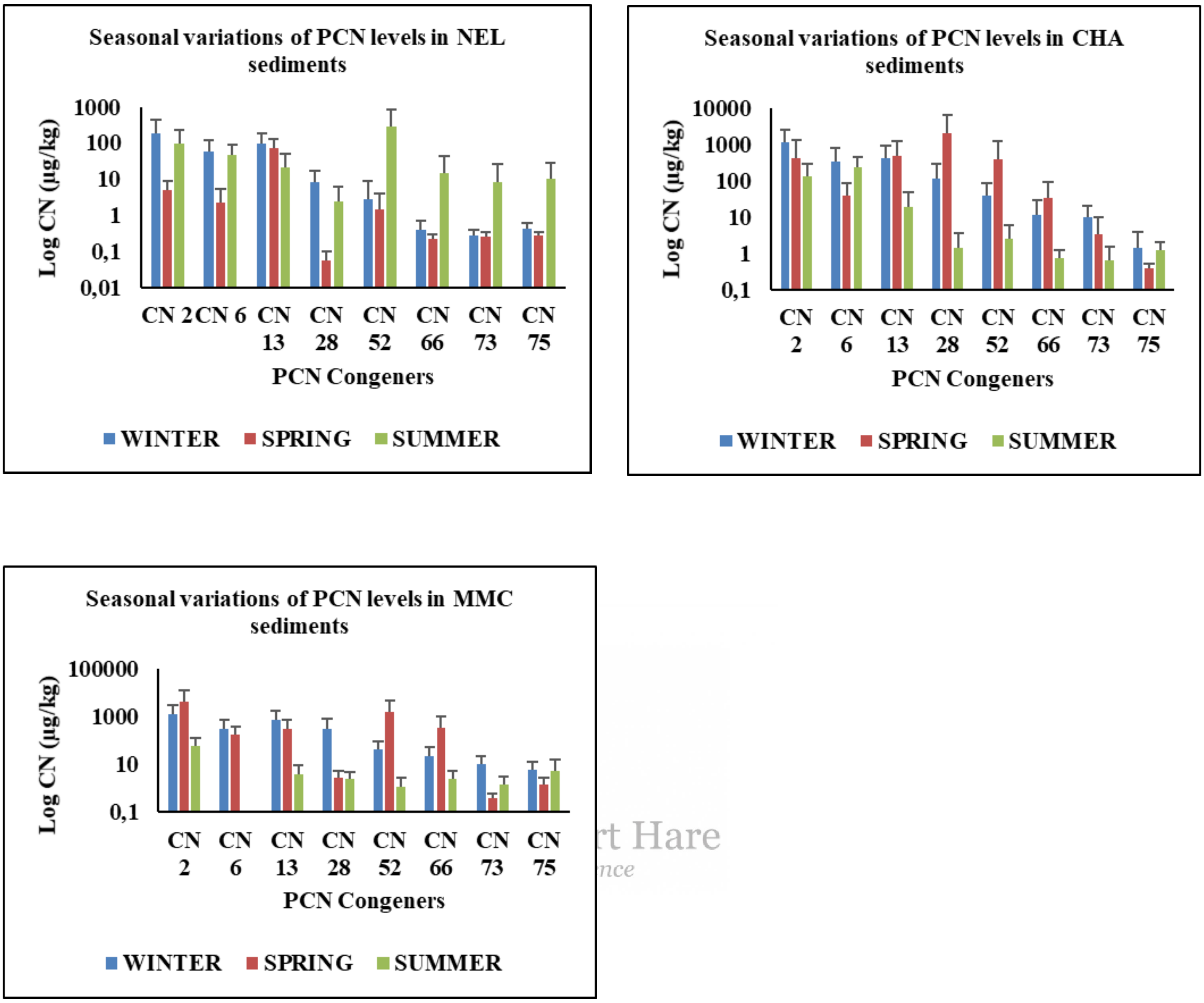

Figure 6. 3 Seasonal variations of PCN levels in NEL, CHA and MMC sediment samples

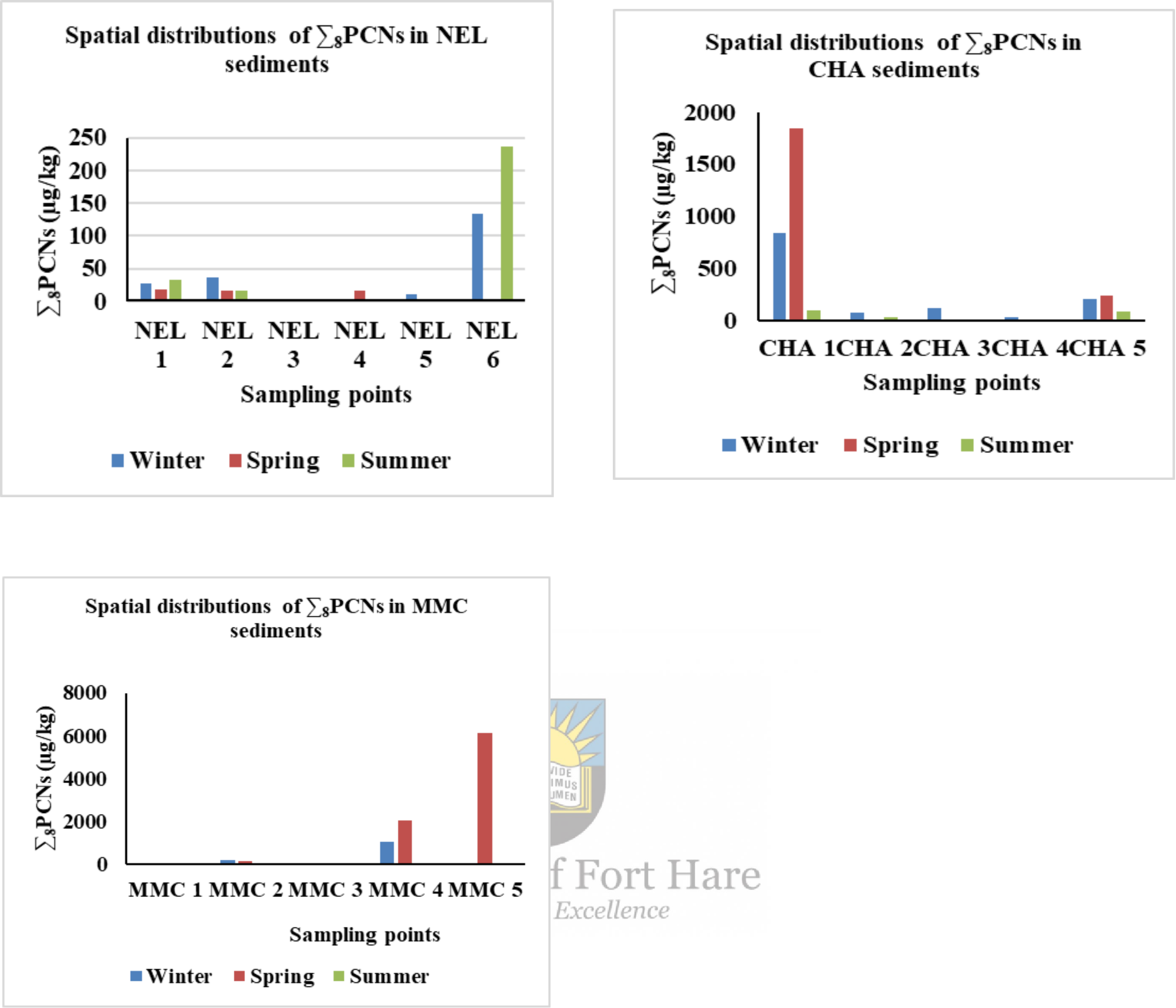

Figure 6. 4 Spatial distributions of $\sum_8$PCNs in NEL, CHA and MMC sediments

The $\sum_8$PCNs in NEL sediments during winter, spring and summer varied from 2.323 to 134 µg/kg, 2.951-20.046 µg/kg and 0.991-237 µg/kg. The decreasing trend was as follows: summer > winter > spring. The highest levels during summer could have arisen from dilution effect caused by POPs' condensation that is most prominent during this period. Winter is usually characterised by drought resulting in POPs' precipitation (Olisah *et al*., 2020; Sibiya *et al*., 2017). The low PCN levels in sediment samples during spring could be that the pollutants were still in the liquid phase during sampling and were yet to sink to the bottom of the lake where they could be adsorbed on the sediment. All the congeners were detected at all selected points on the lake except at NEL 3 where sediment sample could not be obtained throughout the sampling periods. CN 52 had maximum concentration in sediment samples during summer at NEL 6. The $\sum_8$PCNs levels in sediments collected from NEL 6 also exceeded other points. This sampling point (NEL 6) is located opposite an industrial area and very close to a drainage system, which empties municipal and industrial wastes directly into the lake anytime it rained. NEL becomes polluted by these overflows and wastes (Kampire *et al*., 2017); hence, the high PCN levels from this point could be linked to the inflows. NEL 1 and 2 are other points with high $\sum_8$PCNs. Reports have shown that an area with elevated PCN compositions are abundant in fine particles and organic matters (Liu *et al*., 2018). In the case of this lake, NEL 1, 2 and 6 could be regarded as being rich in both particulates and organic matters. The dominant congeners in the sediment were CN 2 (33.1%), followed by CN 52 (32.33%) > CN 13 (21.91%) > CN 6 (7.39%) > CN 66 (1.73%) > CN 75 (1.28%) > CN 28 (1.22%) > CN 73 (1.04%). The prevalence of penta- and mono-CNs are rarely reported, most studies have tri-, tetra- and hepta-CNs as the dominating congeners (Liu *et al*., 2018; Mahmood *et al*., 2014; Pan *et al*., 2011). The dominance of CN 2 at this site could be because of breakdown of the higher chlorinated homologues in this region (Mahmood *et al*., 2014). The $\sum_8$PCNs in CHA sediment samples varied from 32.771-836 µg/kg (winter), 0.429-1888 µg/kg (spring) and 0.846-99 µg/kg (summer). The trend was as follows: spring > winter > summer. CN 2 had maximum value in winter at CHA 1, while CN 28 had the highest concentration during spring at the same CHA 1. The high PCN levels in sediment samples during spring could be from deposition of airborne PCNs with those in soil by raindrops and their eventual release into the waterbody along with the deluge (Pei *et al*., 2018). CN 28 (37.5%) had the highest percentage distribution across the three seasons, followed by CN 2 (28.7%), CN 13 (16.3%), CN 6 (9.3%), CN 52 (7.5%), CN 66 (0.8%), CN 73 (0.2%) and CN 75 (0.1%).

From Figure 6.4, it can be observed that CHA 1 contained higher $\sum_8$PCNs than the remaining points. CHA 1 is positioned within a residential area, from where the river is being polluted with fresh domestic effluents and wastes (Adams *et al*., 2019).

