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Assessment of Persistent Organic Pollutant accumulation in Sediments of the Klip River Wetland, Johannesburg



WITS
UNIVERSITY

By

AYO OLASUPO

A dissertation submitted to the Faculty of Science, University of the Witwatersrand in fulfilment of the requirements for the degree of Master of Science

University of the Witwatersrand, Johannesburg, July 2018

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any university.



(Signature of candidate)

19th July 2018

ABSTRACT

The Klip River wetland located south of Johannesburg is economically significant and serves as an important source of water and purifier of pollutants originating from mining and industrial activities occurring within the Witwatersrand Basin. Importantly, the Klip River is also a source of water to the Vaal Dam, which serves Johannesburg with portable water. Previous investigations have revealed that the upper reaches of the Klip River wetland sequester high levels of inorganic pollutants associated with mining activities. This study was initiated to investigate the accumulation and potential source of Polyaromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) in sediments from the Klip River wetland. PAHs and PCBs were found to be widely distributed in the surface sediments of two main tributaries entering the wetland. Total PAH concentrations were in the range of 44 – 95 mg/kg, while total PCB concentrations ranged from 0.2 – 5.3 mg/kg. The spatial distribution of PAHs showed that upstream sites were more polluted, which was attributed to the proximity of these sites to heavy traffic and industrial complexes. Conversely, the spatial distribution of PCBs showed increasing contamination downstream, which was ascribed to anthropogenic activities from the residential settlements of Soweto and Lenasia. A sediment core from the wetland revealed lower levels of contamination, with total PAH and PCB concentrations in the range of 2.4 – 6.3 mg/kg and 0.17- 0.80 mg/kg, respectively. PAH and PCB concentrations increased with depth, indicating a potential groundwater source of pollution. Potential source identification using a combination of different PAH isomeric ratios, indicated a mix petrogenic and pyrogenic sources of contamination, with petrogenic sources having a stronger influence. PCB congeners indicated a potential source of contamination originating from dielectric fluids in electric transformers and industrial capacitors. Ecological risk assessments conducted using National Oceanic and Atmospheric Administration's (NOAA) sediment quality guidelines indicated a probable adverse effect to aquatic life and possibly human health for most of the PAH and PCB congeners investigated. A further risk characterisation of the sites indicated that about 60% of the investigated sites could be classified as moderately to highly polluted sites with potential ecological risk. A further and more in-depth investigation is therefore needed to assess the bioaccumulation and biomagnification of contaminants within the Klip River system and determine the ecotoxicological impact this has on both aquatic health and humans who rely on resources from the Klip River wetland.

DEDICATIONS

I dedicated this work to God who has been the pillar of my past, the strength of my present, and the hope of my future.

To my parents, for their prayers, support and for leading me in the right part. And my siblings for their encouragements.

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LIST OF ABBREVIATION

ADD	Attention Deficit Disorder
ADHD	Attention Deficit Hyperactivity Disorder
Ant	Anthracene
AMD	Acid Mine Drainage
ATSDR	Agency for Toxic Compounds Disease Registry
BaA	Benzo(a)anthracene
Chr	Chrysene
$C_2H_3NaO_2$	Sodium acetate
$C_2H_9NaO_5$	Sodium acetate trihydrate
DDT	Dichlorodiphenyltrichloroethane
dw	Dry weight
EC	Electrical conductivity
ERL	Effect range low
ERM	Effect range medium
ESKOM	Electricity Supply Commission
Fla	Fluorene
GC-TOFMS	Gas chromatography- Time of Flight Mass Spectrometry
HPLC	High Performance Liquid Chromatography
LOD	Limit of Detection
LOQ	Limit of Quantification
LOI	Loss On Ignition
$MgSO_4$	Magnesium sulphate
NOAA	National Oceanic and Atmospheric Administration

NERSA	National Energy Regulation of South Africa
PAH	Polyaromatic hydrocarbon
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
Phe	Phenanthrene
POPs	Persistent organic pollutants
ppb	Part per billion
PSA	Primary secondary amine
Pyr	Pyrene
QA	Quality Assurance
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
RSD	Relative standard deviation
TOM	Total Organic Matter
TSA	Total Surface Area
UNEP	United Nations Environmental Program
USEPA	United State Environmental Protection Agency

CHAPTER 1: INTRODUCTION

Persistent organic pollutants (POPs) are a group of organic contaminants that are known to persist in the environment because of their long half-lives and ability to resist different degradation processes (Jones and De Voogt, 1999). They are also known to undergo long-range environmental transport due to their semi-volatile nature and as such have been detected in areas such as the Arctic and Antarctic where they have neither been produced or used (Dalla Valle et al., 2007; Mulvad et al., 1996; Solomon and Schettler, 2000). POPs have also been detected in a variety of matrices, including fatty tissues (Gerber et al., 2016; Naigaga et al., 2011; Saldanha et al., 2010), breast milk (Bouwman et al., 2012), blood serum (Darnerud et al., 2010), bird eggs (Polder et al., 2008), water (Zhang et al., 2003), air (Shoeib and Harner, 2002) and sediments (Buah-Kwofie and Humphries, 2017; Jones and De Voogt, 1999; Pheiffer et al., 2018; Rimayi et al., 2017; Wu et al., 1999). A number of health-related problems have been associated with POPs in both aquatic and terrestrial organisms due to their carcinogenic (Karlsson and Viklander, 2008), mutagenic (Ghaeni et al., 2015), reproductive impairment, and endocrine disruption tendencies (Thomas et al., 2007). As a result of the environmental and human health challenges caused by POPs, there is a global effort through the Stockholm Convention to eliminate or reduce the production and use of POP related compounds by 2025 (Bouwman, 2004). Examples of POPs include polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), organochlorines etc.

Polychlorinated biphenyls (PCBs) are a group of persistent organic contaminants characterized by their ability to bioaccumulate, biomagnify, and be transported in different environmental compartments (Gakuba et al., 2015; Pennington, 2001; Sapozhnikova et al., 2004). PCBs are produced and used extensively as dielectric and hydraulic fluids, cooling agents, and plasticizers (El-Shahawi et al., 2010; O'Donovan et al., 2011; Rimayi et al., 2017; Vallack et al., 1998), with an estimated global production of 1.3 million tonnes at inception (Rimayi et al., 2017). Similar to PCBs, polyaromatic hydrocarbons (PAHs) are also a group of organic contaminants made up of two or more fused aromatic rings of carbon and hydrogen (Chen et al., 2003; Pheiffer et al., 2018). Among the different congeners of PAHs, the USEPA has identified 16 as priority pollutants due to their mutagenicity, carcinogenicity, and toxicity (Chen et al., 2003; Karlsson and Viklander, 2008; Pheiffer et al., 2018). PAHs are produced from incomplete combustion of fossil fuel, refuse incineration, sewage incineration, asphalt

paving, vehicular exhaust and other industrial activities (Arruti et al., 2012; Chen et al., 2003; Lee et al., 1995; Li et al., 2001). Diagnostic source identification using a multi-isomer approach is often used to assess the potential origin of PAHs and involves comparing the concentration ratio of different PAH congeners (Pies et al., 2008). For example, concentration ratios of anthracene/phenanthrene [An/(An + Ph)], fluoranthene/pyrene [Fl/(Fl + Py)], and benzo(a)anthracene/chrysene [BaA/(BaA+Chr)] can be used to determine whether the sources of PAHs are of pyrogenic or petrogenic origin (Budzinski et al., 1997; Nieuwoudt et al., 2011; Pies et al., 2008).

Wetlands often function as a medium to removing or reducing contaminants from water (McCarthy et al., 2007), and this is accomplished by various physicochemical processes such as filtration, sedimentation, chemical precipitation and adsorption (Grundling and Marneweck, 1999; Vermaak, 2009). The Klip River wetland located south of Johannesburg (Figure 1.1) is considered one of the most economically significant wetlands in South Africa. It initially served as a local source of water and now functions a purifier of contaminants from various anthropogenic activities occurring within the Witwatersrand Basin (McCarthy et al., 2007). The upper reaches of the wetland receives surface run-off from the Klip River and Klipspruit tributaries, and also groundwater from the underlying dolomite aquifer (McCarthy et al., 2007). The upper reaches is covered by tall reed (*Phragmites australis*) and serves to purify the water entering the Vaal Dam, which is the main source of water to Johannesburg (McCarthy et al., 2007). Potential sources of pollution to the Klip River wetland system include; acid mine drainage (Humphries et al., 2017; McCarthy et al., 2007), treated and untreated sewage discharge from industries around the wetlands (McCarthy and Venter, 2006), vehicular exhaust emissions, refuse burning, industrial/municipal waste disposal and combustion of coal at the Klip River industrial complex (McCarthy et al., 2007).

Large quantities of fossil fuels continue to be used by industries to help boost the country's economy, with the combustion of coal being a major contributor to PAH and PCB emissions. It is estimated that the combustion of coal contributes 65% to total air pollution in South Africa (Balmer, 2017; Jeffrey, 2005). Alberton, located within the Klip River catchment was reported to be a hotspot for dioxin-like compounds (PCBs) as a result of the numerous industrial activities (Jooste et al., 2008). Other investigations on the extent of pollution at the Klip River wetland have reported the presence of PAHs and PCBs in surface sediments from the catchment (Pheiffer et al., 2018). Studies by Humphries et al. (2017) and McCarthy et al. (2007)

reported on the attenuation of pollution arising from acid mine drainage (AMD) within the wetland and the sequestration of large quantities of heavy metals.

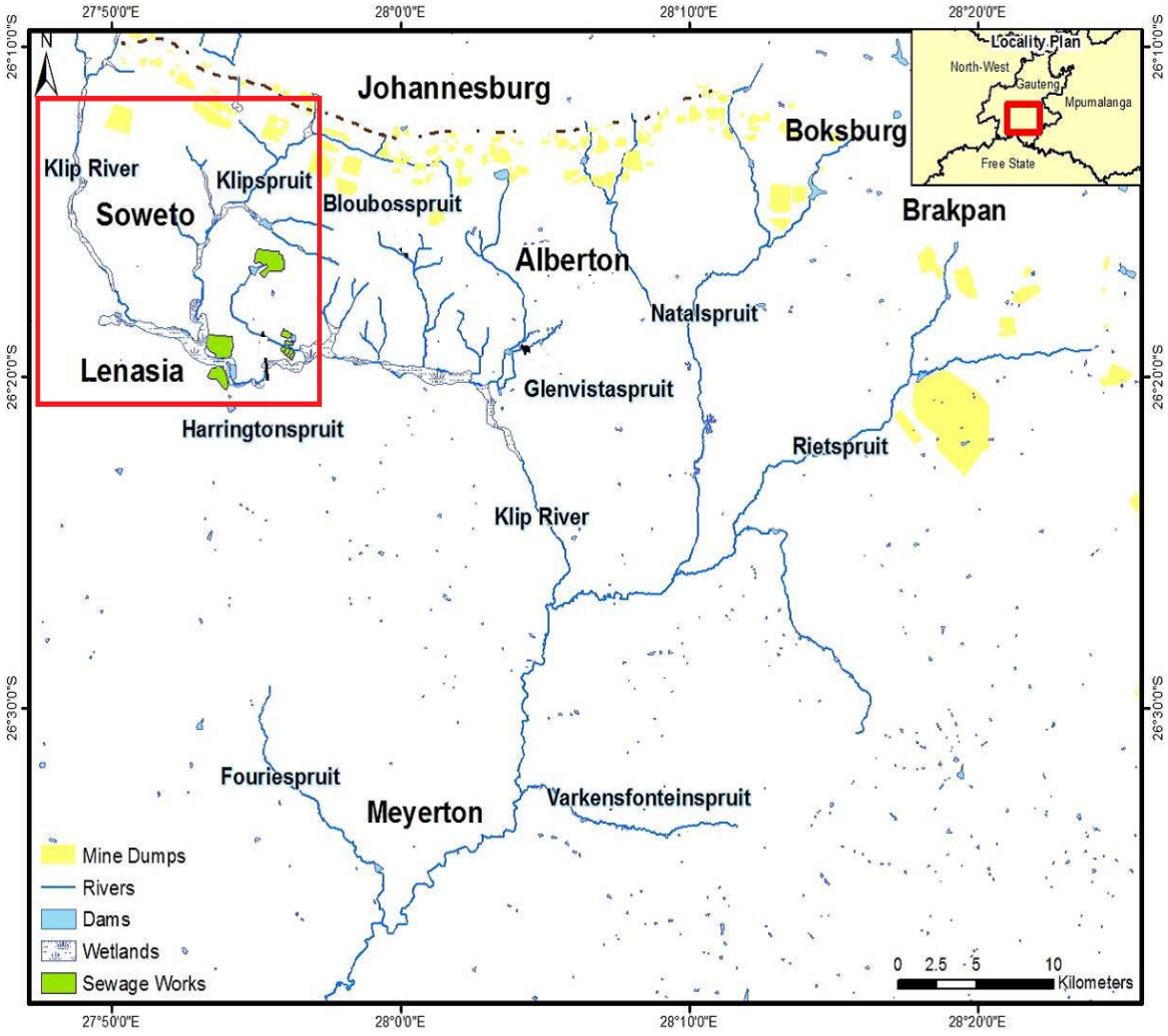


Figure 1.1: Location of the Klip River system, its tributaries and water sources (Vermaak, 2009).

AIM AND OBJECTIVES

The aim of this study is to investigate the accumulation of selected PAHs and PCBs within sediments of the Klip River wetland.

Objectives:

- To identify and quantify the presence of PAHs and PCBs in sediment samples from the Klip River wetland and its catchment.
- To investigate the spatial distribution of contaminants in the catchment area and relate this to potential sources.
- To examine the distribution of contaminants through a sediment core and relate this to pollutant transport and fate.
- To conduct an ecotoxicological risk assessment and provide recommendations for future research.

CHAPTER 2: LITERATURE REVIEW

2.1 Persistent Organic Pollutants

Persistent organic pollutants (POPs) are ubiquitous pollutants in the environment and represent a universal contamination problem (Fu et al., 2003). Potential hazards associated with POPs are as a result of their ability to persist in the environment and their toxicity to human and wildlife (Fu et al., 2003; Jones and De Voogt, 1999). POPs are produced mainly through anthropogenic activities associated with agriculture, industrial waste, and municipal sewage disposal systems (Fu et al., 2003; Jones and De Voogt, 1999). Some POPs are released naturally into the environment from volcanic eruptions and forest fires, while others are intentionally released from the refining of metals, use of pesticides/herbicides, production of chlorinated compounds, and incomplete combustion processes (Bouwman et al., 2012; Jones and De Voogt, 1999).

POPs are hydrophobic compounds which adsorb strongly to organic matter when released into the environment (Jones and De Voogt, 1999). In animals, they are bioaccumulated in fatty tissues and biomagnify in the food chain (Jones and De Voogt, 1999). Despite their persistence in soil and sediment, POPs are volatile and may escape from the surface of soil/sediment into the atmosphere at environmental temperatures (Jones and De Voogt, 1999). POPs can travel very far from their initial point source and be redeposited in another location as a result of their ability to resist reaction breakdown (Qing Li et al., 2006). The global extent of POP pollution became apparent with their detection in areas such as the Arctic, where they have never been used or produced (Mulvad et al., 1996). The contact time of any POP in the environment is dependent on its half-life, however, other factors such as soil characteristics, environmental temperature, and precipitation also determines the bioavailability of POPs (Reid et al., 2000). The toxicity of POPs can be attributed to their chemical and biological stability, and their intense lipophilicity (Björklund et al., 2000).