The $\sum_8$PCNs in MMC sediments varied from 9.535-1055 µg/kg, 11.093-6744 µg/kg, and 0.260-34.3 µg/kg. It followed the order: spring > winter > summer. The concentrations of individual CNs were higher at MMC 4 and 5 during the three seasons. Elevated $\sum_8$PCNs were also recorded at MMC 4 and 5 sediments when compared with other points. Both points are situated within the manufacturing area of the Markman community from where untreated industrial effluents are discharged into the canal (Adams *et al*., 2019). Liu *et al*. (2018) linked high PCN levels in aqueous environment to industrial and municipal wastes. One can infer that these two points were the most polluted. CN 2

(63.7%) was the dominating congener across the three seasons, followed by CN 52 (14.6%), CN 13 (10.5%), CN 6 (4.7%), CN 66 (3.4%), CN 28 (2.8%), CN 73 and 75 (0.1% each)

When the PCN levels in this study are compared with other reports around the world, the values measured here are lower than those recorded in Detroit River, USA (1.23–8200 µg/kg, Marvin *et al*., 2002) and Near Chlor-alkali plant, Georgia, USA (196000–23400 µg/kg, Kannan *et al*., 1998). However, the findings here are above the published reports from Laojie River, Northern Taiwan (0.408–1.47 µg/kg, Dat *et al*., 2019), Yellow River, China (0.618-130 µg/kg, Li *et al*., 2017), Liaohe River Basin, China (0.33-12.49 µg/kg, Li *et al*., 2016), and Lake Ontario, Canada (21–38 µg/kg, Helm *et al*., 2008). However, PCN concentrations from Yangtze River Delta, East China (0.60–4600 µg/kg, Zhang *et al*., 2015) and River Chenab, Pakistan (8.94–414 µg/kg, Mahmood *et al*., 2014) exceeded values obtained from NEL and CHA in this study. MMC sediments were more polluted with PCNs than the other two sites.

6.3.3 Seasonal variations of PBDE levels in sediments

The variations of PBDE levels in sediment samples across the three seasons are depicted in Figures 6.5 and 6.6.

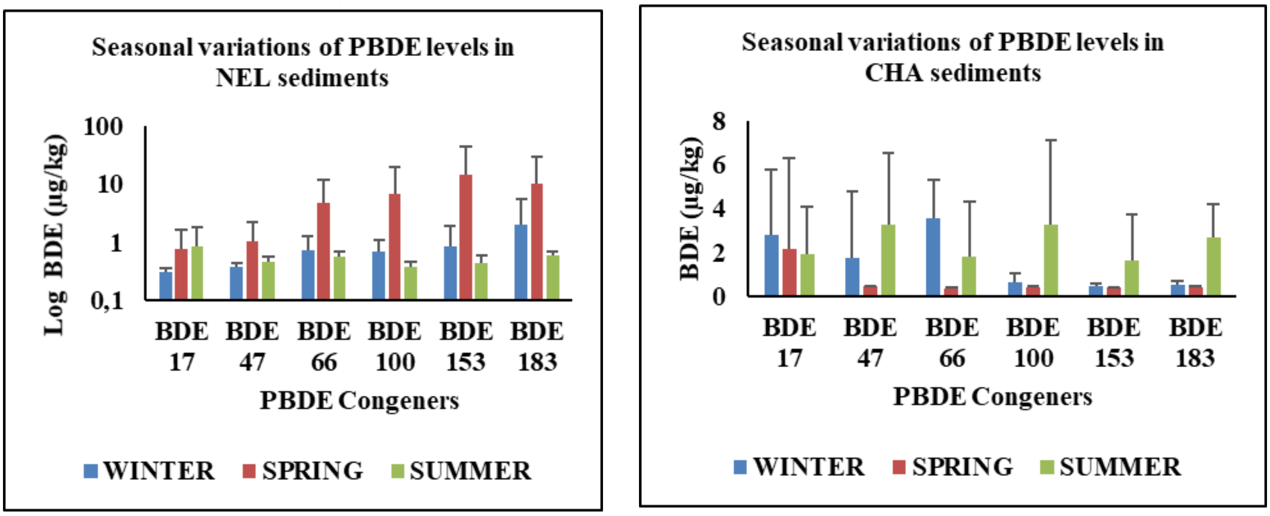

Figure 6. 5 Seasonal variations of PBDE levels in NEL and CHA sediment samples

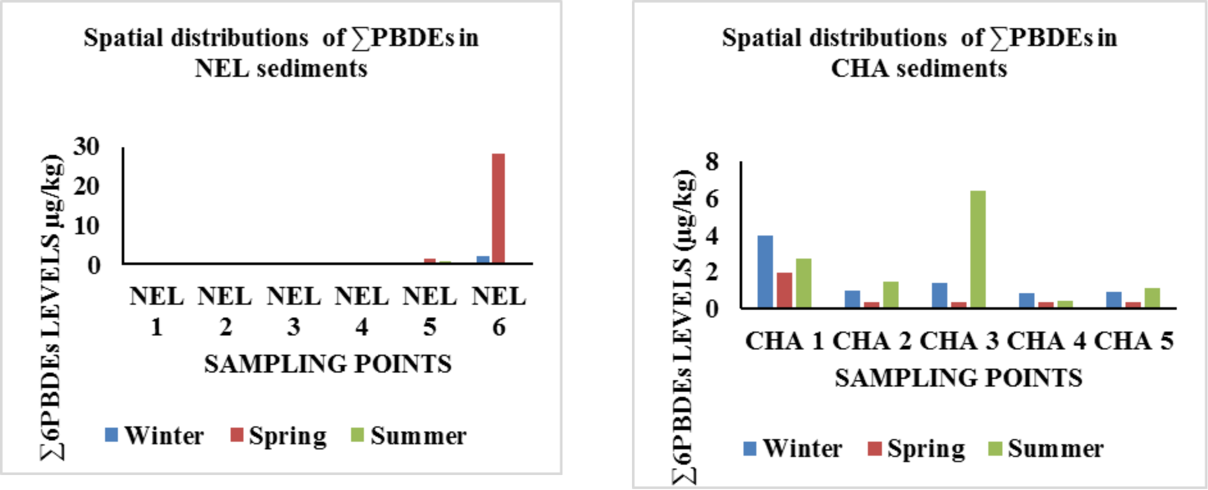

Figure 6. 6 Spatial distributions of $\sum_6$PBDEs in NEL and CHA sediments

The $\sum_6$PBDEs levels in NEL sediment samples across the three seasons ranged from 0.354-2.462 µg/kg in winter, 0.381-28.850 µg/kg (spring), and 0.390-0.851 µg/kg (summer). The decreasing order is spring > winter > summer. All the BDE concentrations were on the high side during spring with BDE 153 recording the highest value. The percentage distribution is BDE 153 (29.4%), BDE 183 (25.6%), BDE 66 (25.2%), BDE 100 (14.7%), BDE 17 (3.6%) and BDE 47 (3.6%). The high PBDE concentrations during spring season could have emanated from existing PBDE residues in the soil being drained into the lake by the rainfall (Lv *et al*., 2015), or precipitation of airborne PBDEs (Pei *et al*., 2018). For the spatial distribution of PBDEs in the lake sediments, the sum $\sum_6$PBDEs were appreciable at all points, but was highest at NEL 6. NEL 6 could be inferred to contain more PBDE levels than any other points on the lake. With the elevated levels of both classes of pollutants in NEL 6 sediments, it can be concluded that this point was most polluted.

Likewise, the $\sum_6$PBDEs concentrations in CHA sediments ranged from 0.806-4.141 µg/kg (winter), 0.347-2.219 µg/kg (spring), and 0.455-6.468 µg/kg (summer). The trend was summer > winter > spring. BDE 17 had the highest percentage (24.2%), while other congeners, BDE 66 (20.1%), BDE 47 (19.3%), BDE 100 (14.6%), BDE 183 (12.9%) and BDE 153 (8.9%) followed the progression. CHA 1 and 3 sediments contained more $\sum_6$PBDEs than other points. With the levels of both pollutants in CHA 1, this point could be said to be the most polluted at this site.

The values obtained in this study were below those recorded in Sundays Estuary, Eastern Cape Province, South Africa (0.08–32.41 µg/kg, Olisah *et al*., 2020), Danube catchment, Czech Republic (0.0057-29.2 µg/kg dw, Kukucka *et al*., 2015), Taihu Lake, China (0.39-34.44 µg/kg, Zhou *et al*., 2012), Niagara River, New York, USA (0.72-148 µg/kg, Samara *et al*., 2006), Pearl River Delta, China (0.04-94.7 µg/kg, Mai *et al*., 2005) and Scheldt River, Belgium (1.4-272 µg/kg dw, Covaci *et al*., 2005). PBDE levels in surface sediment of Beijiang River, South China (0.26-5.64 µg/kg, Xiong *et al*., 2016), Yellow River, China (0.02-0.609 µg/kg, Pei *et al*., 2018), Chaohu Lake basin, China (0.06–5.41 µg/kg, Liu et al., 2018) exceeded those from this study. NEL sediments contained more PBDEs than the other site.

6.3.4 Correlation of PCNs and PBDEs with physicochemical parameters of sediments

A regression analysis was employed to determine the association between congeners and physicochemical parameters, and further corroborated with non-parametric spearman rho and Kendall tau analysis as illustrated in Tables 6.1–6.3. The result indicates that the summed PCNs shared no relationship with either of the physicochemical parameters (Table 6.1). In contrast, the summed PBDE showed a strong correlation with the sediment physicochemical parameters. The variation in the degree of association of the two pollutants with the physicochemical data could be due to the differences in the polarizability of the congeners. Brominated congeners have been posited to exhibit a more substantial degree of polarizability than the chlorinated congeners. This possibly accounted for PBDE consistency with physicochemical parameters of sediments (Falandysz *et al*., 2019). The polarizability of congeners is influenced by the measurement of their hydrophobicity and lipophilicity (Mamy *et al*., 2015).

Table 6. 1 Regression analysis of PCNs and physicochemical parameters of sediments

Regression Statistics	MC-PCN	OM-PCN	OC-PCN
Multiple R	0.018	0.041	0.041
R Square	0.000	0.002	0.002
Adjusted R Square	-0.011	-0.010	-0.010
Standard Error	1002.024	1001.338	1001.338
Significance F	0.869	0.704	0.704

Table 6. 2 Regression analysis of PBDEs and physicochemical parameters of sediments

Regression Statistics	MC-PBDE	OM-PBDE	OC-PBDE
Multiple R	0.294	0.501	0.501
R Square	0.087	0.251	0.251
Adjusted R Square	0.076	0.242	0.242
Standard Error	5.416	4.906	4.906
Significance F	0.005	0.000	0.000

Considering the consistency of the congeners, each of them was examined for their relationship with the sediment physicochemical parameters as shown in Table 6.3. According to Table 6.3, each of the CNs varies randomly, with only CN 13 and CN 28 exhibiting a significant negative relationship with moisture content. In contrast, CN 66 and CN 75 exhibited a positive and significant connection with moisture content. The proportionality existing between PCN molecular mass and moisture content points to the synchronization between the moisture content of highly drained sediments and octanol-water partition coefficient of organics than to the aqueous solubility of the organochlorines. Expectedly, enormous significant synchronization is exhibited between organic matter or carbon and the PCN homologues except for CN 13, whose variance was attested by Kendall-tau and Spearman rho. The brominated congeners exhibited an irregular relationship with moisture content, and this might be due to the variability in their lipophilicity. Their correlation with the OM and OC is strongly significant.

Table 6. 3 Correlation of PCNs, PBDEs and physicochemical parameters of sediments

	Kendall-Tau			Spearman rho		
	MC	**OM**	**OC**	**MC**	**OM**	**OC**
MC	1.000	0.101	0.101	1.000	0.119	0.119
	.	*0.162*	*0.162*	.	*0.268*	*0.268*
OM	0.101	**1.000**	**1.000**	0.119	**1.000**	**1.000**
	0.162	.	.	*0.268*	.	.
OC	0.101	**1.000**	**1.000**	0.119	**1.000**	**1.000**
	0.162	.	.	*0.268*	.	.
CN 2	-0.134	**0.237**	**0.237**	**-0.213**	**0.324**	**0.324**
	0.068	*0.001*	*0.001*	*0.048*	*0.002*	*0.002*
CN 6	-0.045	**0.247**	**0.247**	-0.009	**0.331**	**0.331**
	0.610	*0.005*	*0.005*	*0.943*	*0.010*	*0.010*
CN 13	**-0.225**	0.083	0.083	**-0.318**	0.114	0.114
	0.003	*0.276*	*0.276*	*0.004*	*0.316*	*0.316*
CN 28	**-0.192**	**0.264**	**0.264**	**-0.367**	**0.373**	**0.373**
	0.017	*0.001*	*0.001*	*0.002*	*0.001*	*0.001*
CN 52	0.045	**0.184**	**0.184**	0.034	**0.277**	**0.277**
	0.547	*0.013*	*0.013*	*0.761*	*0.011*	*0.011*
CN 66	**0.161**	**0.271**	**0.271**	0.213	**0.372**	**0.372**
	0.030	*0.000*	*0.000*	*0.051*	*0.000*	*0.000*
CN 73	-0.080	**0.192**	**0.192**	-0.129	**0.290**	**0.290**
	0.283	*0.010*	*0.010*	*0.241*	*0.007*	*0.007*
CN 75	**0.244**	**0.230**	**0.230**	**0.372**	**0.331**	**0.331**
	0.001	*0.002*	*0.002*	*0.001*	*0.002*	*0.002*
BDE17	**0.163**	**0.306**	**0.306**	**0.216**	**0.448**	**0.448**
	0.026	*0.000*	*0.000*	*0.046*	*0.000*	*0.000*
BDE47	**0.342**	**0.229**	**0.229**	**0.493**	**0.368**	**0.368**
	0.000	*0.002*	*0.002*	*0.000*	*0.000*	*0.000*
BDE66	0.136	**0.412**	**0.412**	0.182	**0.556**	**0.556**
	0.060	*0.000*	*0.000*	*0.089*	*0.000*	*0.000*
BDE100	0.132	**0.285**	**0.285**	0.204	**0.421**	**0.421**
	0.069	*0.000*	*0.000*	*0.057*	*0.000*	*0.000*
BDE153	0.100	**0.301**	**0.301**	0.164	**0.419**	**0.419**
	0.169	*0.000*	*0.000*	*0.127*	*0.000*	*0.000*
BDE183	**0.296**	**0.205**	**0.205**	**0.423**	**0.299**	**0.299**
	0.000	*0.005*	*0.005*	*0.000*	*0.005*	*0.005*

Correlation coefficients in bold are statistically significant at p<0.01 and 0.05

6.3.5 Estimated risks due to PCNs

With the application of relative potencies of each PCN congener, the estimated TEQs for NEL, CHA and MMC sediment samples are presented in Table 6.4.

Table 6. 4 Estimated TEQs for dioxin-like PCNs in NEL, CHA and MMC sediments

PCN congeners	TEQ (ug/kg) NEL	TEQ (ug/kg) CHA	TEQ (ug/kg) MMC
CN 2	1.73×10^{-3}	1.04×10^{-2}	3.4×10^{-2}
CN 6	4.29×10^{-5}	2.63×10^{-4}	2.61×10^{-4}
CN 13	2.80×10^{-4}	1.55×10^{-3}	1.60×10^{-3}
CN 52	3.94×10^{-4}	6.33×10^{-4}	1.95×10^{-3}
CN 66	1.96×10^{-2}	6.40×10^{-2}	4.19×10^{-1}
CN 73	9.06×10^{-3}	1.41×10^{-2}	1.22×10^{-2}
CN 75	3.70×10^{-5}	1.10×10^{-5}	4.43×10^{-5}
Σ_7PCNs	3.11×10^{-2}	9.10×10^{-2}	4.69×10^{-1}

Table 6. 5 Comparison of sediments TEQs for PCNs with worldwide reports

Location/Country	TEQ (µg/kg dw)	Prevalent congener	References
North End Lake, South Africa	3.70×10^{-5}- 1.96×10^{-2}	CN 66, 73 and 2	This study
Chatty River, South Africa	1.10×10^{-5}- 6.40×10^{-2}	CN 66, 73	This study
Markman Canal, South Africa	4.43×10^{-5}- 4.19×10^{-1}	CN 66, 2, and 73	This study
Feitsui Reservoir and Laojie river, Taiwan	3.4×10^{-6}-7.1×10^{-4}	CN 66/67, 69 and 73	Dat *et al*., 2019
East China Sea, China	0-0.212	CN 2 and 73	Liu *et al*., 2018
Upper Danube catchment, Czech Republic	0.02×10^{-3} - 0.017		Kukucka *et al*., 2015
Yangtze River, China	1.45×10^{-7}–2.16	CN 66/67 and 73	Zhang *et al*., 2015
River Chenab tributaries, Pakistan	0.1×10^{-3}- 0.057	CN 73, 66/67	Mahmood *et al*., 2014
Daliao River Estuary, Bohai sea, China	8.0×10^{-6} - 2.8×10^{-4}	CN 66/67 and 73	Zhao *et al*., 2011
Canada	0.017	-	Helm *et al*., 2008

The TEQ values for NEL, CHA, and MMC sediment samples ranged from 3.70×10^{-5}- 1.96×10^{-2} ug/kg dw, 1.10×10^{-5}-6.40×10^{-2} µg/kg and 4.43×10^{-5}-4.19×10^{-1} µg/kg sequentially. The highest TEQ value in this report was recorded in MMC, while CNs 66, 73 and 2 were the main contributors to the TEQ values. The TEQ obtained from this study for sediments exceeded those recorded from Daliao River Estuary, China (Zhao *et al*., 2011), Feitsui Reservoir, Laojie River, northern Taiwan (Dat *et al*., 2019), Upper Danube catchment, Czech Republic (Kukucka *et al*., 2015) and from Canada (Helm *et al*., 2008). The reports from Yangtze River, China (Zhang *et al*., 2015) exceeded results from our three sampling sites, but the results from NEL and CHA were far below those recorded in River Chenab tributaries, Pakistan (Mahmood *et al*., 2014) and East China Sea (Liu *et al*., 2018). The high TEQ measured in the East China Sea (ECS) was attributed to influents from industrial and municipal wastes being discharged into the sea (Liu *et al*., 2018).

To further establish the possible toxicity of the sediments to aquatic creatures, PCN concentrations were compared with interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) (Dat *et al*., 2019). The ISQGs and PELs in Canada for dioxins and furans are set at 0.00085 and 0.0215 ug/kg TEQ respectively (CCME, 1999). Although 0.00085 ug/kg dw TEQ represents the summation of TEQ values of all dioxins and dioxin-like compounds (PCDDs/Fs, PCBs, and PCNs) in environmental samples (Zhao *et al*., 2011), the maximum sediment TEQ (due to PCNs) recorded in this study is 0.419 ug/kg TEQ; it exceeded 0.00085 ug/kg dw TEQ (ISQGs) and 0.0215 ug/kg dw TEQ (PELs) approved by Canada. This result revealed that the TEQs due to PCNs exceeded both the ISQGs and PELs of Canada, hence it can be inferred that the waterbodies are not safe for aquatic creatures (Zhao *et al*., 2011).

Conclusions

This research has revealed the extent of pollution of three selected waterbodies (one lake, one river and canal) in Port Elizabeth with PCNs and PBDEs. Recorded PCN levels in the surface sediments were far above that of PBDEs. Although, PBDEs and PCNs were never produced in South Africa, the results obtained from the studied sites have confirmed their pervasive nature in our environment. PCN concentrations in the surface sediments were higher when compared with other related studies globally, with CN 2 as the predominating congener. The correlation analysis revealed a significant relationship between the two pollutants and the physicochemical parameters except the moisture content. TEQ values in sediments were above values obtained in most global reports and this calls for immediate intervention by the Department of Environment to save human and aquatic lives. Additional investigation is necessary to determine the environmental fate of these emerging pollutants and their associated health risks. Also, their concentrations in human samples and other environmental samples should be considered in future studies.

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CHAPTER 7

GENERAL DISCUSSION, CONCLUSION AND RECOMMENDATIONS

7.1 General discussion

The quality of our lakes and other aquatic systems that provide habitats for pelagic creatures and recreational opportunities for human beings are being threatened by different forms of pollution caused by natural and anthropogenic activities (Moon *et al*., 2012). The pollution of water, sediment, flora and fauna of the aqueous environment by trace metals (Awofolu *et al*., 2005) and POPs including polychlorinated biphenyls (Yahaya *et al*., 2018; Kampire *et al*., 2015, 2017), polycyclic aromatic hydrocarbons (Adeniji *et al*., 2019), organochlorine pesticides (Olisah *et al*., 2019), polybrominated diphenyl ethers (Sibiya *et al*., 2017), among others have been reported. Pollution reports due to polychlorinated naphthalenes (PCNs) in Africa and mostly in aqueous matrices are still scanty in the literatures. To this end, this study focussed on evaluation of the levels, seasonal variations and human health risks related with PCNs and PBDEs in South African environment.

The extraction methods' efficiency was evaluated by adding a known volume of calibration standard solutions to each sample before extraction. Solid phase extraction and soxhlet extraction methods were used for extracting the two pollutants (PCNs and PBDEs) from water and sediment samples, respectively. PCNs and PBDEs were eluted from water samples with ethyl acetate (Marti and Ventura, 1997), hexane and acetone (4:1, v/v) mixtures (Barco-Bonilla *et al*., 2015), while dichloromethane and hexane/acetone (3:1) mixture were employed for PCNs extraction (Mahmood *et al.*, 2014) and PBDEs extraction (Covaci *et al.*, 2005) from the solid samples. Average PCNs and PBDEs recoveries from water were 66-95% and 73-87%, while they were 70-88% and 78-96% from pure sand. The recoveries of the surrogate standards in water and pure sand ranged from 63.7-84.4% and 61.2-92.41% respectively. All the samples were extracted and analysed following the validated methods.

The ranges for North End Lake (NEL) water physicochemical parameters (PP) across the three seasons were as follows: temperature (15.3–23°C), pH (7.9–10.3), oxidation-reduction potential (23.4-109.5 mV), atmospheric pressure (14.52-15.56 PSI), turbidity (15.1–167 NTU), electrical conductivity (114–1291 µS/cm), TDS (55-645 mg/L), TSS (20–107 mg/L), and salinity (0.05–0.65 PSU). All the NEL water PP except for turbidity and total suspended solids were within acceptable limits. The sum of eight PCN congeners $\sum_8$PCNs and $\sum_6$PBDEs in NEL water samples varied from 0.164–2.934 µg/L and 0.009-1.025 µg/L, independently. Levels of $\sum_8$PCNs and $\sum_6$PBDEs in NEL sediment samples ranged from 0.991–237 µg/kg and 0.354-28.850 µg/kg, respectively. The calculated hazard quotients (HQs) which is equivalent to the non-carcinogenic health risk due to

PBDEs in NEL water samples ranged from 0.0020-0.1406, while the TEQ values due to PCNs varied from 6.10×10^{-7}-3.12×10^{-3} µg/L in NEL water samples and 3.70×10^{-5}-1.96×10^{-2} ug/kg dw in sediments. Only the highest PCN levels of 0.0005-79.1 µg/L reported from Llobregat aquifer in North East of Spain by Marti and Ventura (1997) exceeded the reported PCN values in this study. NEL water PBDE levels are generally above other reported studies around the globe.