POPs are regarded as endocrine disruptors because they cause reproductive problems when accumulated in the body tissues of animals (Ghaeni et al., 2015; Gray 2004; Jones and De Voogt, 1999; Sibiya, 2012). A study by Jones et al. (1999) revealed that POPs affects some hormones and are major causes of cancers. Despite campaigns by environmental agencies, many developing countries still use POPs due to their low cost and usefulness for agriculture and industrial purposes (Zhang et al., 2003). In South Africa, DDT is still used annually for

malaria vector control in three malaria endemic provinces (i.e. KwaZulu Natal, Limpopo and Mpumalanga) and its metabolites have been found in breast milk of breast-feeding mothers (Bouwman et al., 2012). Other POPs including organochlorine pesticides, PCBs and PAHs have been identified in sediments (Pheiffer et al., 2018; Rimayi et al., 2017), food samples (Nuapia et al., 2016), bird eggs (Bouwman et al., 2008; Polder et al., 2008), and crocodile tissue (Buah-Kwofie et al., 2018) from different regions of South Africa.

2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are non-polar, non-ionic, and neutral organic compounds comprising of two or more fused benzene rings arranged in different conformations (Fu et al., 2003; Zuloaga et al., 2009; Figure 2.1) They are produced mainly from anthropogenic sources, such as the incomplete combustion of coal and other petroleum products (Arruti et al., 2012; Chen et al., 2015; Lee et al., 1995; Li et al., 2001). The United States Environmental Protection Agency (US-EPA) has identified 16 PAHs as priority pollutants due to their toxicity, carcinogenic, mutagenic and endocrine disruption properties (Figure 2.1). As a result of their hydrophobic nature, they adsorb to sediment in the aquatic and terrestrial environment (Latimer et al., 1999).

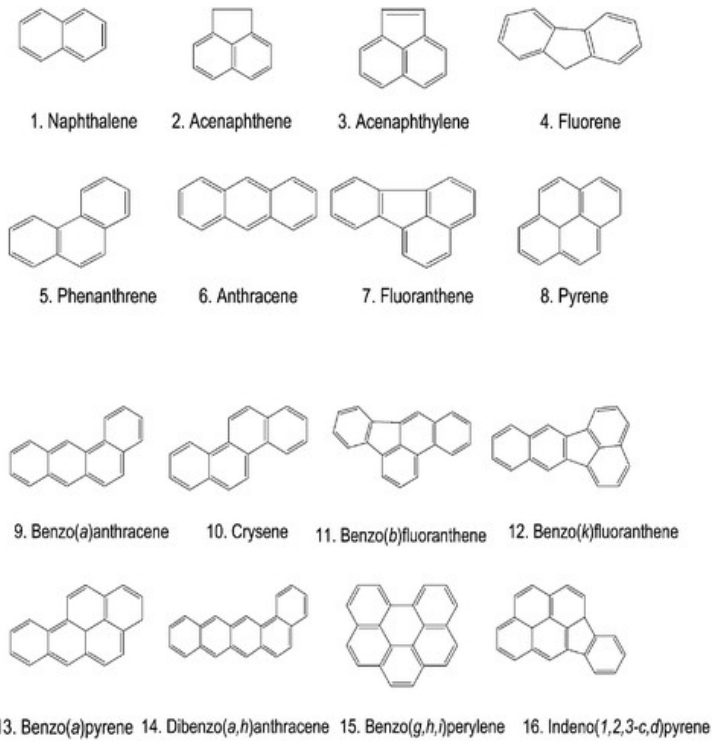


Figure 2.1: Structures and names of the 16 priority PAHs listed by the EPA.

2.2.1 Properties of PAHs and their behaviour in the environment

The properties of PAHs varies depending on the structure and molecular weight of a specific PAH congener (Sibiya, 2012). Chemical properties such as oxidation, solubility and vaporisation increases with an increase in the molecular weight of PAHs (Sibiya, 2012; Wilson and Jones, 1993). PAHs are not easily degradable and their contact time in the environment is dependent on their half-lives (Jones and De Voogt, 1999; Sibiya, 2012). For example, naphthalene has a half-life of 14 weeks in anaerobic sediment, while benzo(a)pyrene has a half-life of 300 weeks under the same conditions (Sibiya, 2012). A dose-response limit was set for the different PAHs due to their carcinogenic, mutagenic and toxic effects. The maximum allowable concentration of PAHs in soil and water compartments is shown in Table 2.1 below.

Table 2.1: Acceptable PAH levels in soil and water according to standards set by the Agency for Toxic Substances and Disease Registry (ATSDR) and United State Environmental Protection Agency (US-EPA).

Congener	ASTDR		US-EPA
	Soil (mg/kg)	Water (mg/l)	Water (mg/l)
Pyrene	3.0	3.0	-
Naphthalene	1.0	3.0	-
Phenanthrene	3.0	3.0	-
Benzo[hgi]perylene	3.0	3.0	-
Benzo(a) pyrene	0.3	0.005	0.002
Anthracene	3.0	3.0	-
Fluoranthene	3.0	3.0	-
Acenaphthene	3.0	3.0	-
Acenaphthylene	3.0	3.0	-
Benzo (a) anthracene	0.15	0.005	0.001
Benzo (b)	0.3	0.005	0.002
fluoranthene	-	-	-
Dibenzo (a) anthracene	0.3	0.005	0.004
Fluorene	3.0	3.0	-
Indeno[1,2,3-ghi]pyrene	0.3	0.005	-
Indene	-	0.3	-
Chrysene	-	-	0.002
Benzo(k)fluoranthene	-	-	0.002
Dibenz (a,h) anthracene	-	-	0.003
Indenol (1,2,3-c,d)pyrene	-	-	0.004

There is no exact allowable amount of PAHs in the atmosphere, but there is a recommendation that the amount of PAHs in the atmosphere should not be more than 0.004 ppm (ATSDR, 2006, US-EPA 2009).

2.2.2 Sources of PAHs

It has been estimated that automobile sources of PAHs account for approximately 90% of total PAHs emission, however, this is only true in urban and suburban areas where there are a lot of automobiles (Caricchia et al., 1999). Domestic activities like cooking and heating contribute immensely to PAHs in the atmosphere and this is commonplace in rural settlements where most of the cooking is done by burning of coal and wood (Ravindra et al., 2008; Sibiya, 2012). The major industrial sources of PAHs are coal gasification, coke production, aluminium, iron, and steel production (Ravindra et al., 2008), thermal power plants, petroleum refining, and pitch and asphalt (bitumen) productions (Bjørseth and Eklund, 1979).

2.3 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a group of persistent organic compounds that contain varying numbers of chlorine atoms, and are characterized by their ability to cause environmental hazards (Gakuba et al., 2015; Pennington, 2001). They are man-made compounds which are intentionally produced in industries and are widely used in transformers as dielectric fluids and in condensers (Rimayi et al., 2017; Samara et al., 2006). This group consists of about 209 congeners, with their environmental properties dependent on the level of chlorination (Vallack et al., 1998). They were first described in literature in 1881, but started being commercially produced in 1920 (Gray, 2004). The United Nations Environmental Program (UNEP) identified PCBs as one of the 12 hazardous POPs (dirty dozen) at the Stockholm Convention in March 1999, which was later ratified in May 2001, with South Africa being a signatory to the treaty. PCBs may accumulate in fatty tissues, causing damage to the neurological, reproductive and immune systems of humans and wildlife (Gray, 2004). They also cause developmental disorders in children and women of childbearing age because they mimic estrogen hormone in the body (Gray, 2004; Table 2.2).

Table 2.2: Known and possible effects of PCBs in humans (Gray; 2004).

Effects of PCBs in human	
Known effects	Possible effects
Cancer	Liver & Kidney Damage
Headaches, Dizziness	Reproductive Damage
Nervousness	Respiratory Illnesses like Asthma
Fatigue	Decreased Learning Potential
Low Birth Weight	Learning and Development
Poor Infant Habituation	Disabilities
Thyroid Dysfunction	Depression/Aggression (ADD &
Chloracne	ADHD)

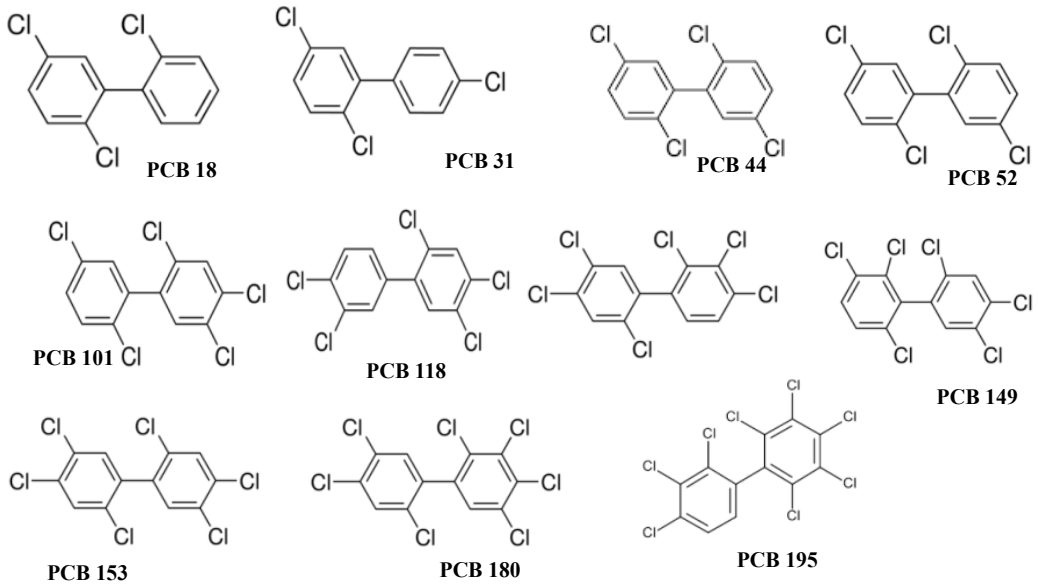


Figure 2.2: Structure and names of PCB congeners investigated in the study

2.3.1 Physicochemical properties of PCBs and their behaviour in the environment

PCBs are non-volatile compounds with a propensity to persist in the environment as a result of their ability to partition strongly in different matrices (Fiedler, 1997). They have been found in almost all compartments of the environment. Ortho-substituted PCBs are found mostly in commercial samples and are very degradable, while the non-ortho substituted varieties are found mostly in environmental matrices and are less degradable (Mackay et al., 1997). Their persistence in the environment is a result of their half-life, which could be days in the air, but several decades in soils and sediment (Jones and De Voogt, 1999). They are generally insoluble in water, with their solubility decreasing with increasing number of chlorine atoms attached to the biphenyl ring and the positional arrangement of the chlorine substituent (Lynn et al., 2007;

Noma et al., 2007). The octanol-water partition coefficient (log $K_{ow)}$ of PCB which determines its hydrophobicity also increases with increasing number of attached chlorine atoms (Hawker and Connell, 1988; Table 2.3)

2.3.2 Sources and uses of PCBs

PCBs are released into the atmosphere unintentionally by burning of fossil fuels and coal (Arruti et al., 2012), recycling of waste, incineration of electrical appliances, and burning of materials containing PCBs (Breivik et al., 2011; Gioia et al., 2011, 2014; Sepúlveda et al., 2010). They were also manufactured and widely used as dielectric fluids in electrical transformers and large capacitors, as pesticide extenders, plasticizers in rubber and sealants (Gioia et al., 2014b), as heat exchange fluids, hydraulic lubricants, and flame retardants (Vallack et al., 1998).

Table 2.3: Log K_{ow} values and total surface area of some selected PCB congeners (Hawker and Connell, 1988)

Congeners	Log K_{ow}	TSA × 10^{-20} m^2
PCB 18	5.24	218.32
PCB 31	5.67	230.66
PCB 44	5.75	233.21
PCB 52	5.84	235.84
PCB 101	6.38	251.62
PCB 118	6.74	262.04
PCB 153	6.92	267.39
PCB 138	6.83	264.76
PCB 149	6.67	260.00
PCB 180	7.36	280.37
PCB 195	7.56	286.12

2.4 Ecological risk assessment of PAHs and PCBs

PAHs and PCBs have also been reported to bioaccumulate in wetland sediments (Han et al., 2018; Pheiffer et al., 2018; Rimayi et al., 2017), making them a possible threat to the environment over a period of time (Neff et al., 2005; Pheiffer et al., 2018). In order to evaluate the ecological risk of PAHs and PCBs in sediments, measured concentrations are usually compared with established international guideline values (Long and MacDonald, 1998). The guideline values of PAHs reported by Long and MacDonald (1998) are based on an effect range low (ERL) and effect range medium (ERM) of individual PAH congeners. Measured PAH

concentrations that are below the respective ERL value indicate that the congener present in that sediment may not be harmful to organisms, but when the PAH concentrations are higher than the reported ERM value, then such a congener or group of congeners are likely to pose risks to the biota (Long and MacDonald, 1998). Contrary to PAHs, evaluating the ecotoxicity of PCBs is based on total PCBs in sediment. If the total PCBs is lower than ERL value, it would be assumed that sediment in the environment is safe, but if the total PCB in sediment is higher than the ERM value it would imply that sediment in that environment has a propensity to cause harm to the biota (Long and MacDonald, 1998).

CHAPTER 3: STUDY AREA

3.1 Description of the Klip River catchments

The Klip River wetland is located south-west of Johannesburg and lies between latitude 26°10'-26°25 S' and longitude 27°45' - 28°05 E (Figure 1.1). It extends from Lenasia and Soweto in the west towards Alberton in the south, and receives runoff from several tributaries such as Klipspruit, Bloubosspruit, Harringtonspruit, Glenvistaspruit, Natalspruit, and Rietspruit (Davidson, 2003; Figure 1.1). The wetland is covered by reed swamps (*Phragmites australis*) and is filled by organic-rich sediment/peat (McCarthy et al., 2007; Figure 3.1).



Figure 3.1: Aerial photograph of the reed-covered swamp of the Klip River wetland along Lenasia to Olifantsvlei, dominated by *Phragmites australis* and surrounded to the left by human settlement (McCarthy et al., 2007).

3.2 History of the Klip River catchments

The Witwatersrand Basin where the Klip River is located literally interprets as the 'ridge of white waters', while the various small springs that surround the ridges in this location informs the name Witwatersrand (Turton et al., 2006; Vermaak, 2009). The availability of water within and around the Witwatersrand attracted various industrial activities (McCarthy et al., 2007; Vermaak, 2009). Coal was found in the East Rand towards the end of the 1880s, gold was discovered on the ridge in early 1886, and towards the end of 1886, Johannesburg was founded

(Turton et al., 2006). These discoveries jointly facilitated the development of this region, leading to migration of people especially miners to the area (McCarthy and Venter, 2006). Today, the Witwatersrand region has an estimated population of about 11 million people, making it one of the most populated industrial settlements in the world (Turton et al., 2006). When mining activities started in this region, the first water used for mining was drawn from the Fordsburgspruit and Natalspruit springs (Turton et al., 2006; Vermaak, 2009). Other sources of water for industrial purposes came from farms in Weltevreden and mining operation plants around Roodepoort (Turton et al., 2006). As a result of increased water demand around the industrial complex, an alternative means was devised, which led to the drawing of water from the dolomite aquifers underlying the Klip River wetland (McCarthy et al., 2007; Vermaak, 2009). Demand for water grew when more gold-mines were discovered and more water was needed to cater for the newly found gold-mines, with an estimated amount of 2000 litres of water required to mine one ton of gold ore (Handley, 2004; Vermaak, 2009). Industrial growth in this region subsequently led to the discharge of effluents from mining activities, sewage treatment plants, and waste disposal, which accumulated in the Klip River wetland either by surface run-off or through groundwater input (McCarthy et al., 2007; Figures 3.2 & 3.3).