The recorded PCN concentrations in NEL sediments were above those recorded from Lake Ontario, Canada (21-38 µg/kg dw, Helm *et al*., 2008), Laojie River, Northern Taiwan (0.408–1.47 µg/kg dw, Dat *et al*., 2019), Yellow River, China (0.618-130 µg/kg dw, Li *et al*. 2017), Laizhou Bay area, North China (0.12-5.1 µg/kg dw, Pan *et al*., 2011), Liaohe River Basin, China (0.33-12.49 µg/kg dw, Li *et al*., 2016), and Danube catchment, Czech Republic (0.03-13.7 µg/kg dw, Kukucka *et al*., 2015). However, PCN levels in NEL sediments were below values obtained from Yangtze River Delta, East China (0.60-4610 µg/kg dw, Zhang *et al*., 2015), River Chenab, Pakistan (8.94-414 µg/kg dw, Mahmood *et al*., 2014), the industrial region of Bitterfeld, Germany (2543 µg/kg dw, Brack *et al*., 2003), Detroit River in the U.S. (1.23-8200 µg/kg dw, Marvin *et al*., 2002), and a chlor-alkali plant in Georgia, USA (19600-23400 µg/kg dw, Kannan *et al*., 1998).

NEL PBDE values were below those reported from sediments of Taihu Lake, China (0.39-34.44 µg/kg, Zhou *et al*., 2012), Sundays Estuary, Eastern Cape Province, South Africa (0.08–32.41 µg/kg, Olisah *et al*., 2020), Danube catchment, Czech Republic (0.0057-29.2 µg/kg dw, Kukucka *et al*., 2015). NEL PBDE levels exceeded that of Paranoá Lake, Brasília, Brazil (2.51-8.1µg/kg, Annunciação *et al*., 2017), Jiaozhou Bay, North China (2.18-10.59 µg/kg, Ju *et al*., 2016), and Beijiang River, South China (0.26-5.64 µg/kg, Xiong *et al*., 2016). It was discovered during sampling that the underneath layer and the sides of the lake were secured with a rock-like materials. This could explain the reason why the pollutants (PCNs and PBDEs) remain more in the liquid phase of the lake than in the particulate phase. Hence, the elevated concentrations of these pollutants in NEL water.

The values of physicochemical parameters for water samples from Chatty River (CHA) were as follows: temperature (15.4–22.9°C), pH (7.7–10.5), TDS (991–1771 mg/L), TSS (6–41 mg/L), turbidity (1.0–197 NTU), electrical conductivity (1981–3542 µS/cm), atmospheric pressure (14.60–14.80 PSI), oxidation-reduction potential (-339.1-51.3 mV), and salinity (1.02–1.87 PSU). The EC, TDS and salinity were on the high side at some points on this site. This was attributed to incessant release of wastewaters from informal settlements surrounding the river. The ORP at some points had negative values; this showed that the water is a reducing system (Copeland and Lytle, 2014). Sum of $\sum_8$PCNs, $\sum_6$PBDEs in CHA water and sediment samples ranged from 0.026–1.054 µg/L, 0.007-0.079

µg/L and 0.429–1889 µg/kg, 0.347-6.468 µg/kg individually. The hazard quotients (HQs) corresponding to the non-carcinogenic health risk associated with PBDEs in CHA water samples ranged from 0.0003-0.0008, while the calculated TEQ values due to PCNs varied from 1.0×10^{-7}-6.62×10^{-5} µg/L in water and 1.10×10^{-5}-6.40×10^{-2} µg/kg in sediments.

Markman Canal (MMC) water samples' temperature was in the range of 15.6-24.5°C, pH (8.4-10.2), TDS (943–4002 mg/L), TSS (7-491 mg/L), turbidity (2.9-154 NTU), electrical conductivity (1885-8004 µS/cm), atmospheric pressure (14.53–14.82 PSI), oxidative reduction potential (7.8-130 mV), and salinity (0.96-4.47 PSU). The turbidity, TSS, EC, TDS and salinity were higher at some points on this site. The industrial wastes could be held accountable for this observation. The average levels of $\sum_8$PCNs in MMC water and sediment samples varied from 0.035–0.699 µg/L and 0.385-18.762 µg/kg correspondingly. The TEQ values in MMC water and sediment samples were 1.19×10^{-7}-1.47×10^{-4} µg/L and 4.43×10^{-5}-4.19×10^{-1} µg/kg respectively, MMC's sediments recorded maximum TEQ values in this study, with CNs 2, 66, and 73 being the major contributors to the TEQ. This could be ascribed to effluents from surroundings' industries (Liu *et al*., 2018).

In all the water samples, the calculated HQ was lower than one, suggesting that usage of the water would not cause a non-carcinogenic health risk (Olisah *et al*., 2020; Martellini *et al*., 2016). The TEQ values for all water samples were also below one, indicating that the waterbodies are safe but there is need for compliant with other water chemical, physical and microbiological quality parameters. However, when the estimated sediments' TEQ in this study was compared with interim sediment quality guidelines (ISQGs, 0.00085 ug/kg TEQ) and probable effect levels (PELs, 0.0215 ug/kg TEQ) of Canada for aquatic lives (CCME, 1999), it was discovered that TEQ values here exceeded both the ISQGs and PELs of Canada, indicating that the waterbodies are not safe for aquatic creatures (Dat *et al*., 2019).

Due to their hydrophobic nature, POPs are more prevalent in sediments than in water, while the highly chlorinated or brominated congeners tend to be less abundant compared to the less chlorinated/brominated congeners. Similar discovery was made in this study where the concentration trends of PCNs and PBDEs vary conversely with the extent of chlorination/bromination of the congeners (Liu *et al*., 2014). The evaluation of POPs especially PCN in water is quite uncommon. Although, there is no set limits for their levels in water or sediment, the findings from our study when compared with previous studies revealed that the PCN levels recorded in all the water samples were above other reported values across the globe except that from Llobregat groundwater in Spain (Marti and Ventura, 1997). It was also discovered that NEL water was composed of more PCNs and PBDEs.

MMC sediments were mostly polluted with PCN followed by CHA. PBDE levels in NEL water and sediments exceeded that of CHA, the elevated pollutants concentrations recorded in NEL could be because of various surface runoffs (from surrounding homes and industrial companies) that empty into the lake and their inability to flow out of the lake (Thomas *et al.*, 1996). Unlike the other two waterbodies, NEL does not flow.

The correlation analysis showed that there is strong a relationship between water salinity, TDS, EC and the pollutants (PCNs and PBDEs). The PCNs have negative significant relationship with temperature and pH; PBDEs have no significant relationship with either temperature or pH. Atmospheric pressure (AP) showed a strong significant and positive relationship with PBDEs, while AP relationship with PCN is insignificant. Pearson's correlation analysis revealed that the selected PCN and PBDE congeners have strong positive association with the organic carbon contents of the sediments; this confirms that sediments' organic matter is a major feature controlling POPs' partitioning in the environment (Moon *et al.*, 2012). The seasonal evaluations showed that more of the pollutants were recorded during the wet seasons and this aligned with previous studies on seasonal variations of POPs (Pei *et al.*, 2018; Li *et al.*, 2017).

7.2 Conclusions

Method validation is very crucial in the analytical determinations of chemical substances qualitatively and quantitatively. Validated methods were employed to determine the pollution state of three waterbodies comprising of NEL, CHA and MMC in Port Elizabeth, ECP, South Africa. This was achieved by measuring the physicochemical parameters, PCN and PBDE levels in both water and sediment samples, alongside their associated health risks. Studies have indicated that industrial and municipal wastes are the main source of these pollutants into our environment. The results from North End Lake indicated that this waterbody is more polluted with PCNs and PBDEs. This is explained by the fact that the maximum TEQ values and calculated hazard quotients (HQs) which correspond to the non-carcinogenic health risk were recorded in NEL water samples. There is need for immediate remediation of the lake and surrounding homes and companies should desist from channelling their effluents into this lake, considering its economic and recreational benefits.

The effects of elevated EC, TDS, and salinity levels in CHA water also became evident by the pollutant levels in the sediments. In addition, the TEQ values also revealed the extent of pollution of this waterbody by effluents from surrounding shantytowns and long distance travelled by this river. Government should construct lined landfills for generated wastes and proper wastewater treatment plants around this catchment area. The elevated EC, TDS, turbidity, PCN concentrations and TEQ values in MMC also confirmed the unsafe status of this waterbody for both humans and animals. The highest TEQ in this study was recorded in MMC sediments. Company owners around this locality should devise ways of treating their generated wastes before disposal into this canal.

7.3 Recommendations

Following this study, these recommendations are proposed:

(1) There is urgent need for immediate remediation and reclamation of the three waterbodies; until this is achieved, the sites should be continuously monitored. Inclusion of more sampling points is suggested in future studies for proper understanding of the spatiotemporal distribution of these pollutants. More advanced extraction methods (accelerated solvent extraction, microwave-assisted extraction) and instrument such as HRGC-HRMS, GC-MS, among others should be employed for the subsequent evaluation of these pollutants to compare extraction efficiency with recovery data.

(2) The Department of Environment and other stakeholders in water and environment sectors should review the waste management policy and the laxity accounting for industrial discharges that compromise river safety and health. The government should construct good drainage systems for our environmental wastes and continuously sensitize the populace on measures to curb surface water pollution.

(3) This study is limited in scope as it provides reference data for PCNs in two different matrices from three waterbodies in economic viable city of Port Elizabeth, South Africa, hence, further studies on PCN levels in aqueous systems and other matrices especially human samples are recommended in Africa and globally.

(4) Fishing for consumption purpose and grazing of cows on these sites should stop forthwith.

7.4 Contributions to knowledge

This study has revealed pollution status of the selected three waterbodies; NEL, MMC and CHA with two emerging pollutants (PBDEs and PCNs). This is among the foremost research on environmental levels of PCNs. Based on the reported data; the following contributions to knowledge can be deduced:

(a) the validated methods employed for the extraction and instrumental analysis can be applied to related liquid and solid samples.

(b) among all the water physicochemical parameters, the pollutant concentrations are mostly influenced by water salinity, TDS and electrical conductivity. Their distribution in sediments is dependent on organic matter and carbon.

(c) the seasonal variations of these two pollutants in both water and sediments is majorly a function of landscapes and other climatic factors.

(d) waste is a major route of releasing these pollutants into our environment as posited by other researchers, hence, proper waste management will go a long way to safeguard both human and the ecosystems from their inimical effects.

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Idowu Victoria Agunbiade, Abiodun Olagoke Adeniji, Anthony Ifeanyi Okoh and Omobola Oluranti Okoh. Seasonal variations and associated health risks of polychlorinated napthalenes in Markman Canal, Eastern Cape Province, South Africa (Submitted to Environmental Geochemistry and Health).

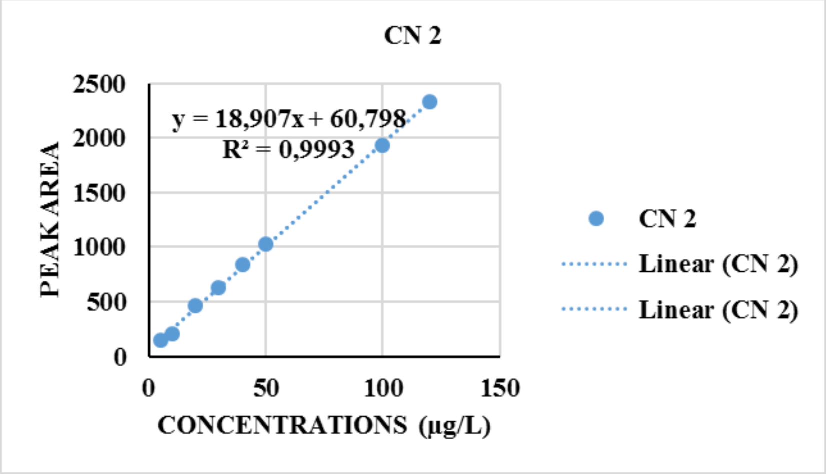
CONFERENCE PRESENTATION

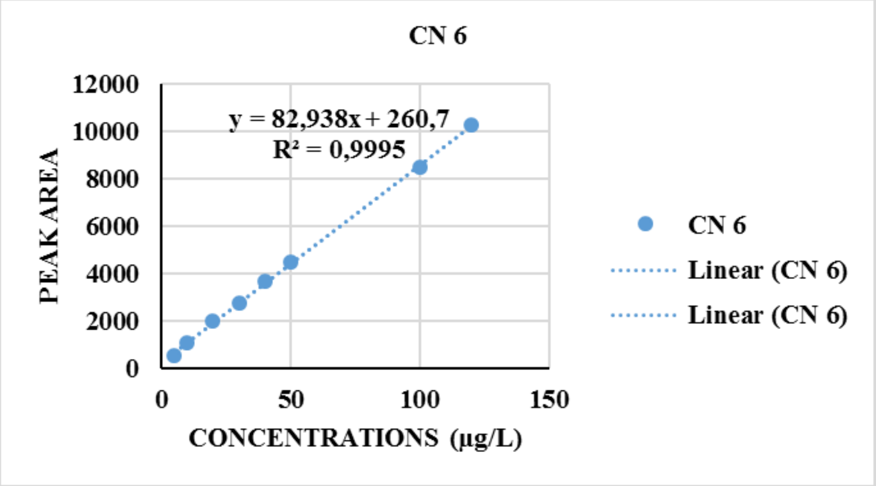
Idowu Victoria Agunbiade, Abiodun Olagoke Adeniji, Anthony Ifeanyi Okoh, Omobola Oluranti Okoh**.** Occurrence of polychlorinated naphthalenes in the North End Lake; an important recreational resort in Eastern Cape Province, South Africa - Oral presentation. 6th Biennial conference, organized by Young Water Professionals, WISA, between 20th to 23rd October, 2019 in Durban, South Africa.

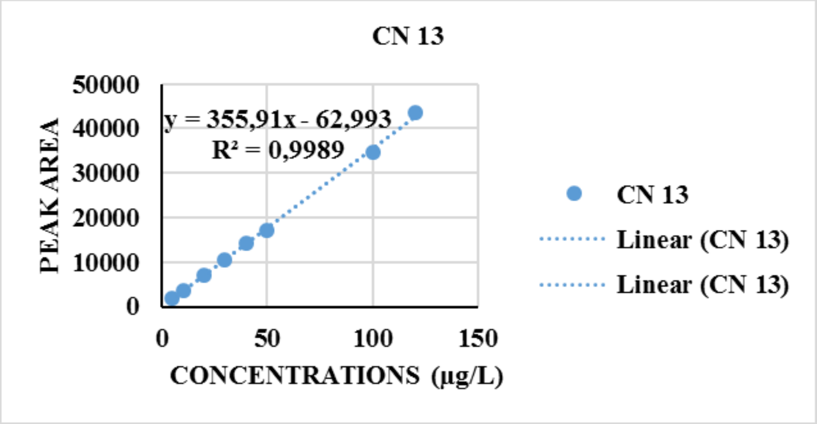
APPENDICES

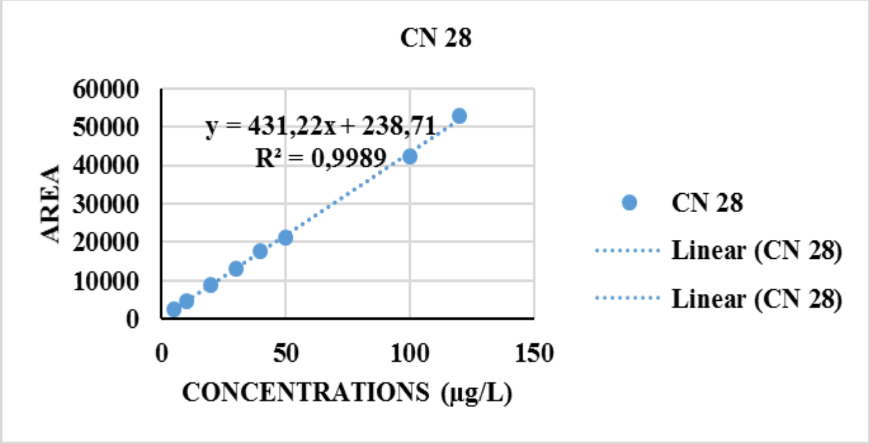
Appendix 1

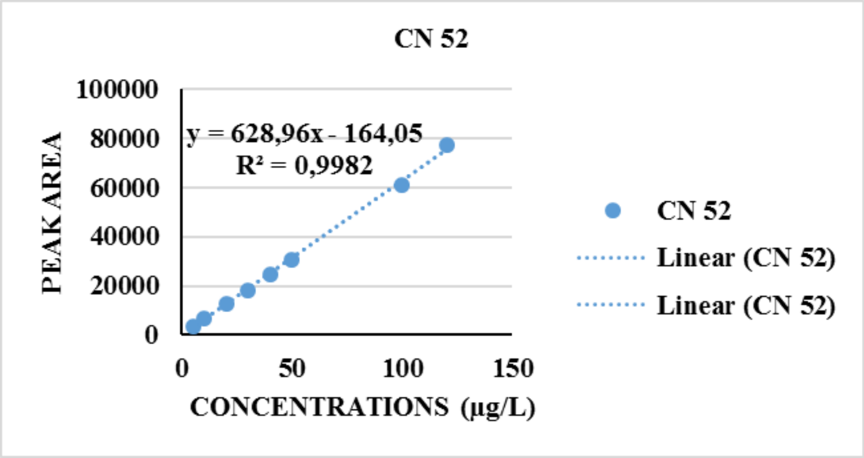
Calibration curves for studied congeners

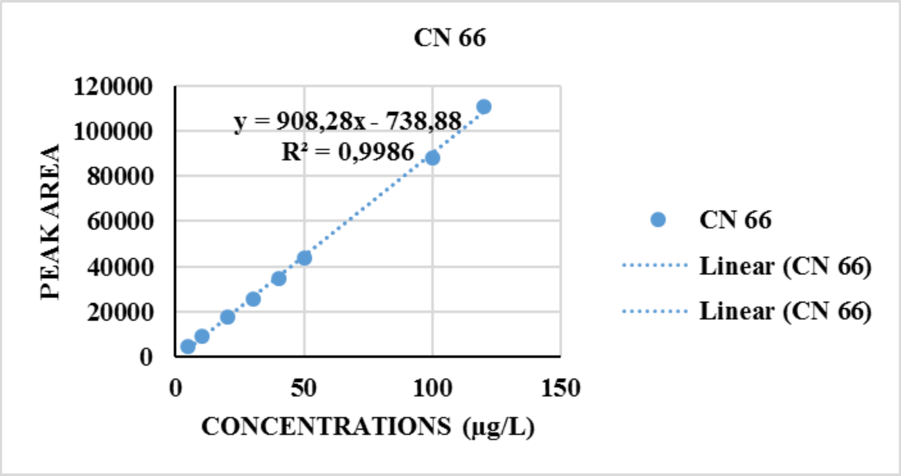


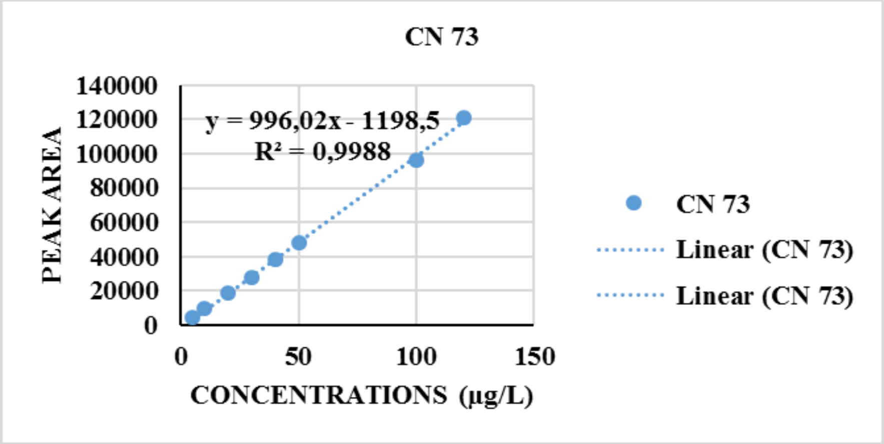


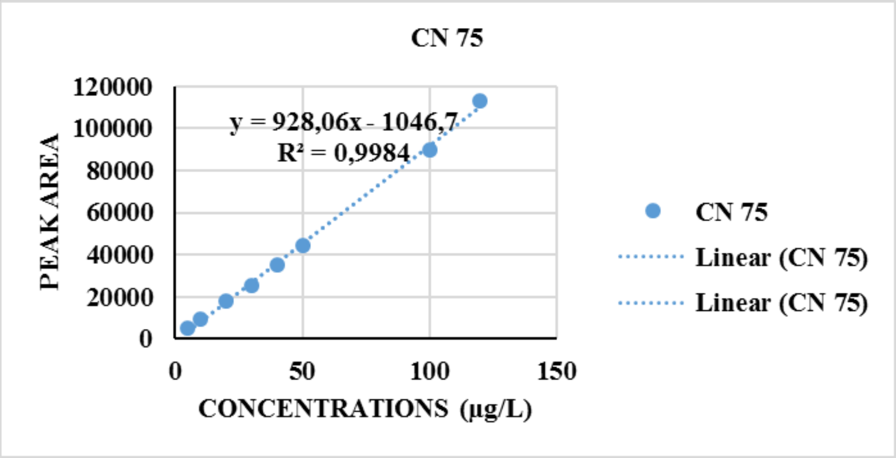


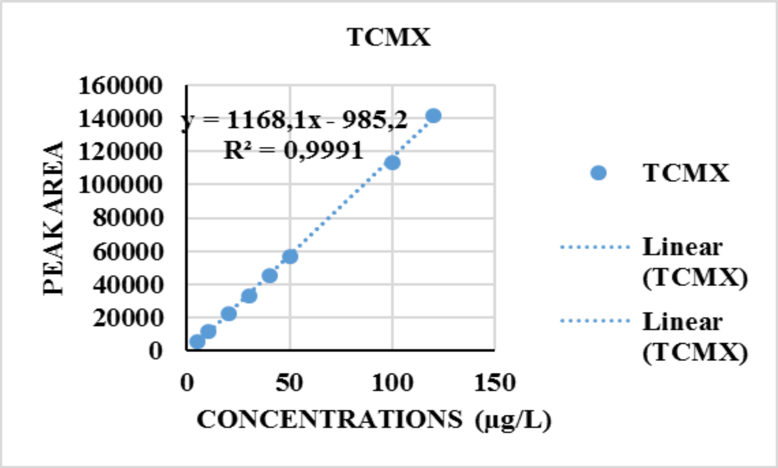


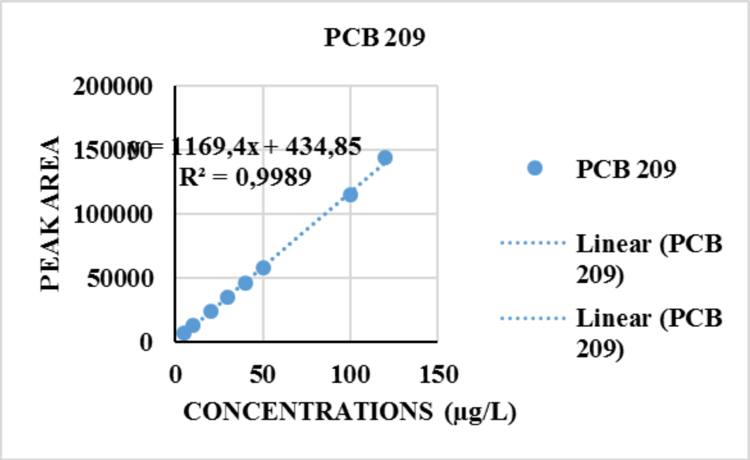

CN 52
PEAK AREA
100000
80000
60000
40000
20000
0
0
50
100
150
CONCENTRATIONS (µg/L)
y = 628,96x - 164,05
R² = 0,9982
CN 52
Linear (CN 52)
Linear (CN 52)