3.3 Climate, hydrology and geohydrology of the Klip River

The climate of the region is sub-humid with a maximum average temperature of 26 ^{o}C in January and 16 ^{o}C in June (Vermaak, 2009). Precipitation occurs mainly in the summer (October to March) and comes in the form of high intensity rainfall, which enhances surface run-off (Partridge, 1968; Vermaak, 2009). The average precipitation is around 600-750 mm per annum (Grundling and Marneweck, 1999).

The Klip River wetland is underlain mainly by dolomite rock of the Malmani subgroup (Figure 3.4). The dolomite aquifer was a major source of water at the wetland (McCarthy et al., 2007), increased population in this region due to industrialization and over-dependence on the water coming from the dolomite aquifer, led to a drastic fall in the water table at the wetland, and subsequent deterioration in surface water quality due to influx of effluents from gold treatment plants and sewage purification plants (Kafri and Foster, 1989; Vermaak, 2009). Other man-made water sources like communal dams, ponds, and recreational/farm dams were constructed to meet the need of the fast-growing industries/population in the region (Davidson, 2003; Vermaak, 2009).

3.4 Pollution of the Klip River and other anthropogenic impacts

Industrial growth started in the lower reaches of the Klip River system along the southern haunch of the Witwatersrand Ridge, which is the main watershed that divides the Vaal River basin to the south and the Limpopo River basin to the north (Vermaak, 2009). This region is otherwise known as the Witwatersrand urban industrial mining complex (McCarthy et al., 2007). Majority of the industrial activities (wastewater treatments, mining, and waste disposal) are concentrated in the catchments of the Klip River tributaries and wetland, leaving industrial wastes and effluents to be deposited into the Klip River wetlands (McCarthy et al., 2007). Different researchers have worked on the extent of pollution at the Klip River wetland and catchments. Pollution arising from acid mine drainage was reported by Humphries et al. (2017) and Tutu et al. (2008), while the presence of organic contaminants were reported by Pheiffer et al. (2018) and Rimayi et al. (2016, 2017). These contaminants are released into the Klip River by a combination of surface run-off and seepage from conduits pipes transporting treated and untreated industrial waste (McCarthy and Venter, 2006). About 85% of the wastewater which enters the Klip River is anthropogenic, with a high concentration of nitrates and phosphates (Davidson, 2003; McCarthy and Venter, 2006). Without the wetland's ability to sequester and retain pollutants, the quality of water entering into the Vaal River from the Klip River system through the Vaal barrage would likely deteriorate (McCarthy et al., 2007).



Figure 3.2: Discharge point of the Olifontsvlie sewage treatment plant ponds into the Klip River Wetland in August 2008 (Vermaak, 2009).



Figure 3.3: Aerial photograph of the discharge point of the Bushkoppies sewage treatment plant ponds into the Klip River Wetland (McCarthy et al., 2007).

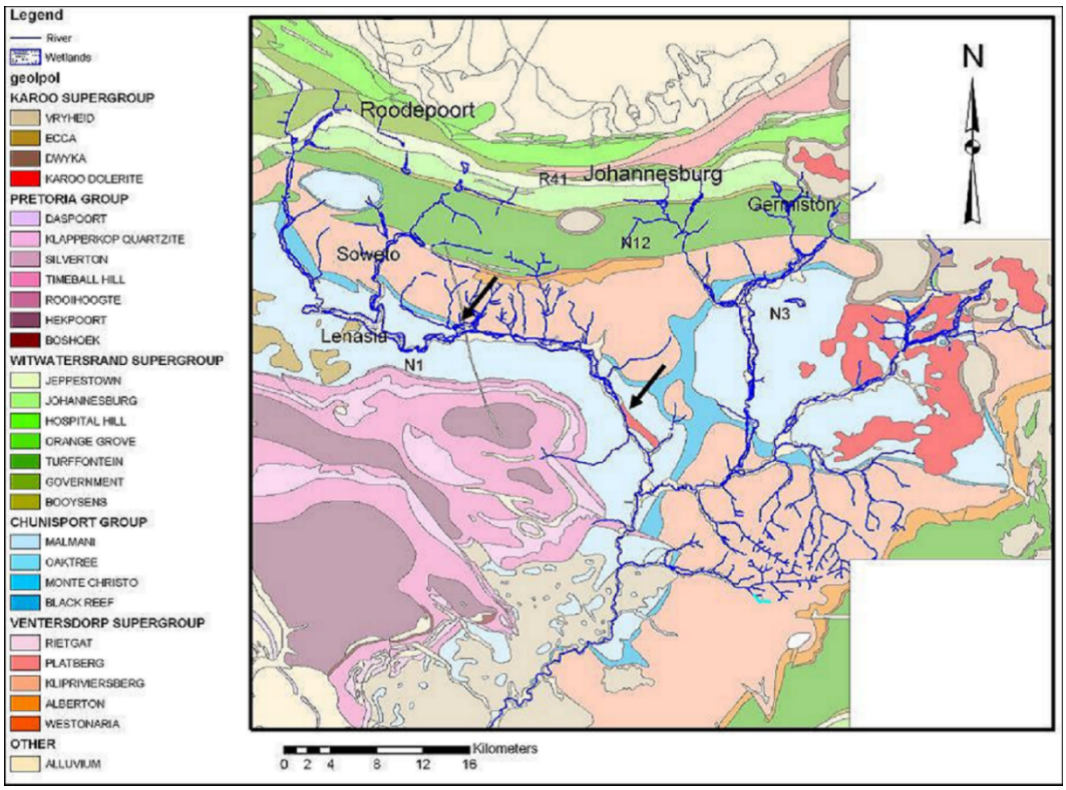


Figure 3.4: Surface geology of the Klip River catchments with arrows indicating dykes (Vermaak, 2009).

CHAPTER 4: MATERIALS AND METHODS

All solvents used for extraction were of HPLC grade (≥ 99.9% purity) and were purchased from Sigma Aldrich, South Africa. PAH and PCB standards were also purchased from Sigma Aldrich. The PAH standard solution contained the 16 priority PAHs as classified by the United States Environmental Protection Agency (USEPA). The PCB standard solution contained 12 common congeners. Ultrapure water (milli-Q, Billerica MA USA) was used throughout the experimental procedure.

4.1 Field work

Surface sediment samples (Table 4.1) were collected from two main tributaries within the Klip River catchment (Figure 4.1). Sampling targeted the major tributaries draining into the upper section of the Klip River wetland. A sediment core from the upper section of the wetland was collected (site C_1) using a Russian corer. Coring was conducted to a depth of 3.5 m with subsamples taken at approximately 10 cm intervals to examine the vertical distribution of pollutants within wetland. The pH, electrical conductivity, and redox potential were determined using a multipurpose electrode (ORION Thermo Scientific) by directly inserting electrodes into the sediment. Collected sediment samples were stored in the refrigerator at 4 ^{o}C prior to analysis.

Table 4.1: Locations of sampling sites

Sampling site	Area description	Latitude	Longitude
S1A Klip River tributary	Bard street Roodeport	26.171151° S	27.819250° E
S2A Klip River tributary	Main street	26.294708° S	27.99374° E
S3 Klip River tributary	Moroka bypass west bound	26.294708° S	27.836590° E
S1B Klipspruit tributary	Crownwood road and Soweto highway	26.227054° S	28.002361° E
S2B Klipspruit tributary	Crown mines golf club	26.388861° S	27.341666° E
S3B Klipspruit tributary	Sheffield road Soweto	26.431944° S	28.013888° E
S4B Klipspruit tributary	Eldorado park shooting range	26.306051° S	27.883410° E
C1 Core wetland site	Near Lenasia	26.305600° S	27.871800° E

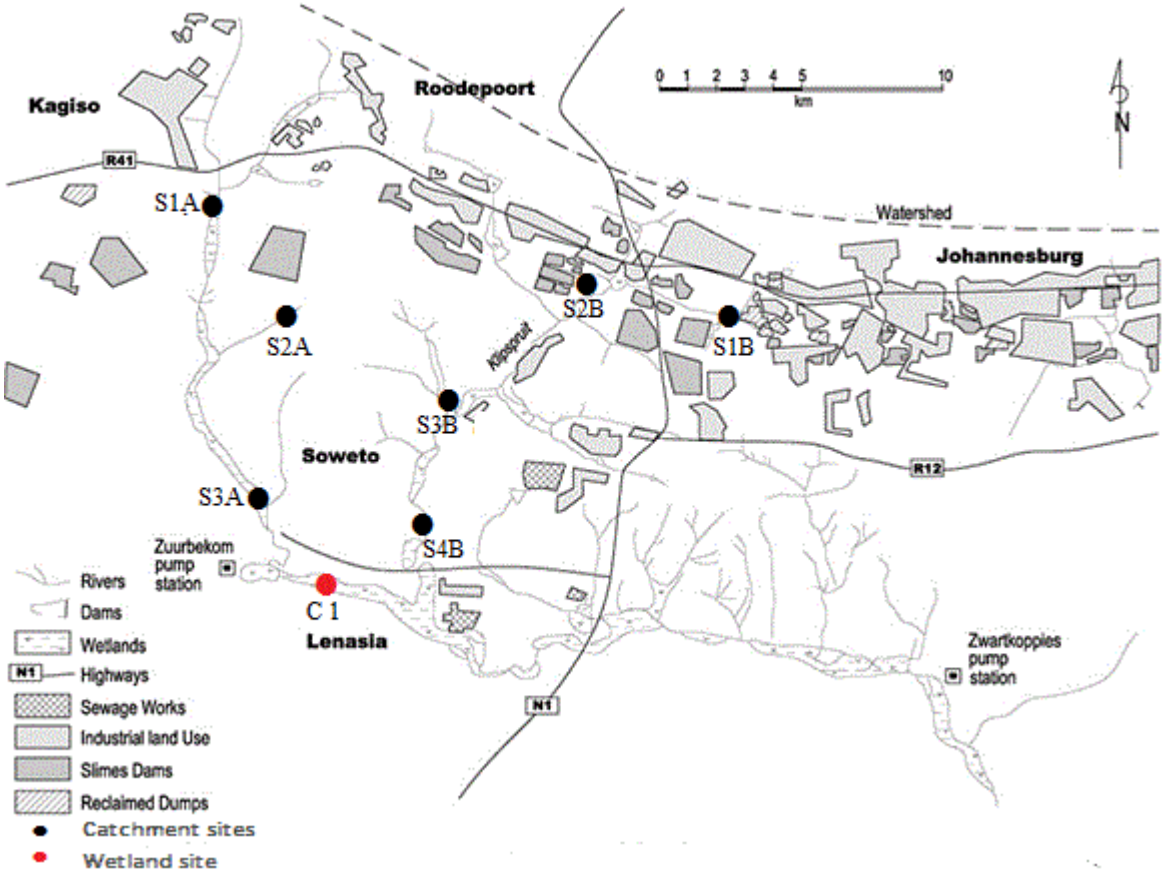


Figure 4.1: Map of the Klip River system showing the location of sediment sampling sites relative to industrial activities (McCarthy et al., 2007).

4.2 Sample Preparation

Samples were air-dried at room temperature and later milled using a ball mill (Retsch MM 200) to ensure homogeneity. Milled samples were stored in amber bottles in a cool, dry and dark place to avoid photodegradation of target compounds. Total organic matter was estimated on sub-samples by loss on ignition (LOI). Sediment samples of ~1.5 g were weighed before and after heating to a temperature of 500 ^{o}C for 6 hours according to the method described by Byers et al.(1978).

4.3 Extraction and Cleanup

A modified QuEChERS method was adopted for the extraction of target PAH and PCB compounds (Salem et al., 2016). Samples of approximately 1 g were weighed into a 50 ml centrifuge tube and hydrated with 6 mL of millipore water. Acetonitrile (6 mL), containing 1% glacial acetic acid was added, followed by vigorous shaking using a vortex mixer for 2 minutes to obtain homogeneity. To this mixture, 3 g magnesium sulphate ($MgSO_4$), 0.7 g sodium acetate ($C_2H_3NaO_2$) and 0.7 g sodium acetate trihydrate ($C_2H_9NaO_5$) was added, followed by

vigorous shaking to ensure complete dispersion. Samples were then centrifuged at 5000 rpm for 10 minutes. The organic extract (supernatant) was transferred into a centrifuge tube containing 0.5 g $MgSO_4$, 0.2 g C18 and 0.2 g primary secondary amine (PSA). This mixture was vortexed, then centrifuged to collect the supernatant (clean extract). The extract was evaporated to dryness under vacuum and reconstituted in 1 mL hexane before transferring into a GC vial for analysis.

4.4 Analysis

Analysis was performed using two-dimensional gas chromatography-Time-of-Flight mass spectrometry (Agilent 7890B GC x GC-TOFMS) equipped with a BPX5 capillary column (30 m, 0.25 mm, 0.25 μm film thickness). Samples of 2 μl were injected (triplicate) in a splitless mode using He (99.999%) as a carrier gas at a flow rate of 1.4 mL/min. The transfer line and inlet temperature was set at 260 and 250 ^oC, respectively. The ion source temperature was set at 250 ^oC, with an acquisition delay time of 3 minutes and acquisition voltage of 1850 V. The initial oven temperature was set at 80 ^oC, held for 0.5 min, and then increased to 180 ^oC at a rate of 20 ^oC/min. The oven temperature was systematically adjusted until a final temperature of 300 ^oC. The secondary oven and modulator temperatures were offset at 5 ^oC and 15 ^oC, respectively, relative to the primary oven temperature. The ion trap mass detection was scanned from 45 to 900 amu. Peak identification and data processing were performed using the Leco ChromaTOF software and databases. Peaks were identified based on the retention time of specific ions and confirmed by two identifier ions (Figure 4.2).

4.5 Quality assurance and quality control

Quantification was performed against a series of multicomponent PAH and PCB reference standards. The correlation coefficient (R^2) values for calibration curves were all greater than 0.99 (Table 4.2). Extraction efficiency of the procedure was determined by spiking blank samples (triplicate) with a known concentration of the multicomponent standard solution. The blank sample was collected from a different location relative to the field of study, it was extracted and analysed repeatedly (>10) using the method stated in sections 4.3 and 4.4 to ensure the absence of the target analytes. Recoveries ranged from 68 – 110% for PAHs and 76 – 112% for PCBs (Table 4.2).