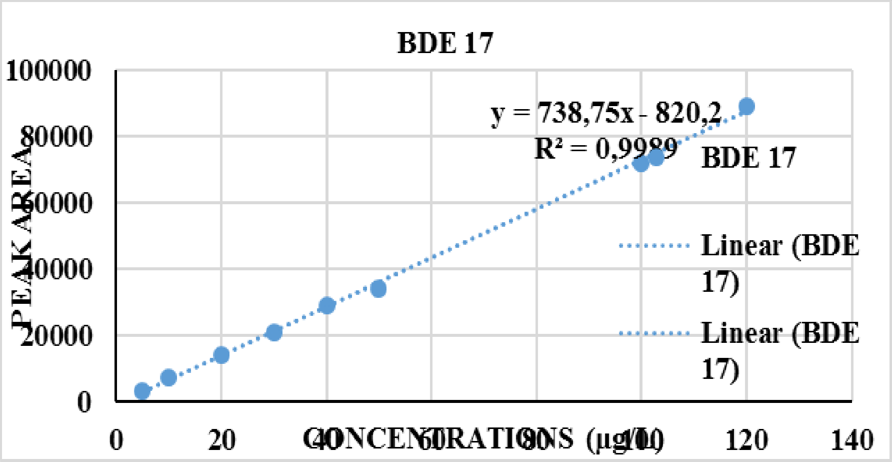

CN 66
PEAK AREA
120000
100000
80000
60000
40000
20000
0
0
50
100
150
CONCENTRATIONS (µg/L)
y = 908,28x - 738,88
R² = 0,9986
CN 66
Linear (CN 66)
Linear (CN 66)

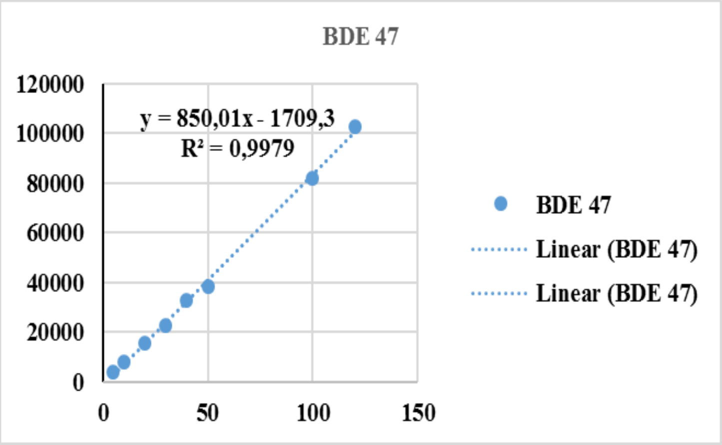

CN 73
PEAK AREA
140000
120000
100000
80000
60000
40000
20000
0
0
50
100
150
CONCENTRATIONS (µg/L)
y = 996,02x - 1198,5
R² = 0,9988
CN 73
Linear (CN 73)
Linear (CN 73)

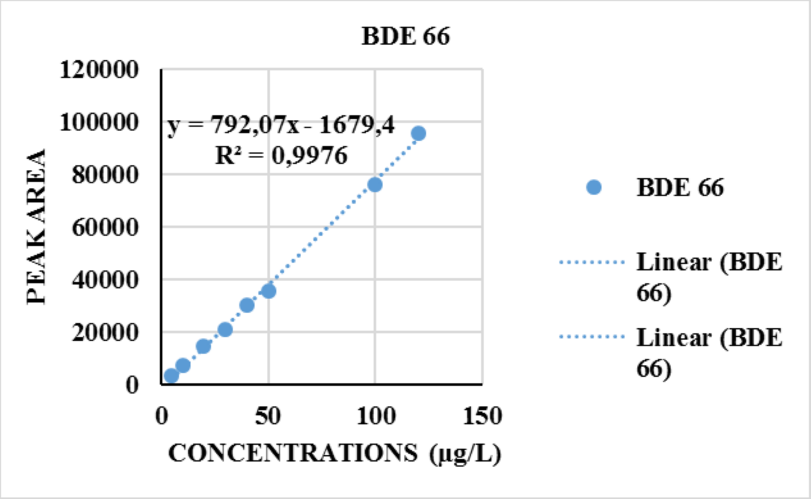

CN 75
PEAK AREA
120000
100000
80000
60000
40000
20000
0
0
50
100
150
CONCENTRATIONS (µg/L)
y = 928,06x - 1046,7
R² = 0,9984
CN 75
Linear (CN 75)
Linear (CN 75)

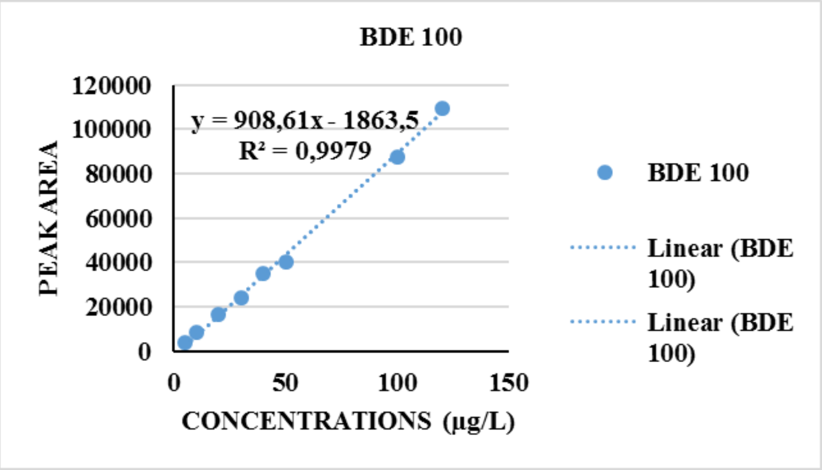

TCMX
160000
140000
120000
100000
80000
60000
40000
20000
0
PEAK AREA
y = 1168,1x - 985,2
R² = 0,9991
0
50
100
150
CONCENTRATIONS (µg/L)
TCMX
Linear (TCMX)
Linear (TCMX)

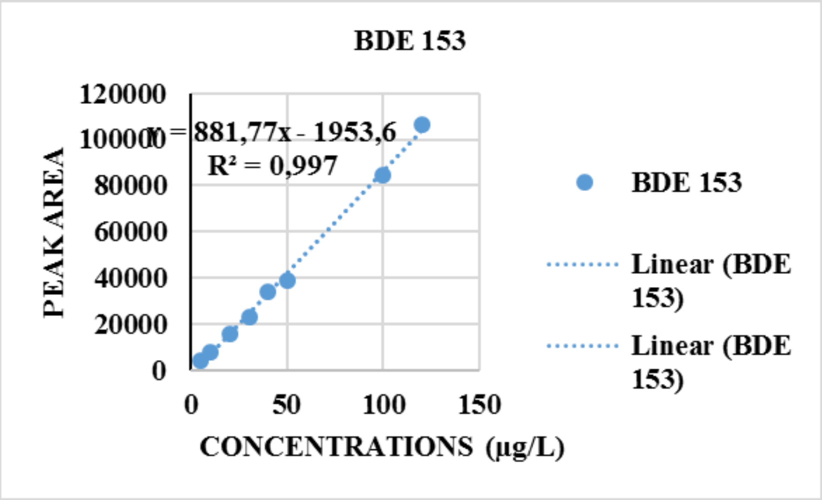

PCB 209
200000
150000
100000
50000
0
PEAK AREA
y = 1169,4x + 434,85
R² = 0,9989
0
50
100
150
CONCENTRATIONS (µg/L)
PCB 209
Linear (PCB 209)
Linear (PCB 209)

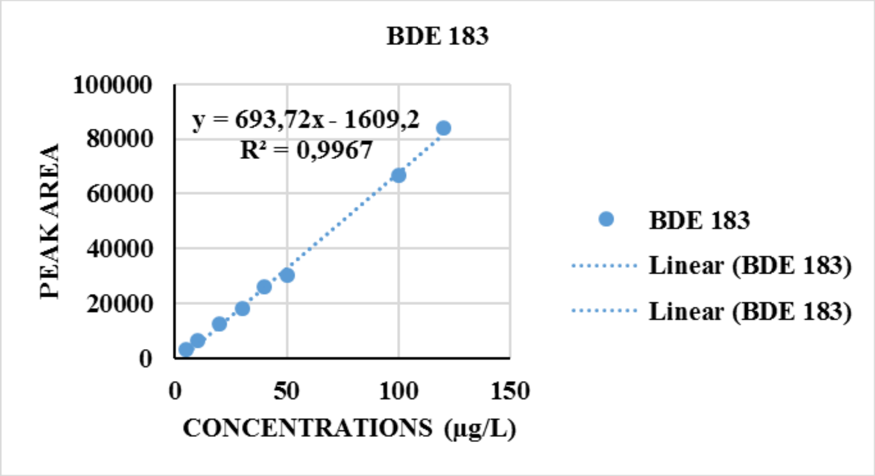

BDE 17
100000
80000
60000
40000
20000
0
PEAK AREA
y = 738,75x - 820,2
R² = 0,9989
0
20
40
60
80
100
120
140
CONCENTRATIONS (µg/L)
BDE 17
Linear (BDE 17)
Linear (BDE 17)

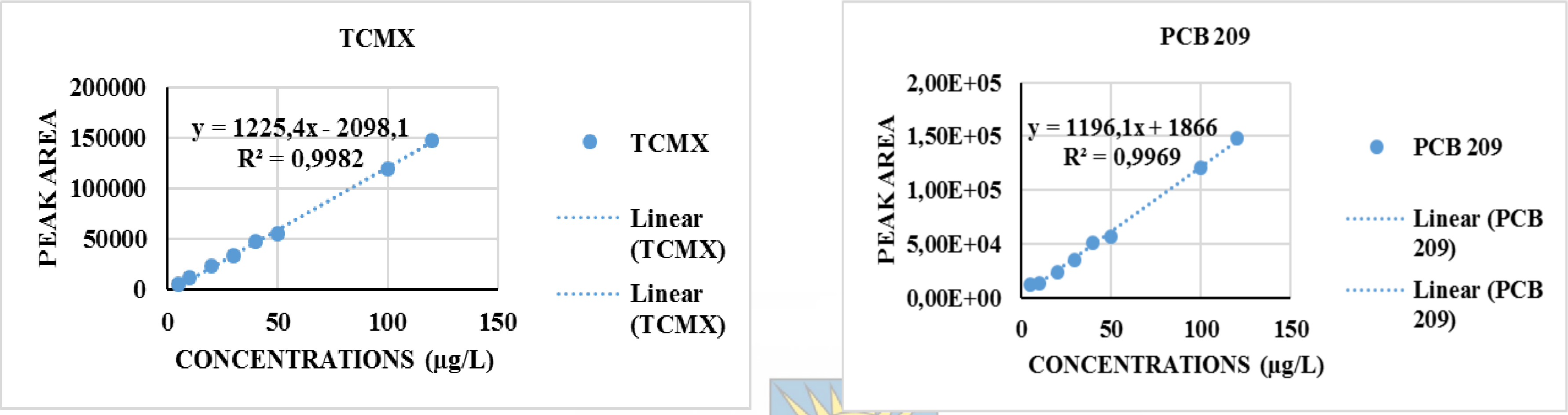

BDE 47
120000
100000
80000
60000
40000
20000
0
y = 850,01x - 1709,3
R² = 0,9979
0
50
100
150
BDE 47
Linear (BDE 47)
Linear (BDE 47)


BDE 66
120000
100000
80000
60000
40000
20000
0
PEAK AREA
y = 792,07x - 1679,4
R² = 0,9976
0
50
100
150
CONCENTRATIONS (µg/L)
BDE 66
Linear (BDE 66)
Linear (BDE 66)


BDE 100
120000
100000
80000
60000
40000
20000
0
PEAK AREA
y = 908,61x - 1863,5
R² = 0,9979
0
50
100
150
CONCENTRATIONS (µg/L)
BDE 100
Linear (BDE 100)
Linear (BDE 100)


BDE 153
120000
100000
80000
60000
40000
20000
0
PEAK AREA
y = 881,77x - 1953,6
R² = 0,997
0
50
100
150
CONCENTRATIONS (µg/L)
BDE 153
Linear (BDE 153)
Linear (BDE 153)


BDE 183
100000
80000
60000
40000
20000
0
PEAK AREA
y = 693,72x - 1609,2
R² = 0,9967
0
50
100
150
CONCENTRATIONS (µg/L)
BDE 183
Linear (BDE 183)
Linear (BDE 183)



Appendix 1: Calibration curves for analysed congeners and surrogate standards in this study

Appendix 2: Seasonal levels of the physicochemical parameters of NEL, CHA and MMC water samples

	Winter				**Spring**				**Summer**			
Parameters (NEL)	**Mean± STD**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	Mean± STD	Min	Max	**n(det)**
Temperature (°C)	15.5±0.21	15.3	16	12/12	19.7±0.5	19.1	20.6	12/12	22.2±0.6	21.5	23.0	12/12
pH	8.2±0.2	7.9	8.4	12/12	8.7±0.4	8.1	9.1	12/12	9.7±0.4	9.2	10.3	12/12
ORP (mV)	45.6±27.10	24.6	97.2	12/12	67.1±15.2	43.7	92.9	12/12	71.6±29.6	23.4	109.5	12/12
EC (µS/cm)	1078.1±450.7	114	1291	12/12	1237.6±12.2	1220	1256	12/12	1250.4±10.7	1237	1266	12/12
TDS (mg/L)	538.1±225.6	55	645	12/12	618.8±6.2	610	628	12/12	625.2±5.3	618	633	12/12
Salinity (PSU)	0.54±0.23	0.05	0.65	12/12	0.62±0.01	0.61	0.63	12/12	0.62±0.01	0.62	0.63	12/12
Atm. pressure (PSI)	14.69±0.3	14.52	15.56	12/12	14.81±0.01	14.79	14.83	12/12	14.78±0.02	14.76	14.81	12/12
Turbidity (NTU)	18.3±1.5	15.1	19.4	12/12	73.2±56.0	15.4	167	12/12	43.5±6.3	33.4	52.3	12/12
TSS (mg/L)	34.8±8.6	20	46	12/12	62.2±25.7	38	107	12/12	39.5±5.5	31	48	12/12
Parameters (CHA)	**Mean± STD**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	Mean± STD	Min	Max	**n(det)**
Temperature (°C)	16.0±0.5	15.4	16.9	10/10	21.1±0.7	20.2	22	10/10	20.2±1.5	18.8	22.9	10/10
pH	8.9±0.4	8.4	9.3	10/10	8.8±0.1	8.6	8.9	10/10	9.4±1.0	7.7	10.5	10/10
ORP (mV)	-154.1±155.2	-339.1	-0.2	10/10	-75.16±85.82	-185.60	7.5	10/10	-65.62±102.13	-244.2	51.30	10/10
EC (µS/cm)	2655.2±351.5	1981	2907	10/10	3292.6±265.77	2837	3542	10/10	2865.3±184.6	2623	3138	10/10
TDS (mg/L)	1327.8±175.6	991	1454	10/10	1646.4±132.89	1419	1771	10/10	1433.6±93.98	1311	1576	10/10
Salinity (PSU)	1.38±0.2	1.02	1.52	10/10	1.73±0.15	1.48	1.87	10/10	1.5±0.11	1.36	1.65	10/10
Atm. pressure (PSI)	14.62±0.01	14.60	14.63	10/10	14.67±0.0	14.67	14.68	10/10	14.78±0.02	14.74	14.80	10/10
Turbidity (NTU)	12.02±6.1	2	17.5	10/10	60.01±76.61	2.50	197.6	10/10	16.36±17.13	1.0	47.60	10/10
TSS (mg/L)	18.3±10.92	7	35	10/10	11.4±2.01	9	15	10/10	16.60±12.52	9	41	10/10
Parameters (MMC)	**Mean± STD**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
Temperature (°C)	16.1±0.3	15.6	16.4	8/10	23.9±0.61	22.8	24.5	10/10	21.4±0.74	20.4	22.5	10/10
pH	8.6±0.2	8.4	8.8	8/10	9.6±0.44	9.0	10.2	10/10	8.8±0.22	8.6	9.1	10/10
ORP (mV)	30.1±18.45	7.8	49.2	8/10	34.76±18.28	9.0	50.7	10/10	115.92±10.49	103.10	130	10/10

EC (µS/cm)	7151.25±529.52	6755	8004	8/10	3823.90±606.69	3043	4815	10/10	3118.20±850.07	1885	4025	10/10
TDS (mg/L)	3575.63±264.75	3378	4002	8/10	1912±303.27	1522	2407	10/10	1560±423.17	943	2012	10/10
Salinity (PSU)	3.96±0.31	3.73	4.47	8/10	2.02±0.34	1.58	2.58	10/10	1.64±0.47	0.96	2.14	10/10
Atm. pressure (PSI)	14.66±0.14	14.53	14.82	8/10	14.70±0.10	14.60	14.81	10/10	14.73±0.03	14.70	14.77	10/10
Turbidity (NTU)	59.99±62.80	2.9	142	8/10	59.37±58.60	15.0	154.2	10/10	49.8±47.35	12.20	118.10	10/10
TSS (mg/L)	76.50±69.18	7	168	8/10	170.90±196.98	26	491	10/10	20.6±19.16	4	54	10/10

Appendix 3: Percentage moisture, organic matter and organic carbon contents of NEL, CHA, MMC sediment samples

	Winter				**Spring**				**Summer**			
Parameters NEL	**Mean± STD**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
% Moisture content	0.09±0.05	0.04	0.20	10/10	3.45±1.70	1.25	6.07	10/10	5.72±1.11	4.31	7.99	10/10
% organic matter	0.78±0.37	0.39	1.56	10/10	0.69±0.78	0.08	2.24	10/10	0.74±0.59	0.14	1.77	10/10
% organic carbon	0.45±0.21	0.22	0.91	10/10	0.40±0.45	0.05	1.30	10/10	0.43±0.34	0.08	1.03	10/10
	Winter				**Spring**				**Summer**			
Parameters CHA	**Mean± STD**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
% Moisture content	0.06±0.05	0.01	0.16	10/10	1.83±0.30	1.23	2.36	10/10	6.66±2.17	4.17	10.18	10/10
% organic matter	0.87±0.23	0.44	1.19	10/10	0.24±0.04	0.17	0.30	10/10	0.60±0.34	0.18	1.30	10/10
% organic carbon	0.50±0.13	0.26	0.69	10/10	0.14±0.02	0.10	0.17	10/10	0.35±0.20	0.10	0.75	10/10
	Winter				**Spring**				**Summer**			
Parameters MMC	**Mean± STD**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
% Moisture content	1.09±0.85	0.41	2.62	8/10	6.75±2.46	3.16	9.51	10/10	10.84±4.86	4.29	18.92	10/10
% organic matter	1.90±1.41	0.39	4.47	8/10	0.55±0.31	0.16	1.07	10/10	1.13±0.63	0.36	2.03	10/10
% organic carbon	1.10±0.82	0.23	2.59	8/10	0.32±0.18	0.09	0.62	10/10	0.65±0.36	0.21	1.18	10/10

Appendix 4: PCN concentrations (μg/L) in NEL, CHA and MMC water samples during winter, spring and summer

	Winter				**Spring**				**Summer**			
Congeners	**Mean± STD (NEL)**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
CN 2	1.488±0.352	0.817	1.981	12/12	1.988±1.949	0.422	6.757	12/12	0.764±0.156	0.513	0.915	8/12
CN 6	0.162±0.082	0.056	0.309	10/12	1.428±1.901	0.097	6.489	12/12	1.467±0.653	0.650	2.774	12/12
CN 13	0.066±0.024	0.029	0.111	12/12	0.262±0.305	0.013	0.893	12/12	0.089±0.070	0.014	0.236	12/12
CN 28	0.033±0.010	0.020	0.057	8/12	0.518±0.752	0.016	1.913	8/12	0.187±0.060	0.072	0.285	12/12
CN 52	**	**	**	**	0.632±0.056	0.576	0.688	2/12	0.041±0.034	0.013	0.109	8/12
CN 66	**	**	**	**	1.184±0.873	0.271	2.188	4/12	0.034±0.004	0.031	0.038	4/12
CN 73	**	**	**	**	0.528±0.521	0.007	1.055	4/12	0.017±0.012	0.007	0.040	8/12
CN 75	0.019±0.02	0.007	0.055	12/12	0.629±0.620	0.009	1.256	2/10	0.011±0.005	0.007	0.020	8/12
$\sum_8$CNs	0.379±0.072	0.284	0.490	12/12	0.870±0.874	0.164	2.934	12/12	0.381±0.101	0.209	0.543	12/12
Congeners	**Mean± STD (CHA)**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
CN 2	2.286±1.476	1.263	5.290	10/10	1.115±0.896	0.395	2.597	4/10	0.522±0.172	0.348	0.703	4/10
CN 6	0.431±0.450	0.056	1.092	6/10	0.083±0.006	0.074	0.090	4/10	0.548±0.126	0.337	0.743	10/10
CN 13	0.271±0.187	0.084	0.640	10/10	0.089±0.067	0.027	0.216	10/10	0.041±0.029	0.018	0.093	6/10
CN 28	0.087±0.069	0.016	0.173	4/10	0.031±0.00	0.031	0.031	2/10	0.229±0.079	0.118	0.339	8/10
CN 52	0.151±0.029	0.121	0.180	2/10	0.011±0.001	0.010	0.012	2/10	0.016±0.005	0.010	0.027	10/10
CN 66	0.040±0.004	0.036	0.044	2/10	0.015±0.010	0.008	0.037	6/10	0.008±0.001	0.008	0.011	4/10
CN 73	0.008±0.001	0.007	0.009	2/10	**	**	**	0/10	0.007±0.000	0.007	0.007	4/10
CN 75	0.010±0.002	0.007	0.015	10/10	**	**	**	0/10	**	**	**	0/10
$\sum_8$CNs	0.572±0.249	0.391	1.054	10/10	0.187±0.264	0.026	0.885	10/10	0.214±0.055	0.155	0.317	10/10
Congeners	**Mean± STD (MMC)**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
CN 2	1.924±0.871	0.480	2.959	8/10	0.715±0.166	0.545	0.881	4/10	0.935±0.993	0.996	0.999	6/10
CN 6	0.358±0.136	0.223	0.640	8/10	0.178±0.092	0.084	0.272	4/10	0.393±0.403	0.376	0.383	10/10
CN 13	0.374±0.325	0.087	0.941	8/10	0.045±0.007	0.035	0.053	8/10	0.057±0.071	0.065	0.072	6/10
CN 28	0.082±0.060	0.016	0.195	8/10	0.024±0.001	0.023	0.024	2/10	0.061±0.026	0.027	0.095	6/10
CN 52	0.028±0.011	0,015	0.045	6/10	**	**	**	0/10	**	**	**	0/10
CN 66	0.049±0.042	0.007	0.091	4/10	**	**	**	0/10	0.016±0.0	0.015	0.016	2/10
CN 73	0.007±0.0	0.007	0.007	2/10	0.010±0.0	0.010	0.010	2/10	0.009±0.0	0.009	0.009	2/10
CN 75	0.014±0.005	0.008	0.021	6/10	0.012±0.0	0.012	0.012	2/10	0.007±0.0	0.007	0.007	2/10
$\sum_8$CNs	0.439±0.178	0.192	0.699	8/10	0.154±0.209	0.035	0.553	10/10	0.247±0.123	0.076	0.368	10/10