Table 4.2: Calibration coefficients (R^2), n=3, percentage recoveries, LOD and LOQ

Congeners	**Recovery (%)**	**R^2**	**LOD (µg/l)**	**LOQ (µg/l)**
Naphthalene	75±5.5	0.9986	0.09	0.29
Acenaphthylene	68±7.1	0.9989	0.04	0.13
Acenaphthene	82±2.3	0.9980	0.04	0.13
Fluorene	81±5.6	0.9995	0.07	0.24
Phenanthrene	80±11	0.9921	0.06	0.18
Anthracene	81±9.0	0.9998	0.08	0.26
Fluoranthene	98±4.3	0.9972	0.09	0.29
Pyrene	77±4.1	0.9945	0.29	0.95
Chrysene	95±8.2	0.9939	1.09	3.61
Benzo[a]anthracene	79±6.3	0.9797	0.39	1.29
Benzo[k]fluoranthene	102±12	0.9900	1.10	3.64
Benzo[b]fluoranthene	101±7.0	0.9965	0.83	2.75
Benzo[a]pyrene	110±1.5	0.9943	1.06	3.51
PCB 18	94±3.4	0.9970	0.04	0.12
PCB 31	86±2.4	0.9988	0.03	0.09
PCB 44	91±8.3	0.9935	0.04	0.12
PCB 52	112±4.2	0.9930	0.04	0.14
PCB 101	86±8.9	0.9933	0.05	0.18
PCB 118	87±1.8	0.9937	0.07	0.23
PCB 153	94±4.6	0.9975	0.16	0.54
PCB 138	92±5.7	0.9946	0.08	0.27
PCB 149	76±9.1	0.9954	0.12	0.39
PCB 180	78±3.2	0.9947	0.17	0.58
PCB 195	82±4.2	0.9906	0.39	1.30

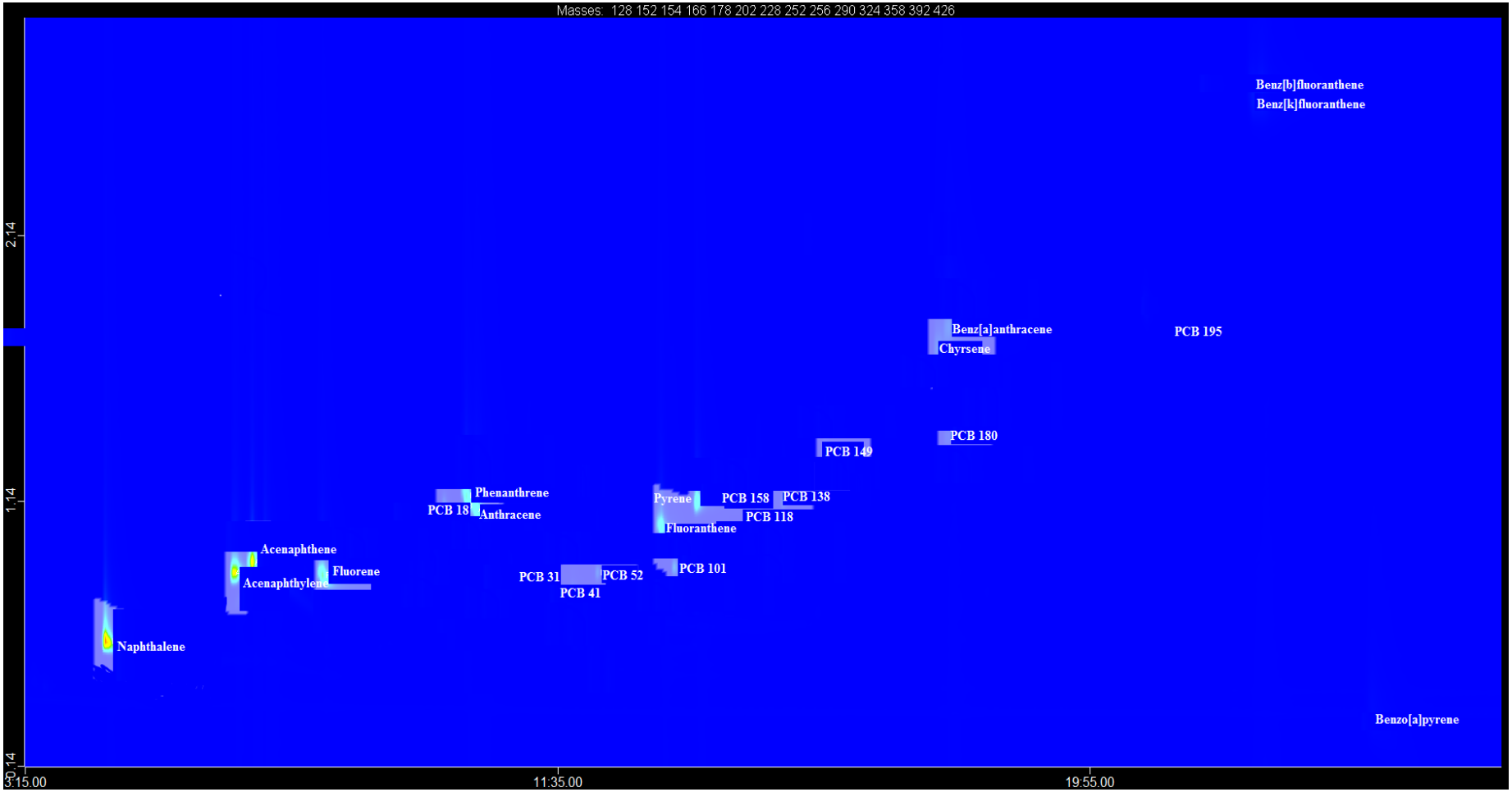


Figure 4.2: A representative 2D chromatogram of the separation of mixed PAH and PCB reference standard using Agilent 7890B GC x GC-TOFMS.

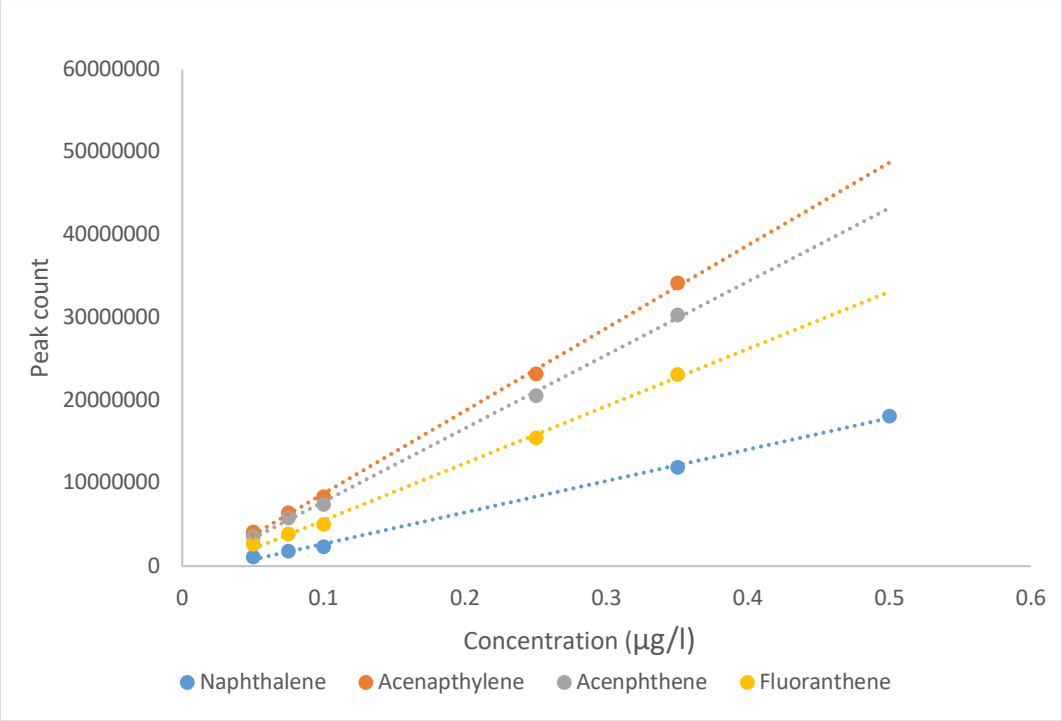


Figure 4.3: Calibration curves of some congeners in PAH multicomponent reference standard

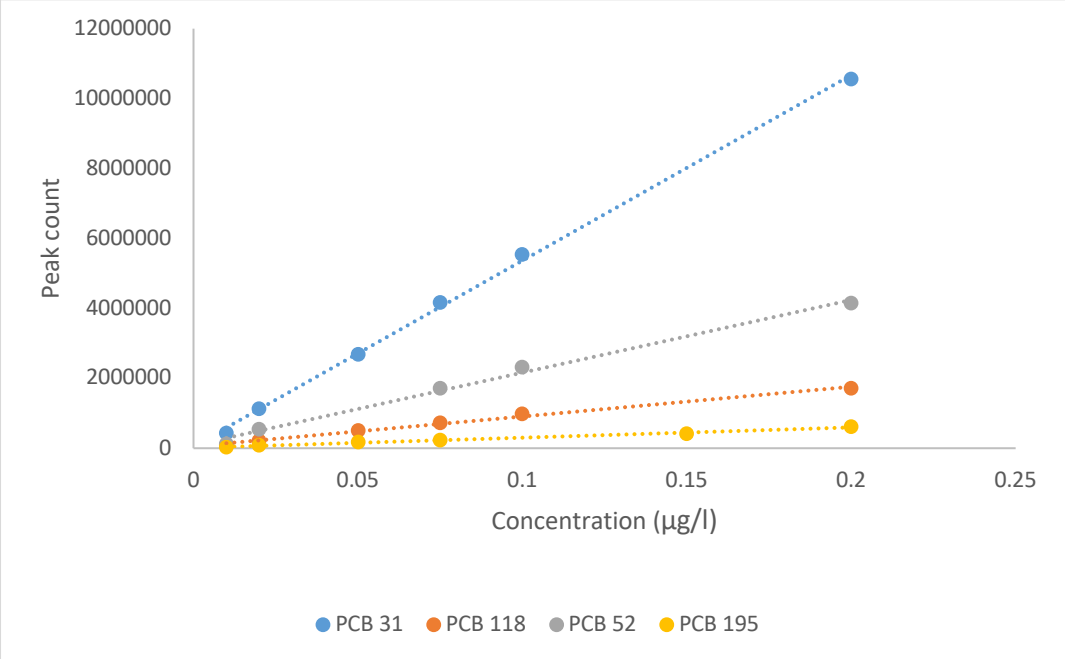


Figure 4.4: Calibration curves of some congeners in PCB multicomponent reference standard

After approximately every 10 sediment samples, a standard solution (PAH at 250 ppb and PCB 50 ppb) was analysed to monitor instrumental response. RSD values ranged from 0.72 - 9.0 for PAHs and 1.6 - 11 for PCBs (Table 4.3). Limits of detection (LOD) for each analyte was estimated based on international guidelines and determined as 3 times the ratio of the standard deviation of the y-intercept to the slope of regression line, while the LOQ was estimated as 10 times the value of the LOD. LOD values for PAHs ranged from 0.04 – 1.1 µg/kg and 0.03 – 0.39 µg/kg for PCBs, while the LOQ ranged from 0.13 – 3.64 µg/kg for PAHs and 0.09 – 1.30 µg/kg for PCBs. Final concentrations were normalized to total organic matter content to take into account variations in sediment composition.

Table 4.3: Analysis of a spiked sample containing PAH congeners at 250 **µg/l** and PCB congeners at 50 **µg/l**, (n=3) which was analysed periodically between samples

Congeners	**Concentrations (µg/l)**			**% RSD**
Naphthalene (Nap)	206	210	221	3.6
Acenaphthylene (Acey)	195	208	193	4.1
Acenaphthene (Acea)	188	173	184	4.2
Fluorene (Flu)	185	183	157	8.8
Phenanthrene (Phe)	244	243	248	1.0
Anthracene (Ant)	165	188	184	6.9
Fluoranthene (Fla)	162	188	192	9.0
Pyrene (Pyr)	168	176	178	2.8
Chrysene (Chr)	245	242	243	0.72
Benzo[a]anthracene (BaA)	237	244	247	2.3
Benzo[k]fluoranthene (BkF)	186	193	207	5.3
Benzo[b]fluoranthene (BbF)	175	190	181	4.3
Benzo[a]pyrene (BaP)	171	173	176	1.3
PCB 18	43	41	44	3.7
PCB 31	43	46	42	5.6
PCB 44	47	43	45	4.2
PCB 52	41	42	43	1.6
PCB 101	38	34	39	7.1
PCB 118	36	40	32	11
PCB 153	46	44	46	2.8
PCB 138	45	51	45	7.0
PCB 149	40	43	36	9.0
PCB 180	41	49	41	11
PCB 195	51	43	44	9.9

CHAPTER 5: RESULTS

The total organic matter (TOM) content of surface sediment samples collected ranged from 12% – 29% with sites S1A (Klip River tributary) and S2B (Klipspruit tributary) recording the highest percentages of 29% and 27%, respectively (Table 5.1). Site S2A had the lowest TOM of 12%. Due to variability in the organic content of samples, TOM values were used to normalise measured PAH and PCB concentrations.

PCB and PAH congeners investigated in this study were found to be widely distributed in sediments collected from the Klip River wetland and its tributaries. Total PCB concentrations in surface sediments collected from the catchment (Klip River and Klipspruit) ranged between 1.1 – 5.3 mg/kg and between 0.17 – 0.80 mg/kg within the wetland. Total PAH concentrations were higher and ranged from 44 – 95 mg/kg within the catchment and 2.4 – 6.3 mg/kg within the wetland.

5.1 Spatial distribution of PAHs and PCBs in surface sediments

Highest ∑PAH concentrations were detected at site S1B of the Klipspruit tributary, with a total mean concentration of 95 ± 6.7 mg/kg, whilst site S3A of the Klip River tributary recorded the lowest mean concentration of 44 ± 2.6 mg/kg (Table 5.1). ∑PAH concentrations at sites S1A (52 ± 4.1 mg/kg) and S2A (60 ± 4.1 mg/kg) both on the Klip River tributary, which drains into the wetland at site S3A (44 ± 2.6) revealed little downstream variation (Table 5.1). Additionally, ∑PAH concentrations at sites S1B (53 ± 2.9 mg/kg) and S2B (57 ± 3 mg/kg), both on the Klipspruit tributary which drains into the wetland at site S4B showed little downstream variation. Chrysene (20.5%), benzo(a)anthracene (13.0%) and pyrene (12.7%) were the predominant PAHs detected and together accounted for approximately 47% of ∑PAH concentrations (Table 5.1). On average, the Klipspruit tributary (69 ± 4.6) showed a higher level of contamination of ∑PAH compared to the Klip River tributary (52 ± 3.6).

Table 5.1: Average concentration (mg/k ± SD, n=3) and percentage contribution of individual PAH congeners and physico-chemical parameters present in the surface sediments from the Klip River catchment

	Klip River			**Klipspruit**				
Congeners	**S1A (mg/kg)**	**S2A (mg/kg)**	**S3A (mg/kg)**	**S1B (mg/kg)**	**S2B (mg/kg)**	**S3B (mg/kg)**	**S4B (mg/kg)**	**% Contribution**
PAHs								
Naphthalene	3.1±0.2	4.3±0.4	2.7±0.02	4.4±0.08	0.23±0.007	0.41±0.002	2.6±0.05	4.1
Acenaphthylene	0.61±0.1	1.1±0.007	0.53±0.006	1.9±0.04	1.3±0.027	2.5±0.02	1.3±0.02	2.1
Acenaphthene	0.55±0.04	0.49±0.008	0.36±0.009	1.0±0.05	1.1±0.07	1.5±0.05	1.0±0.02	1.4
Fluorene	0.47±0.02	0.80±0.003	0.92±0.02	2.5±0.04	3.6±0.1	2.4±0.02	1.3±0.01	2.7
Phenanthrene	5.5±0.1	13±0.3	3.6±0.02	1.8±0.03	4.4±0.06	6.2±0.02	4.7±0.05	9.1
Anthracene	1.4±02	1.1±0.02	2.7±0.02	1.6±0.04	3.4±0.03	2.1±0.02	0.10±045	3
Fluoranthene	2.6±0.1	4.5±0.04	4.5±0.03	5.1±0.06	2.5±0.03	5.7±0.01	5.5±0.1	7
Pyrene	11.0±0.4	8.3±0.03	5.8±0.004	8.4±0.07	5.2±0.3	8.1±0.01	8.1±0.1	13
Chrysene	13.0±0.3	12.0±0.06	9.8±0.4	24±0.2	2.3±0.09	18 ±0.2	9.8±0.08	21
Benzo[a]anthracene	5.2±0.1	3.9±0.02	4.5±0.06	16±0.07	10 ±0.6	10±0.01	6.6±0.01	13
Benzo[k]fluoranthene	4.5±0.05	2.3±0.02	2.6±0.02	11±0.3	7.6±0.2	7.2±0.004	3.3±0.05	8.8
Benzo[b]fluoranthene	1.6±0.1	3.5±0.04	1.7±0.03	7.8±0.08	7.1±0.1	4.3±0.006	5.2±0.2	7.2
Benzo[a]pyrene	2.2±0.07	4.6±0.04	4.4±0.06	9.6±0.08	7.8±0.2	4.0±0.05	3.1±0.07	8.3
Total PAHs	**52**	**60**	**44**	**95**	**57**	**73**	**53**	
Organic (%)	29	12	22	15	27	13	24	
pH	7.0	7.3	6.9	6.5	6.7	7.3	6.7	
Redox (mV)	25	8.2	32	54	48	7.2	39	

Table 5.2: Average concentration (mg/kg±stdev, n=3) and percentage contribution of individual PCB congeners present in the surface sediments from the Klip River catchment

	Klip River			Klipspruit				
Congeners	**S1A (mg/kg)**	**S2A (mg/kg)**	**S3A (mg/kg)**	**S1B (mg/kg)**	**S2B (mg/kg)**	**S3B (mg/kg)**	**S4B (mg/kg)**	**% contribution**
PCB 18	0.085±0.01	0.40±0.002	0.077±0.001	0.062±0.002	0.025±0.003	0.50±0.016	0.22±0.001	8.4
PCB 31	0.048±0.05	0.27±0.001	0.061±0.001	0.064±0.003	0.067±0.002	0.39±0.002	0.14±0.001	6.4
PCB 44	0.072±0.006	0.47±0.02	0.079±0.005	0.025±0.001	0.066±0.006	0.32±0.006	0.15±0.001	7.0
PCB 52	0.023±0.005	0.13±0.001	0.045±0.001	0.040±0.001	0.066±0.001	0.15±0.001	0.065±0.001	3.1
PCB 101	0.084±0.005	0.45±0.004	0.11±0.001	0.057±0.003	0.11±0.003	0.44±0.01	0.21±0.002	8.7
PCB 118	0.12±0.010	0.58±0.001	0.16±0.009	0.17±0.001	0.16±0.002	0.68±0.04	0.34±0.02	13
PCB 153	0.078±0.010	0.32±0.001	0.073±0.008	0.11±0.001	0.093±0.004	0.53±0.01	0.22±0.001	8.5
PCB 138	0.059±0.003	0.24±0.001	0.071±0.004	0.12±0.001	0.061±0.006	0.38±0.001	0.17±0.01	6.5
PCB 149	0.059±0.003	0.25±0.06	0.097±0.001	0.21±0.003	0.071±0.002	0.51±0.002	0.21±0.001	8.4
PCB 180	0.19±0.002	0.46±0.002	0.22±0.002	0.39±0.002	0.21±0.003	0.78±0.003	0.32±0.005	15
PCB 195	0.25±0.006	0.47±0.01	0.20±0.003	0.40±0.01	0.23±0.004	0.64±0.008	0.30±0.01	15
Total PCBs	**1.1**	**4.0**	**1.2**	**1.6**	**1.2**	**5.3**	**2.4**	

PAHs with four-member rings (pyrene, chrysene and benzo(a)anthracene) contributed 41% of ∑PAHs across all sites, while three-membered ring PAHs (acenaphthylene, acenaphthene, fluoranthene, phenanthrene, and anthracene) contributed about 40%. Two-membered rings (naphthalene) contributed the least (0.3%), while PAHs with five-member rings (benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene) contributed about 15% (Figure 5.1). Overall, four- and three-member rings were the most dominant PAH congeners detected within the study area (Figure 5.1). Site S1B of the Klipspruit tributary recorded the highest percentage of the four-membered ring PAHs, while the site S2A (Klip River tributary) had the highest percentage of the three-membered ring PAHs (Figure 5.1).

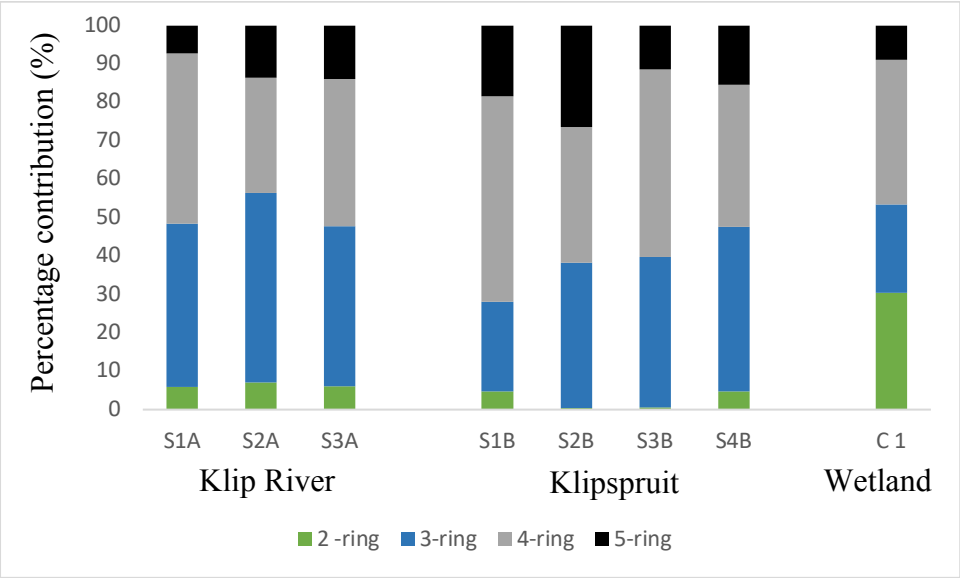


Figure 5.1: Percentage contribution of PAH membered rings within the study area.

Diagnostic source identification of PAHs in sediments of the Klip River wetland was performed using Fla/(Fla+Pyr), Ant/(Ant+Phe), and BaA/(BaA+Chr) ratios. The Ant/(Ant+Phe) values of all sites were > 0.1, which suggests a pyrogenic source of contamination from the combustion of coal and biomass (Figure 5.2). Fla/(Fla+Pyr) values suggest approximately 63% of the sites pollution to be from dominantly petrogenic sources (incomplete combustion of petroleum), while the remaining 37% are from combustion of petroleum (Figure 5.2 and 5.3). The BaA/(BaA+Chr) values also suggest approximately 63% of all sites to be contaminated with petroleum combustion while the remaining 37% from mixed petrogenic and pyrogenic sources (Figure 5.3).

Sites S3B located on the Klipspruit (5.3 ± 0.2 mg/kg) and S1A on the Klip River (1.1 ± 0.07 mg/kg) recorded highest and the lowest mean ∑PCB concentrations, respectively (Table 5.2). Additionally, site S4B on the Klipspruit (2.4 ± 0.08 mg/kg) recorded a higher residual concentration of ∑PCB compared to site S3A on the Klip River (1.2 ± 0.06 mg/kg), which is a similar observation made for ∑PAH concentrations (Table 5.2). ∑PCB concentrations along both tributaries showed variable downstream trends. Generally, average ∑PCB concentrations along the Klipspruit (2.6± 0.2) were higher than that detected along the Klip River (2.1 ± 0.09) (Table 5.2). PCB 118 (13%), PCB 149 (8.4%), PCB 180 (15%) and PCB 195 (15%) accounted for approximately 52% of the total PCB concentrations detected in catchment samples (Table 5.2).

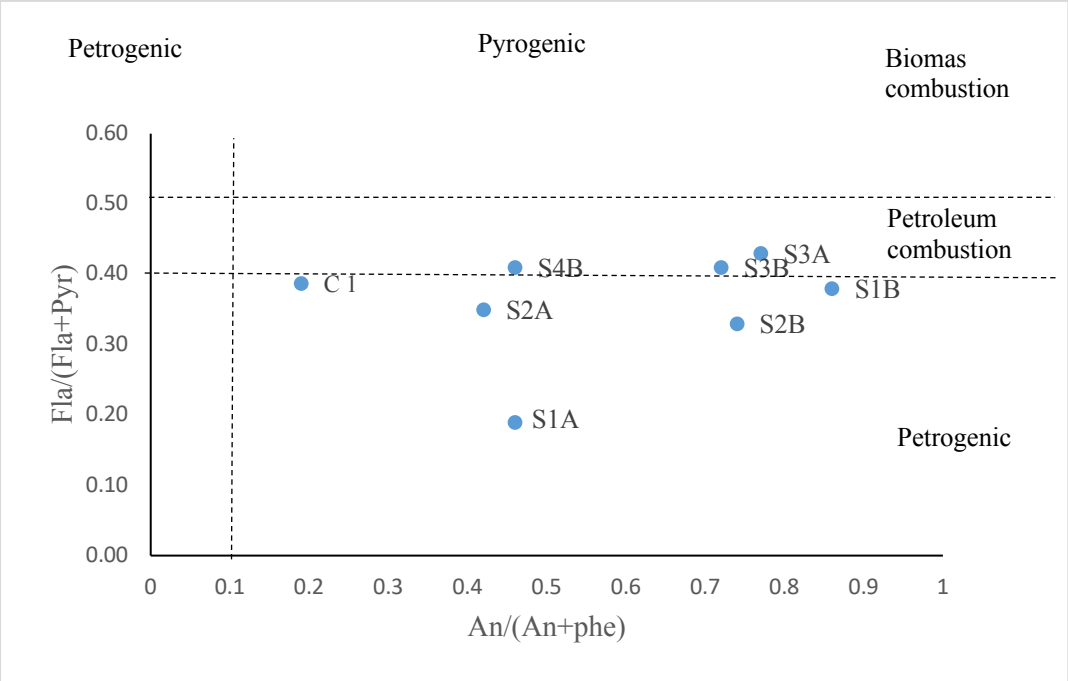


Figure 5.2: PAH source fingerprinting using fluoranthene, pyrene, anthracene and phenanthrene ratios to identify source of contamination.

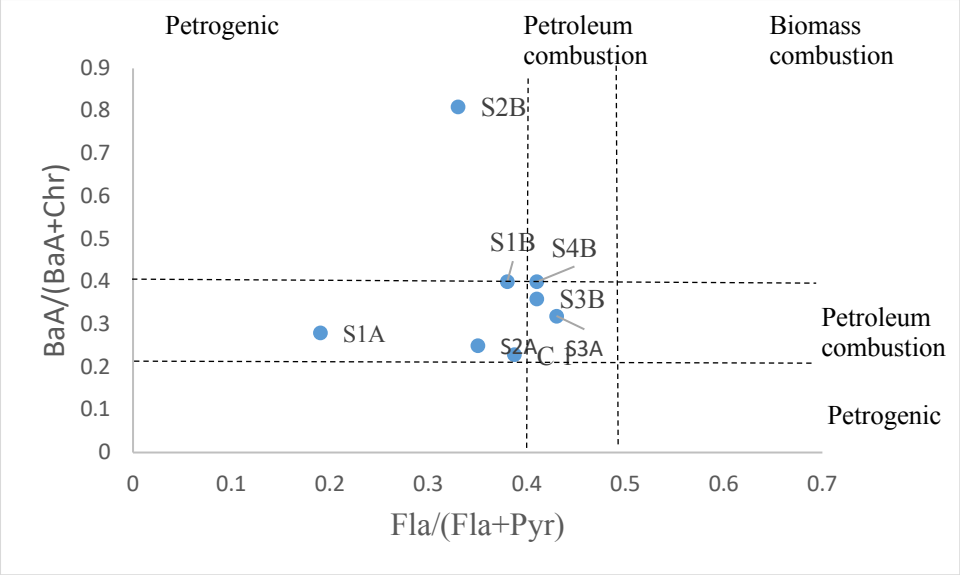


Figure 5.3: PAH source fingerprinting using benzo(a)anthracene, chrysene, fluoranthene and pyrene ratios to identify source of contamination.

At all catchment sampling sites, PCB congeners with 4-6 chlorine substituents were the most dominant (about 45%), followed by congeners with 7-8 chlorine atoms (30%) (Figure 5.4). The percentage of 4-6 chlorinated PCBs were fairly evenly distributed across all sites, but the highest percentage of 7-8 chlorinated PCBs was recorded at the S1B site on the Klipspruit (Figure 5.4). On average, the mean concentration of 4-6 (2.7 ± 0.19 mg/kg) and 7-8 (1.8 ± 0.29 mg/kg) chlorinated PCBs at the Klip River tributary were lower than those detected along the Klipspruit tributary; 4.9 ± 0.3 mg/kg and 3.3 ± 0.15 mg/kg, respectively (Table 5.2; Figure 5.4).

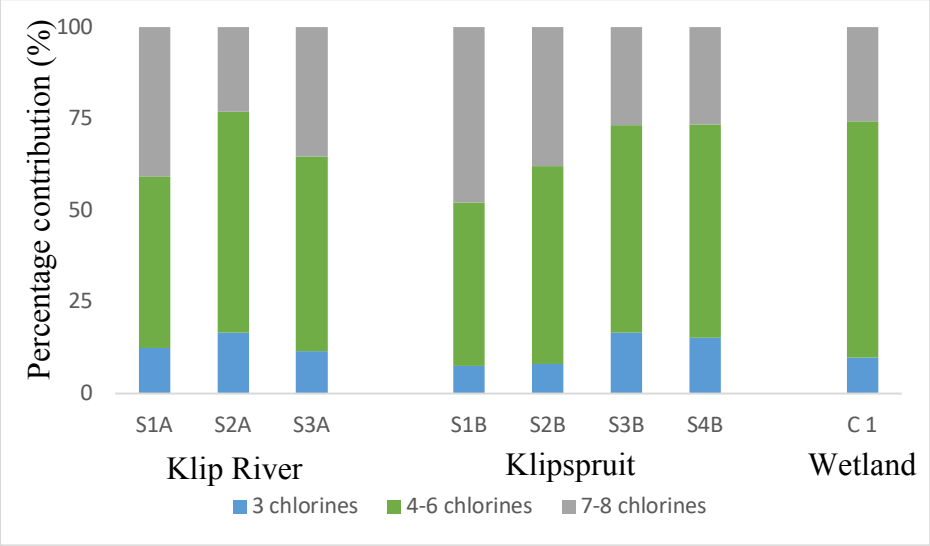


Figure 5.4: Percentage contribution of PCBs with varying number of chlorine atoms attached to the biphenyl ring

5.2 Downcore variation in the distribution of PAHs and PCBs

The sediment core from the wetland showed a wide variation in the total organic matter content, with percentages ranging from 23% near the base of the core to 92% at 90 cm depth (Figure 5.5). The upper 260 cm of the core was comprised of peat and was characterised by an organic content that varied between 23% - 92%. The sediment core samples showed a wide variation in redox potential, with the highest value of -109 mV recorded at 100 cm while the lowest value -316.5 mV recorded at 220 cm (Figure 5.5).