Appendix 5: PBDE concentrations (µg/L) in NEL and CHA water samples during winter, spring and summer

NEL	**Winter**				**Spring**				**Summer**			
Congeners	**Mean± STD**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
BDE 17	0.083±0.130	0.005	0.401	12/12	0.756±0.676	0.046	1.569	12/12	0.117±0.181	0.004	0.519	12/12
BDE 47	0.034±0.021	0.007	0.072	12/12	1.104±0.792	0.232	2.913	12/12	0.128±0.235	0.007	0.657	12/12
BDE 66	0.025±0.013	0.008	0.046	12/12	0.521±0.377	0.066	1.046	8/12	0.111±0.154	0.010	0.442	12/12
BDE 100	0.010±0.003	0.006	0.017	12/12	0.492±0.404	0.039	1.106	12/12	0.036±0.040	0.009	0.123	12/12
BDE 153	0.011±0.002	0.008	0.014	12/12	0.015±0.012	0.008	0.051	2/12	0.010±0.004	0.008	0.021	10/12
BDE 183	0.022±0.003	0.017	0.024	6/12	**	**	**	**	**	**	**	**
$\sum_6$BDEs	0.031±0.025	0.010	0.086	12/12	0.599±0.363	0.079	1.025	12/12	0.080±0.113	0.009	0.298	12/12
CHA	**Winter**				**Spring**				**Summer**			
Congeners	**Mean± STD**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
BDE 17	0.022±0.018	0.004	0.052	10/10	0.041±0.026	0.004	0.072	10/10	0.101±0.098	0.052	0.153	10/10
BDE 47	0.009±0.004	0.007	0.017	10/10	0.023±0.021	0.007	0.054	10/10	0.037±0.042	0.008	0.140	10/10
BDE 66	0.011±0.001	0.009	0.013	10/10	0.009±0.002	0.007	0.012	8/10	0.013±0.002	0.010	0.016	10/10
BDE 100	0.007±0.001	0.007	0.008	10/10	0.007±0.000	0.007	0.008	10/10	0.013±0.002	0.011	0.017	10/10
BDE 153	0.009±0.002	0.008	0.013	10/10	0.009±0.001	0.008	0.010	6/10	0.010±0.001	0.008	0.011	4/10
BDE 183	0.016±0.002	0.014	0.018	6/10	**	**	**	0/10	**	**	**	0/10
$\sum_6$BDEs	0.075±0.027	0.048	0.122	10/10	0.089±0.050	0.033	0.156	10/10	0.174±0.145	0.090	0.306	10/10

Appendix 6: PCN concentrations (µg/kg) in NEL, CHA and MMC sediment samples during winter, spring and summer

	Winter				**Spring**				**Summer**			
Congeners	**Mean± STD (NEL)**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
CN 2	188.422±232.926	14.264	663.446	10/10	4.885±3.471	1.349	11.608	10/10	94.912±129.677	1.719	350.202	10/10
CN 6	59.573±56.718	13.503	149.322	6/10	2.229±2.857	0.109	6.299	6/10	45.540±39.218	0.468	98.640	6/10
CN 13	95.955±83.754	0.914	248.923	10/10	73.208±53.485	5.629	148.647	10/10	21.583±27.427	0.752	87.409	10/10
CN 28	8.250±7.869	0.050	21.225	10/10	0.056±0.039	0.014	0.108	6/10	2.348±3.676	0.013	9.568	10/10
CN 52	2.801±5.463	0.053	14.190	10/10	1.453±2.547	0.056	6.554	10/10	277.262±524.600	0.375	1335.451	10/10
CN 66	0.386±0.294	0.148	0.957	10/10	0.217±0.073	0.139	0.360	10/10	14.444±27.780	0.226	71.163	10/10
CN 73	0.283±0.103	0.199	0.550	10/10	0.265±0.084	0.199	0.435	10/10	8.507±16.421	0.264	41.980	10/10
CN 75	0.417±0.167	0.205	0.656	10/10	0.285±0.052	0.203	0.374	10/10	10.399±17.257	1.161	49.891	10/10
$\sum_8$CNs	41.856±49.786	2.323	134.307	10/10	11.152±7.053	2.951	20.046	10/10	57.166±94.808	0.991	237.437	10/10
Congeners	**Mean± STD (CHA)**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
CN 2	1098.750±1297.766	196.338	3671.415	10/10	414.186±812.978	0.220	2065.980	10/10	130.280±139.729	0.300	363.474	4/10
CN 6	320.615±416.088	35.950	1145.168	10/10	39.620±42.047	2.681	104.239	6/10	226.293±203.055	0.274	532.335	10/10
CN 13	413.915±444.556	13.020	1281.368	10/10	490.888±713.413	1.483	1900.800	10/10	19.324±26.116	0.285	60.270	6/10
CN 28	114.461±170.801	8.628	418.761	8/10	2001.623±4001.739	0.014	10042.530	10/10	1.434±2.156	0.015	5.190	8/10
CN 52	37.877±44.949	2.466	127.996	10/10	381.694±780.656	0.099	2279.925	10/10	2.597±3.278	0.076	8.127	10/10
CN 66	11.738±16.183	0.149	44.116	10/10	33.617±54.739	0.155	141.465	10/10	0.739±0.499	0.185	1.595	4/10
CN 73	9.976±9.543	0.750	28.679	10/10	3.427±6.179	0.248	17.745	10/10	0.666±0.766	0.204	2.610	4/10
CN 75	1.449±2.286	0.174	6.601	10/10	0.385±0.121	0.246	0.593	8/10	1.189±0.818	0.360	2.387	10/10
$\sum_8$CNs	253.341±312.967	32.771	836.801	10/10	419.258±754.003	0.429	1888.468	10/10	44.907±42.176	0.846	99.142	10/10
Congeners	**Mean± STD (MMC)**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
CN 2	1259.971±1536.057	13.821	3945.225	8/10	4224.798±7150.010	1.091	20185.650	10/10	54.859±59.178	0.234	161.264	10/10
CN 6	284.592±399.458	0.060	1043.719	8/10	164.256±197.620	0.405	473.546	10/10	**	**	**	0/10
CN 13	708.548±939.111	56.102	2390.535	8/10	303.204±357.984	46.265	1015.225	10/10	3.656±5.011	0.073	11.450	6/10
CN 28	290.00±429.199	0.137	1055.216	8/10	2.554±2.403	0.145	4.965	4/10	2.485±2.062	0.066	5.320	8/10
CN 52	41.770±44.547	0.068	113.300	8/10	1467.782±2742.014	0.072	7931.430	8/10	1.113±1.395	0.071	4.127	10/10
CN 66	21.850±25.130	0.212	63.383	8/10	324.606±564.080	0.321	1438.436	8/10	2.378±2.584	0.141	6.657	10/10
CN 73	10.085±11.569	0.268	31.056	8/10	0.395±0.175	0.186	0.631	6/10	1.423±1.420	0.240	3.984	10/10
CN 75	5.670±6.749	0.247	16.950	8/10	1.358±1.186	0.296	3.220	6/10	5.270±9.379	0.188	25.443	10/10
$\sum_8$CNs	327.811±446.533	9.535	1054.670	8/10	1686.953±2492.532	11.093	6744.160	10/10	11.288±12.617	0.260	34.295	10/10

Appendix 7: PBDE concentrations (μg/kg) in NEL and CHA sediment samples during winter, spring and summer

	Winter				Spring				Summer			
Congeners	**Mean± STD (NEL)**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
BDE 17	0.301±0.044	0.246	0.385	10/12	0.777±0.809	0.218	2.324	10/12	0.820±0.933	0.185	2.672	10/12
BDE 47	0.381±0.048	0.334	0.481	10/12	1.055±1.084	0.317	3.277	10/12	0.454±0.099	0.361	0.712	10/12
BDE 66	8.019±14.446	0.428	37.060	10/12	4.718±6.837	0.345	19.113	10/12	0.548±0.133	0.424	0.889	10/12
BDE 100	0.702±0.356	0.364	1.377	10/12	6.656±12.096	0.353	31.626	10/12	0.369±0.086	0.320	0.608	10/12
BDE 153	0.854±1.009	0.352	3.500	10/12	14.206±27.307	0.350	68.991	10/12	0.427±0.147	0.338	0.849	10/12
BDE 183	1.976±3.334	0.360	10.607	10/12	9.860±18.653	0.400	49.197	10/12	0.599±0.100	0.391	0.709	10/12
$\sum_{6}$BDEs	0.821±0.772	0.354	2.462	10/12	6.212±11.578	0.381	28.850	10/12	0.536±0.183	0.390	0.851	10/12
	Winter				**Spring**				**Summer**			
Congeners	**Mean± STD (CHA)**	**Min**	**Max**	**n(det)**	**Mean ± STD**	**Min**	**Max**	**n(det)**	**Mean± STD**	**Min**	**Max**	**n(det)**
BDE 17	2.823±2.766	0.176	8.995	10/10	2.171±4.320	0.204	9.899	10/10	1.917±2.302	0.221	5.744	10/10
BDE 47	1.747±2.844	0.315	8.958	10/10	0.440±0.048	0.363	0.484	10/10	3.267±3.429	0.454	8.330	10/10
BDE 66	3.552±1.673	2.002	6.883	10/10	0.353±0.029	0.328	0.398	10/10	1.792±2.642	0.485	6.512	10/10
BDE 100	0.657±0.373	0.352	1.363	10/10	0.409±0.053	0.340	0.469	10/10	3.262±4.059	0.419	10.352	10/10
BDE 153	0.477±0.128	0.362	0.750	10/10	0.393±0.031	0.357	0.435	10/10	1.654±2.212	0.441	5.579	10/10
BDE 183	0.546±0.126	0.358	0.774	10/10	0.414±0.032	0.369	0.457	10/10	2.682±1.572	0.706	4.864	10/10
$\sum_{6}$BDEs	1.634±1.256	0.807	4.141	10/10	0.696±0.688	0.347	2.219	10/10	2.429±2.227	0.455	6.468	10/10