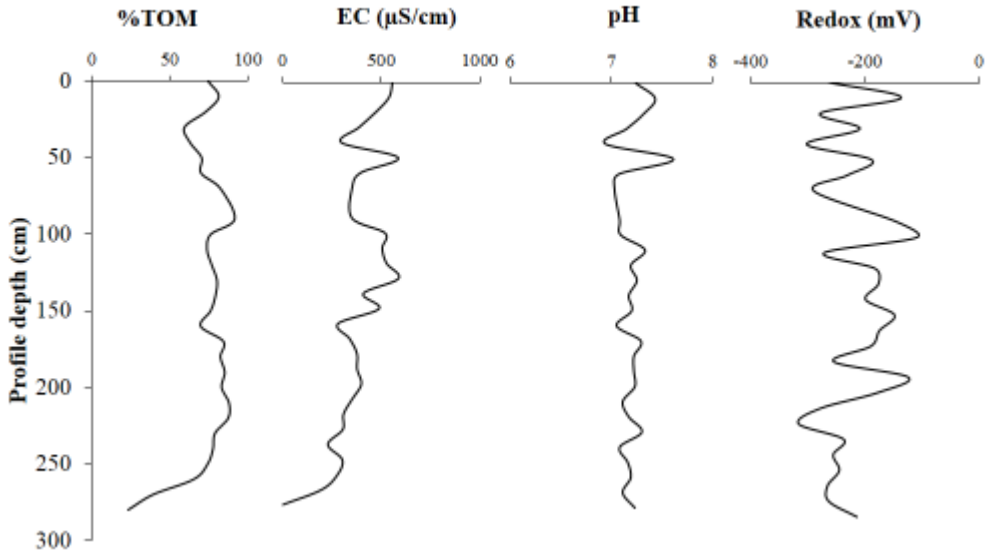


Figure 5.5: Variation in physicochemical parameters (% TOM, EC, REDOX, and pH) with depth at the Klip River wetland

There was no apparent trend in the redox potential through the core. Sediment pH ranged between 6.9 and 7.6, and showed no obvious trend with depth (Figure 5.5). Electrical conductivity (EC) ranged from 0.17 to 591 µS/cm. The highest value of EC (591 µS/cm) was recorded at depth of 130 cm while the lowest value (0.17 µS/cm) was recorded near the bottom of the profile.

Mean ∑PAH concentrations ranged between 2.4 – 6.3 mg/kg, and were lower than that detected in surface sediments from the catchment (Figure 5.6). There was an inconsistent but gradual increase in mean ∑PAH concentrations with increasing depth to ~ 160 cm where a highest concentration of 6.3 ± 0.49 mg/kg was detected. Lowest ∑PAH concentrations (2.4 ± 0.22 mg/kg) were detected within surface samples from the wetland (Figure 5.6)

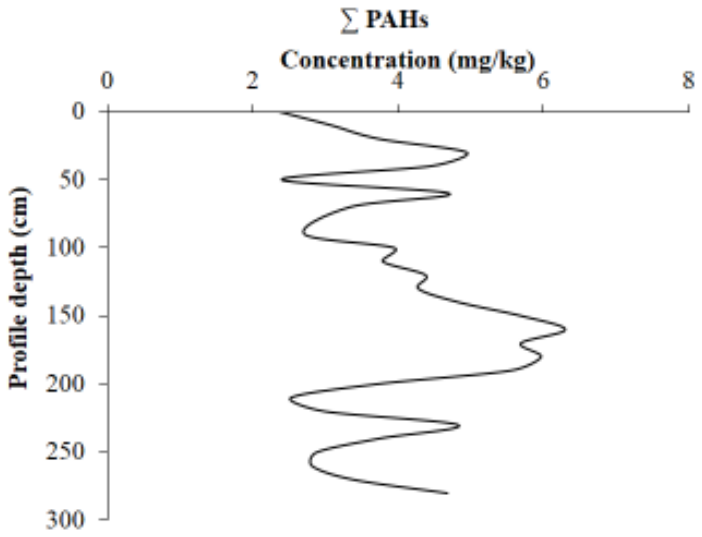


Figure 5.6: Mean distribution of ∑PAH (mg/kg) at the core sampling site of the wetland.

Approximately 62% of the ∑PAH concentration in the sediment core was accounted for by only three congeners i.e. naphthalene (30%), phenanthrene (12%) and chrysene (20%) (Supplementary Table 1). Naphthalene and chrysene showed a gradual increase down the core. On the contrary, phenanthrene recorded its highest concentration towards the base of the peat (Figure 5.7).

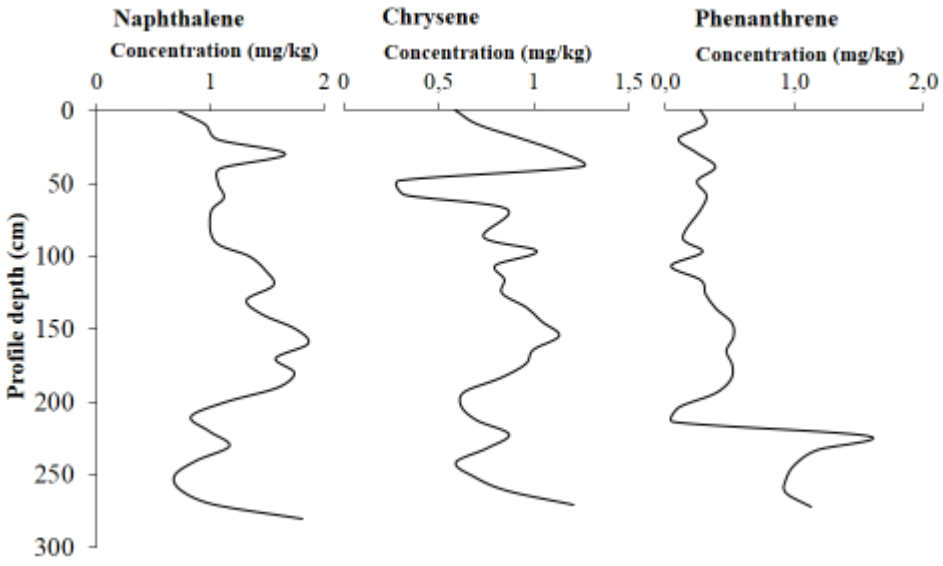


Figure 5.7: Distribution of the most dominant PAH congeners through the Klip River wetland core

Chrysene, benzo(a)anthracene, and benzo(k)fluoranthene, which are known for their carcinogenic properties, contributed approximately 28% to ∑PAH concentrations (Supplementary Table 1). These compounds all showed similar trends, with a gradual increase down the core followed by a decrease towards the bottom of the core. Benzo(k)fluoranthene was not detected in samples below 200 cm depth (Figure 5.8).

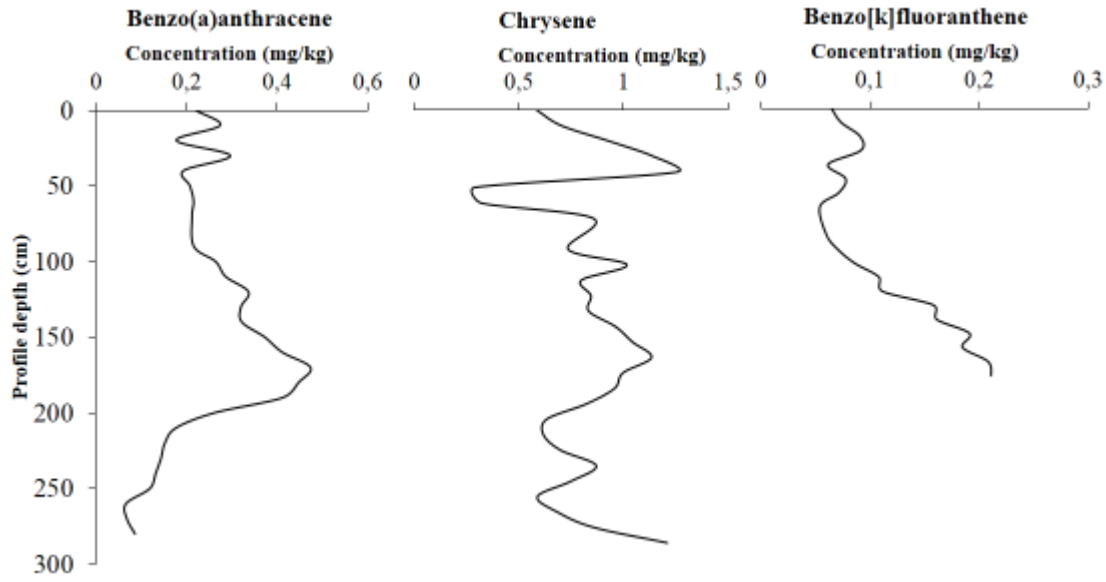


Figure 5.8: Distribution of carcinogenic PAHs through the Klip River wetland core.

Naphthalene (0.71 - 1.9 mg/kg), benzo(a)anthracene (0.07 - 0.47 mg/kg), benzo(b)fluoranthene (0.03 - 0.4 mg/kg), and benzo(a)pyrene (0.03-0.21 mg/kg) are all considered highly toxic compounds and together accounted for about 44% of ∑PAH concentrations. All compounds displayed similar downcore trends except for naphthalene which increased at the base of the core (Figure 5.9; Supplementary Table 1).

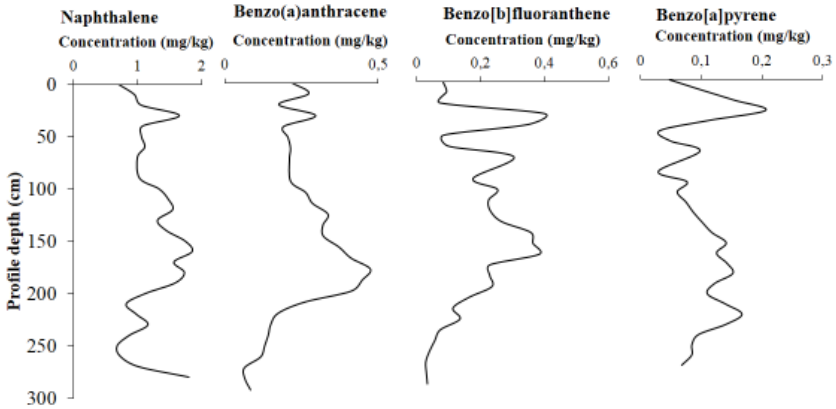


Figure 5.9: Distribution of highly toxic PAHs through the Klip River wetland core.

The distribution of PAHs varied according to the number of aromatic rings (Figure 5.10). Four-membered ring compounds had the highest representation (37%) followed by the two-membered ring compounds (30%). The three- and five-membered rings recorded approximately 23% and 9%, respectively (Supplementary Table 1). The two and three rings showed similar downcore trends, with a substantial increase in concentration around 180 cm. The four- and five-membered rings also showed similar downcore trends with highest concentrations measured between 40-60 cm and 150-180 cm (Figure 5.10).

Total PCB concentrations through the sediment core showed substantial variations, with concentrations ranging between 0.17 mg/kg and 0.8 mg/kg (Figure 5.11). Highest concentrations (0.8 ± 0.028 mg/kg) were detected at 160 cm, but were lower than that measured in surface sediment samples (1.1 – 5.3 mg/kg). The congeners detected in highest concentration were ∑PCB 195 (1.6 ± 0.04 mg/kg), ∑PCB 180 (1.6 ± 0.021 mg/kg), ∑PCB 101 (1.7 ± 0.029 mg/kg), and ∑PCB 44 (1.7 ± 0.03 mg/kg) together contributed about 53% to ∑PCB concentrations (Supplementary Table 2).

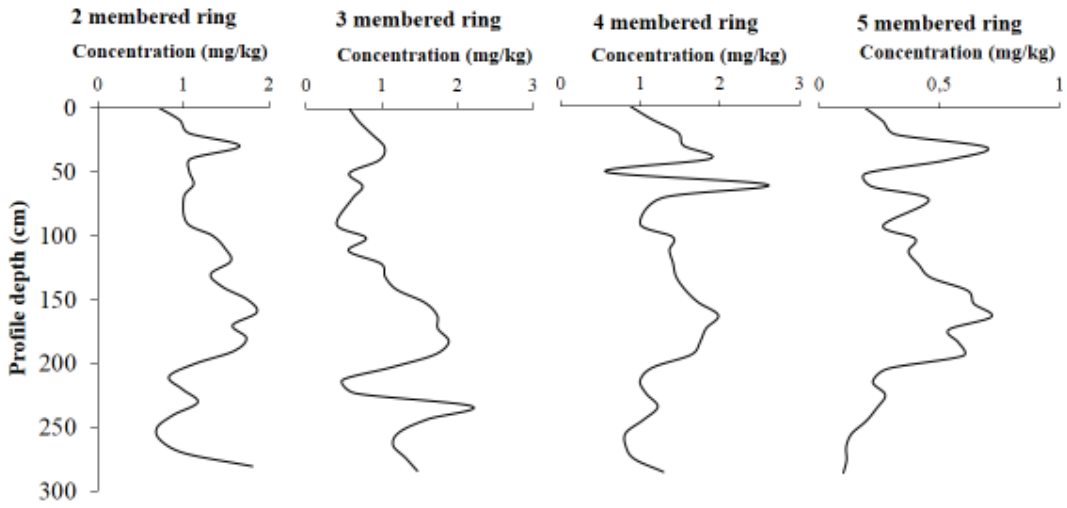


Figure 5.10: Distribution of PAHs according to the number of aromatic rings.

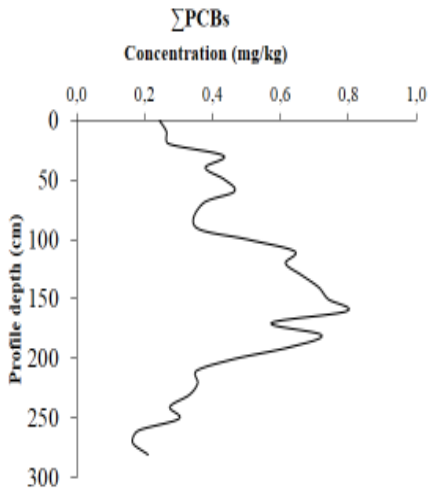


Figure 5.11: Mean distribution of ∑PCB concentrations through the wetland core.

The two most persistent PCB congeners; PCB 180 and 195 (both with a half-life of 9.9 years) accounted for approximately 26% of ∑PCB concentrations. Concentrations ranged between 0.001-0.2 mg/kg for PCB 195 and 0.02-0.1 mg/kg for PCB 180 (Figure 5.12; Supplementary Table 2). Both compounds showed similar trends, with a gradual increase in concentration down the core to 190 cm.

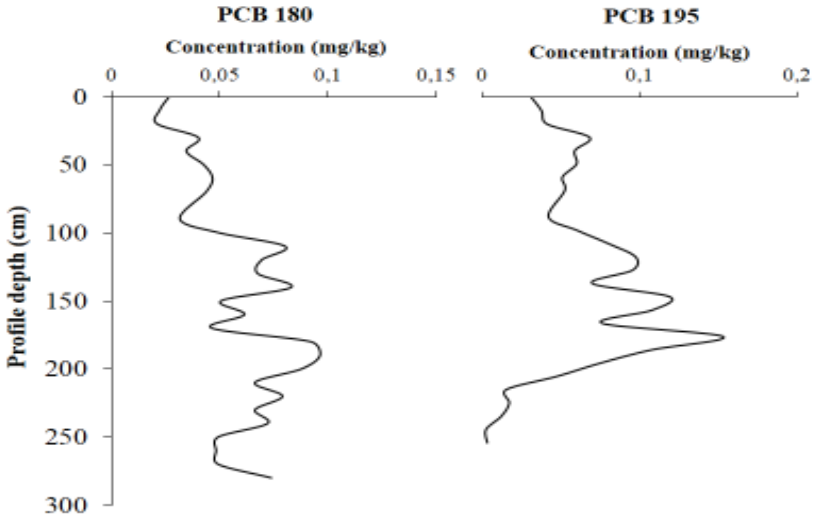


Figure 5.12: Distribution of highly persistent PCBs through the Klip River wetland core.

Less persistent PCB congeners containing two and three chlorine atoms i.e. PCB 52 (7.4%; with half-life of 2.6 years), PCB 44 (11%; half-life 1.6 years), PCB 31 (2.9%; half-life of 5 months), and PCB 18 (4.9%; half–life of few weeks) contributed about 30% to ∑PCB concentrations (Supplementary Table 2). PCB 52 showed a gradual increase in concentration

down the core to a depth of 190 cm, after which a decrease in concentration was recorded towards the end of the peat. PCB 44 concentrations were variable down the core with noticeable increases in concentration at 70 cm and 150 cm. PCB 31 recorded its highest concentration at 170 cm, but was not detected after 200 cm. PCB 18 recorded its highest concentration at 130 cm and subsequently could no longer be detected below 250 cm (Figure 5.13).

The distribution of PCBs according to the number of chlorine atoms attached to biphenyl ring was investigated, with 4-6 chlorinated PCB compounds being the dominant group (PCBs; 118, 153, 138 and 149). This group contributed 64% to ∑PCB concentrations followed by the 7-8 chlorinated PCBs (PCB 180 & 195) at almost 25%. The 3 chlorinated PCBs (PCB 18 & 31) contributed the least with about 10%. (Supplementary Table 2; Figure 5.4). All three classes of PCBs showed similar patterns down the core with gradual increases in concentration from the surface to 180 – 200 cm (Figure 5.14).

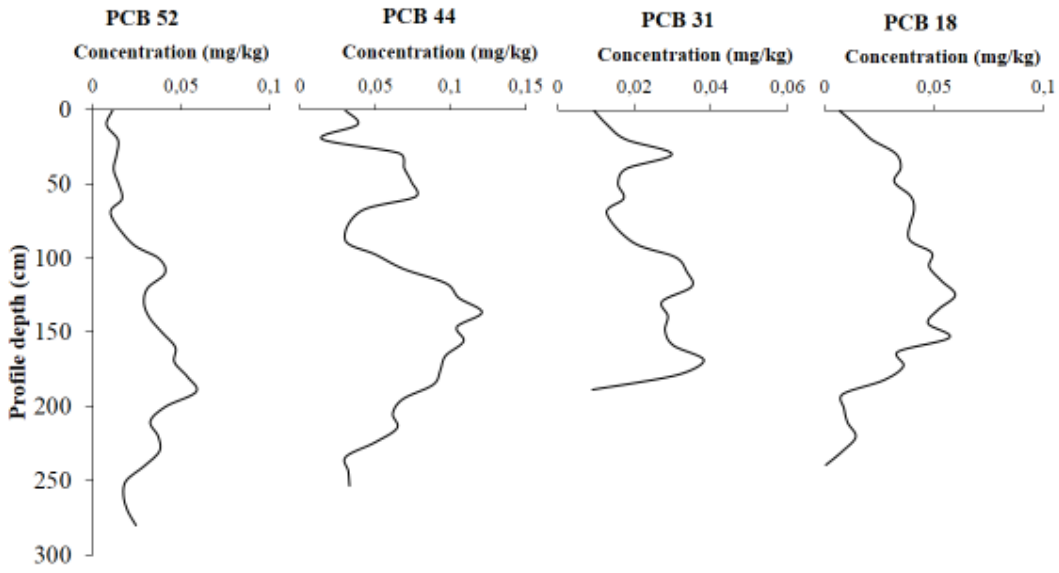


Figure 5.13: Distribution of less persistent PCBs in the core sample from Klip River wetland.

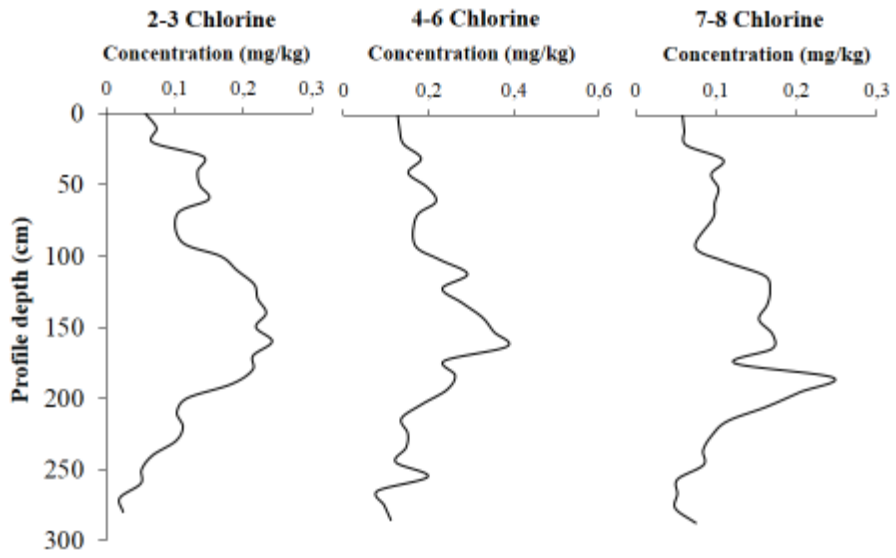


Figure 5.14: Distribution of PCBs according to the number of chlorine atoms attached to the biphenyl ring of the PCB.

5.3 Ecological Risk Assessments

Ecological risk assessment using ERL (effect range low) and ERM (effect range medium) guidelines show that compounds of major concern are those greater than the ERM, phenanthrene, and chrysene were greater than ERM values at four sites while benzo[a]anthracene at two sites and fluorene, pyrene, benzo[k]fluoranthene, benzo[b]fluoranthene, and benzo[a]pyrene were above the ERM guideline at one site. ERL and ERM guidelines only provide an acceptable limit for ∑PCBs (Table 5.3). In all investigated sites, ∑PCB were above the ERL limit, however only 3 samples had total PCB concentration above the ERM guideline value (Table 5.3).

Long and MacDonald (1998) recommended a more comprehensive approach to assessing the combined ecological risk from multi-toxic PAHs on the M-ERM-Q method, calculated according to equation 1.

$$M - ERM - Q = \frac{\sum(Ci/ERMi)}{n} \qquad \text{Equation 1}$$

Where C*i* concentration of congener *i* in the sediment, ERMi is the ERM value for congener *i* and *n* is the number of compounds. Values less than the ERM are below the lowest acceptable limit and are said to be non-toxic, while values exceeding the ERM are greater than the acceptable limit and are considered highly toxic. Based on this assessment, the most

contaminated sites were S2B and S1B along the Klipspruit, while sites S1A and S2A on the Klip River fell in the medium-high category (Figure 5.15)

Table 5.3: Toxicity risk assessment of PAHs and PCBs based on the guidelines of Long and MacDonald (1998), in sediments (µg/kg dw) of the Klip River catchments and wetland.

Compounds	ERL (µg/kg)	ERM (µg/kg)	PAH range in the study sites (µg/kg)	Number of sites > ERL	Number of sites > ERM
Naphthalene	160	2100	53-900	6	0
Acenaphthylene	16	500	90-355	All	0
Acenaphthene	44	640	31-289	7	0
Fluorene	19	540	34-964	8	1
Phenanthrene	240	1500	206-1582	7	4
Anthracene	85	1100	19-907	7	0
Fluoranthene	600	5100	19-1320	6	0
Pyrene	665	2500	58-3228	7	1
Chrysene	384	2800	440-3869	8	4
Benzo[a]anthracene	261	1600	164-2723	7	2
Benzo[k]fluoranthene	280	1620	49-2048	7	1
Benzo[b]fluoranthene	320	1880	61-1918	7	1
Benzo[a]pyrene	430	1600	36-2115	7	1
∑PCB	50	400	183-692	5	3

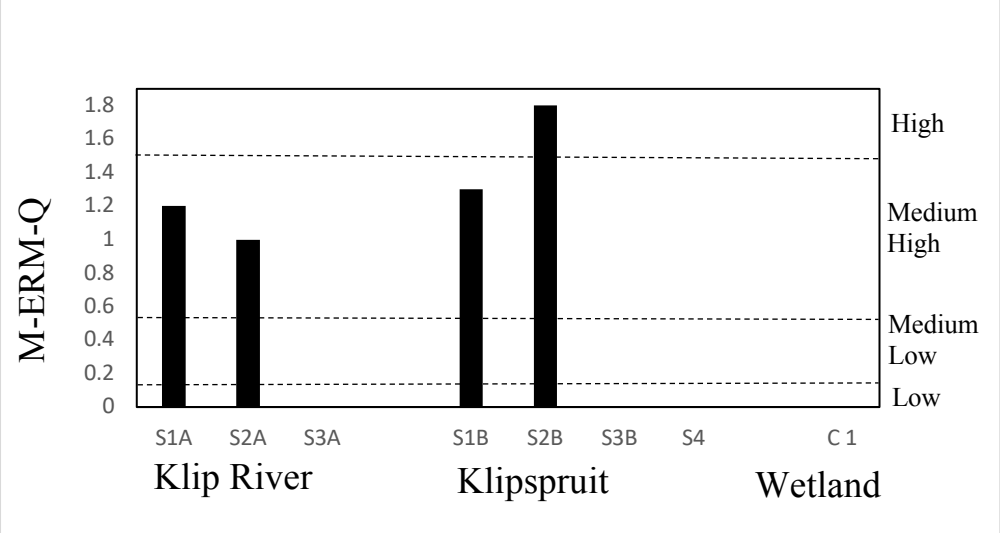


Figure 5.15: Distribution of multiple toxic compounds exceeding the ERM values (M – ERM – Q) in sediments of the Klip River catchments and wetland for PAHs.

CHAPTER 6: DISCUSSION

6.1 Distribution and composition of PAHs and PCBs within the tributaries

The results of this study indicate that organic contaminants, specifically PCBs and PAHs have accumulated in sediments of the Klip River system. This is consistent with recent studies that have reported the presence of organic pollutants such as PAHs (Pheiffer et al., 2018), PCBs, PCDD, and PCDF (Rimayi et al., 2016, 2017) in sediments of the Klip River system. Accumulation studies can provide useful information on contaminant specific bioavailability, which assist in identifying potential agents of toxicity and relate contaminant burden to biomagnification (Gerber et al., 2016; Rainbow, 2002).

The distribution of ∑PAHs within the study area indicates that the Klipspruit tributary is more contaminated compared to the Klip River tributary (Figures 6.1). Highest PAH concentrations were recorded at the most upstream sites along the Klipspruit tributary, with concentrations decreasing downstream towards the wetland. Similarly, the Klip River tributary also recorded high residual concentrations at the most upstream site, before decreasing downstream towards the wetland (Figure 6.1). The upstream sites of the Klipspruit are proximal to a number of major highways including N1, R41 and to a lesser extent R12 (Figure 6.1). In the case of Klip River, the R41 is the only major road that crosses this site. The N1 highway is known to be one of the busiest highways running through the city of Johannesburg and in combination with the two other highways may account for the greater concentration of PAHs detected at Klipspruit tributary relative to Klip River tributary. According to Caricchia et al. (1999), 90% of the total PAH emissions worldwide are from stationary sources, but this is not true in urban settlements where mobile sources from vehicular exhaust are dominant. Sibiya (2012) calculated a 5% increase in the amount of PAHs released from vehicular emissions in the city of Johannesburg from 2005 to 2011. This could be a result of an increase in the number of vehicles that use these roads due to a growing middle class, particularly in Johannesburg. In addition, emissions from industrial activities, which are more predominant along the Klipspruit tributary may account for the high amount of PAHs at these sites compared to the Klip River tributary (Figure 6.1).

The downstream sites of both tributaries are in close proximity to the residential settlements of Soweto and Lenasia (Figure 6.1). Coal contributes 75% of the total energy consumption in South Africa, of which 3% is used in household cooking and heating. However, this 3% is

estimated to contribute to 65% of the total air pollution in South Africa (Balmer, 2017; Jeffrey, 2005). Hence, the amount of PAH burden contributed downstream of both Klip River and Klipspruit tributaries could be attributed to domestic combustion of coal/wood for cooking and heating within and around the densely populated areas of Soweto and Lenasia (Figure 6.1).

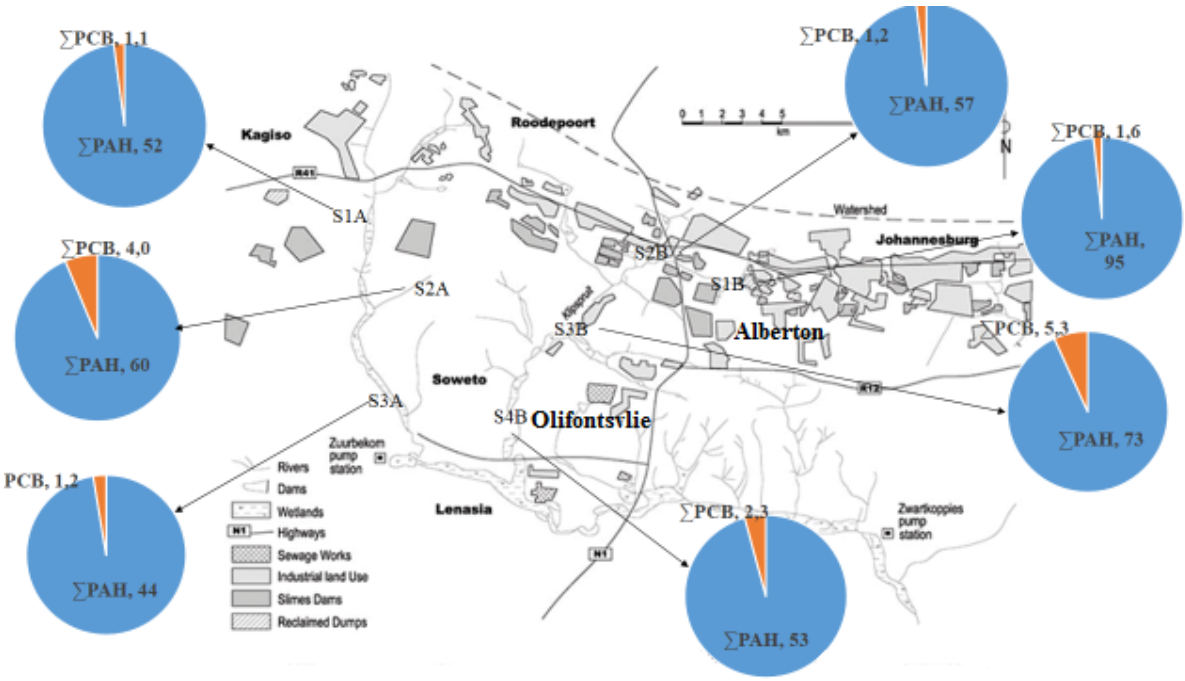


Figure 6.1 Map of the Klip River showing charts of the spatial distribution of ∑PAHs (mg/kg) and ∑PCBs (mg/kg) at the tributary sites

The most dominant PAH congeners in both tributaries were chrysene, pyrene, and benzo(a)anthracene. According to the US-EPA benzo(a)anthracene is considered a human carcinogen. The ability for PAHs to persist in the environment is dependent on their half-life (Jones and De Voogt, 1999) and solubility (Reid et al., 2000). A study by Sibiya (2012) reported the half-life of naphthalene to be 14 weeks, while that of benzo(a)pyrene is 300 weeks under the same conditions. The dominance of the aforementioned congeners (chrysene, pyrene, and benzo(a)anthracene) could be a result of their extended half-lives and high Log K_{ow} values

Similar to PAHs, ∑PCB concentrations detected within the Klipspruit tributary were higher compared to the Klip River tributary. The highest concentration in Klipspruit was recorded at site S3B, with concentrations decreasing at site S4B downstream toward the wetland. Trends in concentration within the Klip River tributary revealed a similar pattern downstream towards the wetland. Alberton is an industrial town which is located upstream of the Klip/Vaal River catchments, which is associated with many industrial activities (Rimayi et al., 2016). Jooste et

al. (2008) reported Alberton to be a potential hotspot for dioxin-like compounds like PCBs. PCBs like other POPs have an ability to travel long distances from their initial point of release to places where they have never used or produced (Dalla Valle et al., 2007). Hence, the concentrations of PCBs detected in the Klip River and Klipspruit tributaries could be as a result of numerous anthropogenic activities in and around the industrial complex of Alberton, such as incineration of PCB equipment, coal combustion and leakages from transformer oil (Rimayi et al., 2017; Samara et al., 2006). Additionally, the National Energy Regulation of South Africa (NERSA) reported leakage of transformer oil as a common occurrence at electricity substations in Gauteng and other provinces (NERSA, 2015).

The residual concentrations detected at the downstream sites of both tributaries could be from anthropogenic activities such as municipal solid waste incineration, hospital waste incineration, sewage waste disposal (Brent and Rogers, 2002; Rimayi et al., 2016), domestic coal combustion, and effluents from sewage works located within proximity of the downstream sites. Furthermore, the levels of PCBs detected downstream of both tributaries could also be due to lack of air pollution regulations which were non-existent prior to April 2015 in South Africa, and resulted in the uncontrolled and unregulated release of incomplete combustible gasses into the environment. According to Hawker and Connell (1988), hydrophobicity increases with an increase in the number of chlorine atoms, and also influences their ability to be persistent in an environment. The predominant PCB congeners recorded at both tributary sites were PCBs 180 and 195. The persistence of these compounds in both tributaries may be as a result of their low solubility (high Log Kow values).

6.2 Vertical distribution of PAHs and PCBs in the Klip River wetland

Industrial and agricultural activities inflict high contaminant pressure on groundwater quality, which can affect groundwater dependent wetland ecosystems (Dimitriou et al., 2008). A number of sewage treatment plants are situated at the Olifontsvlie which is located along the upper reaches of the wetland system (Figure 6.2). According to McCarthy et al. (2007), discharge of wastewater from the sewage treatment plants into the Klipspruit tributary led to the widening of old irrigation canals which were previously dug to support agricultural activities. One such occurrence of groundwater contamination through leakage and subsequent seepage at the Klip River wetland was documented by Naiker et al. (2012). The high level of ∑PAHs and ∑PCBs at the lower end of the core could be attributed to seeping of effluents from the sewage treatment plants located on the wetland which may have caused groundwater

contamination and subsequent influx into the wetland aquifer. Other anthropogenic activities like the indiscriminate disposal and dumping of municipal waste into water bodies from the residents of Soweto, could also contribute to the contamination of groundwater. A study by Humphries et al. (2017) reported a groundwater source of contamination for some inorganic contaminants at the Klip River wetland. The low amount of ∑PAHs and ∑PCBs recorded at the upper sections of the core compared to the bottom could be attributed the Klip River wetland's inability to retain contaminants for a long period hence their downward migration (McCarthy et al., 2007).

The predominant PAH congeners at the peat site were naphthalene, phenanthrene, and chrysene. The dominance of chrysene may be a result of its half-life and solubility, which are higher than most other congeners investigated in this study. The dominance of naphthalene and phenanthrene can be attributed to congener specific sources such as gasoline and diesel engine automobiles, which have been reported to be the dominant sources of PAH congeners in South Africa (Nekhavhambe, 2008; Nieuwoudt et al., 2011; Sibiya, 2012).

6.3 Identification of potential sources of PAHs and PCBs

Three and four membered-ring congeners were the most dominant PAH compounds detected at all sites, similar to what was reported by Pheiffer et al. (2018). The Klipspruit tributary recorded higher contaminant burdens compared to the Klip River tributary, with two membered-ring congeners dominating the core samples. The presence of two and three membered-ring congeners is typically indicative of a petrogenic source (petroleum combustion), while four and five membered-rings are generally introduced into the environment by pyrogenic sources (combustion of biomass) (Culotta et al., 2006). Both tributaries and wetland indicated a mix of petrogenic and pyrogenic sources of contamination.

Petrogenic processes promote the formation of phenanthrene over anthracene because it is thermodynamically more stable, leading to [An/(An + Ph)] ratios less than 0.1. Conversely, the high temperature required for pyrogenic processes in producing PAHs favours the formation of anthracene, thereby increasing the [An/(An + Ph)] ratio above 0.1 (Nieuwoudt et al., 2011; Pies et al., 2008). Similarly, fluoranthene and pyrene ratios can also be used to diagnostically identify PAH sources. Fl/(Fl + Py) ratios greater than 0.5 usually indicate pyrogenic sources, while a ratio of less than 0.5 indicates a petrogenic source (Nieuwoudt et al., 2011; Yunker et al., 2002). Petrogenic sources of contamination are related to incomplete combustion in petrol

and diesel engines, while pyrogenic sources of contamination are typically associated with the combustion of wood and coal (Pheiffer et al., 2018). In this study, [An/(An + Ph)] ratios suggested a pyrogenic source of contamination (Figure 5.2) at all sites. The [BaA/(BaA+Chr)] ratio suggested a petrogenic source of contamination at almost all sites and this is most likely because benzo(a)anthracene is typically associated with vehicular emissions (Dickhut et al., 2000). The [Fl/(Fl + Py)] ratio indicated petrogenic (petroleum or diesel combustion) sources of contamination at the upstream sites of both tributaries and within the wetland, while pyrogenic (biomass combustion) sources of contamination were detected at downstream sites of both tributaries (Figure 5.2). The petrogenic sources of contamination at upstream sites speak to their proximity to major highways (N1, R41, and R12), while the pyrogenic sources further downstream is indicative of anthropogenic activity such as sewage treatment, municipal waste incineration, and domestic coal combustion from nearby residential settlements of Soweto and Lenasia (Figure 6.2).

Contamination patterns characterizing the source and distribution of PCBs are not well understood in South Africa (Hu et al., 2011). Major sources of PCBs are attributed to Aroclor 1242, 1254, and 1260; trade names for commercial PCB mixtures (Rimayi et al., 2017). Aroclor 1242 is dominated by 2-3 chlorinated PCBs, while Aroclor 1254 is dominated by 4-6 chlorinated PCBs, and 7-8 chlorinated PCBs are signature to Aroclor 1260 (Rimayi et al., 2017). Aroclor 1242, 1254 and 1260 were commonly used in electrical transformers imported by the energy utility provider of South Africa (ESKOM), most of which are still in use (Gray, 2004). The 4-6 chlorinated PCBs were the predominant congeners across all sites investigated and were widely detected in both tributaries and the wetland (Figure 5.4). The 7-8 chlorinated PCBs were more dominant upstream of both tributary sites, followed by a decrease downstream towards the wetland (Figure 5.4). The 2-3 chlorinated PCBs were the least dominant at all sites (Figure 5.4), which is consistent with previous studies conducted on the Klip River and Jukskei tributaries (Rimayi et al., 2017). The distribution of PCBs in the environment can be influenced by the loss of less chlorinated PCB congeners through volatilisation, sedimentation, and microbial degradations (De et al., 2006; Gakuba et al., 2015). Low chlorinated PCBs (2-3 chlorines) are generally more soluble in water than the high chlorinated ones (Borja et al., 2005; Rimayi et al., 2017). The low concentrations of 3-chlorinated PCBs at all sites in this study may be attributed to their relatively higher solubility in water, losses through volatilisation, and microbial degradation. Despite transformer oil leakages reported by NERSA (2015) in Gauteng

province including areas surrounding Klip River and its tributaries, Aroclor 1242 (mixture of low chlorinated PCBs) were found in relatively low concentrations in this study.

6.4 Comparison with other relevant studies

Mindful of the fact that quantitative comparison between different data sets is complicated by differences in time of sampling, nature of the sediment analysed, analytical methods used, storage conditions, duration before analysis, and number of congeners investigated, this nonetheless allows data from the current study to be placed within context. Compared to a recent study conducted by Pheiffer et al. (2018) within the same study area (Klip River system), ∑PAH concentrations reported in this study are 3 times lower. Other regional studies conducted within the Jukskei River (Sibiya, 2012) and Vaal triangle (Nieuwoudt et al., 2001) report ∑PAH concentrations in sediments that are >2-3 times higher than the concentrations detected in the current study (Table 6.1).

The levels of ∑PAH reported in the current study are within the same order of magnitude as those detected in other international studies from Europe, the Americas and Asia (e.g. Pereira et al., 1996; Anderson et al., 1996; Budzinski et al., 1997; Mai et al., 2002; Chen et al,. 2015; Hussain et al,. 2015) (Table 6.1). An exception is Shi et al., (2005) where ∑PAH were found to be about 100 folds more than was detected in the current study (Table 6.1).

Generally, ∑PCB concentrations detected in this study were greater than the concentrations detected in samples from the Umgeni River in Durban, South Africa (Gakuba et al., 2015) However, ∑PCB concentrations were found to be within the range (n.d.-104 mg/kg) of several other international studies (Table 6.2). However, studies from the Americas (Alonso-Hernandez et al., 2014; Combi et al., 2013) and from Yamuna River in Delhi, India (Kumar et al., 2013) had ∑PCB concentrations that were significantly lower than what was detected from the current study. On the contrary, the levels of ∑PCBs detected in other studies did not differ substantially from the current study, with the exception of a study conducted by Li et al. (2005) on sediments from Sheboygan River, Wisconsin USA, where ∑PCB levels were more than 100 times the levels of the current study.

Table 6.1 Comparison of ∑PAH dry weight concentrations in sediments at different locations around the world

Research area	No of PAHs	∑PAH (mg/kg)	Reference
Klip River, Johannesburg	13	8-15	Current study
Regional Studies			
Jukskei River, Johannesburg	16	0.06-45	(Sibiya, 2012)
Vaal triangle, South Africa	16	4-39	(Nieuwoudt et al., 2001)
Klip River, Johannesburg	16	0.3-5	(Pheiffer et al., 2018)
International Studies			
Pearl River Delta, China	16	0.4–11	(Mai et al., 2002)
Daya Bay South China	16	0.04–0.1	(Yan et al., 2009)
Weihe River in Northwest China	16	0.4–16	(Chen et al., 2015)
Rivers in Tianjin, China	16	0.8–1943	(Shi et al., 2005)
Masan Bay in Korea	16	0.2–3	(Khim et al., 1999)
River Brahmaputrai Guwahati, India	16	0.3–23	(Hussain et al., 2015)
San Francisco Bay in USA	16	3–28	(Pereira et al., 1996)
San Diego Bay in USA	17	0.08–20	(Anderson et al., 1996)
Arcachon Bay in France	16	0.03–4	(Baumard et al., 1998)
Gironde Estuary in France	16	0.02–5	(Budzinski et al., 1997)
Todos os Santos Bay in Brazil	16	0.01–2	(Nascimento et al., 2017)

Table 6.2. Comparison of ∑PCB dry weight concentrations in sediments at different locations around the world, n.d = not detected

Research area	∑PCB (mg/kg)	Reference
Klip River	0.2- 0.7	Current study
Regional Studies		
Umgeni River, Durban	0.1-0.4	(Gakuba et al., 2015)
International studies		
Minjiang Estuary China	1.0	(Xing et al., 2005)
Haihe Estuary, China	n.d-0.3	(Zhao et al., 2010)
Yangtze Estuary, China	0.002–0.2	(Gao et al., 2013)
Liaohe River, North China	0.005–0.2	(Lv et al., 2015)
Yamuna River in Delhi in India	0.0002–0.02	(Kumar et al., 2013)
Eastern Romania	0.02–0.2	(Dragan et al., 2006).
Urban river (Huveaune) in France	0.003–0.4	(Kanzan et al., 2014)
Naple Harbour, Italy	0.001–0.9	(Sprovieri et al., (2007)
Sheboygan River, Wisconsin in USA	0.1-104	(Li et al., 2005)
Sea Lots, Trinidad	0.06–0.6	(Mohammed et al., 2011)
Gulf of Batabanó, Cuba	0.0001–0.0003	(Alonso-Hernandez et al., 2014)
Guaratuba Bay, Brazil	nd-0.006	(Combi et al., 2013)

6.5 Ecological Risk assessment

A congener-based approach of analysing PAH toxicity using ERM and ERL guideline values was used for all the investigated sites. According to Long et al. (1998), congener concentrations exceeding ERM guideline values poses ecotoxicity to the biota and human health. PAH congeners such as fluorene, pyrene, benzo(k)fluoranthene, benzo(b)fluoranthene, and benzo(a)pyrene all exceeded ERM guideline values at one site each (Table 5.2). Furthermore, US-EPA (2002) has classified benzo(a)anthracene and benzo(k)fluoranthene particularly as human carcinogens.

A more comprehensive, site-specific approach was used to analyse the distribution of combined ecological risk for toxic PAHs (Long and MacDonald, 1998). According to the benchmark suggested by Han et al. (2018), toxicity levels of <0.1, 0.1-0.5, 0.51-1.5, and >1.5 were classified as sites of low, medium-low, medium-high and high toxicity, respectively (Figure 6.2). The only site identified to display a high level of PAH toxicity was located upstream of the Klipspruit tributary (S2B) and is surrounded by heavy industrial activities and motorways. The other upstream site of the Klipspruit tributary (S1B) and the two upstream sites of the Klip River tributary (S1A and S2A) all showed medium levels of toxicity (Figure 6.2).

All sites investigated exceeded the ERL guideline values for ∑PCBs with three of the sites exceeding the ERM guideline values. The toxic ∑PCB sites which exceeded ERM levels were located downstream of the Klipspruit tributary (S3B and S4B), while the only site which exceeded ERM on the Klip River tributary (S2A) was located further upstream of the Klip River tributary (Figure 6.2).

The direct environmental effects of PAHs to nearby residents can be considered moderate, however, the presence of the two carcinogenic congeners which exceeded their respective ERM guideline values for multiple sites upstream may result in possible adverse impacts on both the ecology of the wetland as well as humans who rely on resources from the wetland.

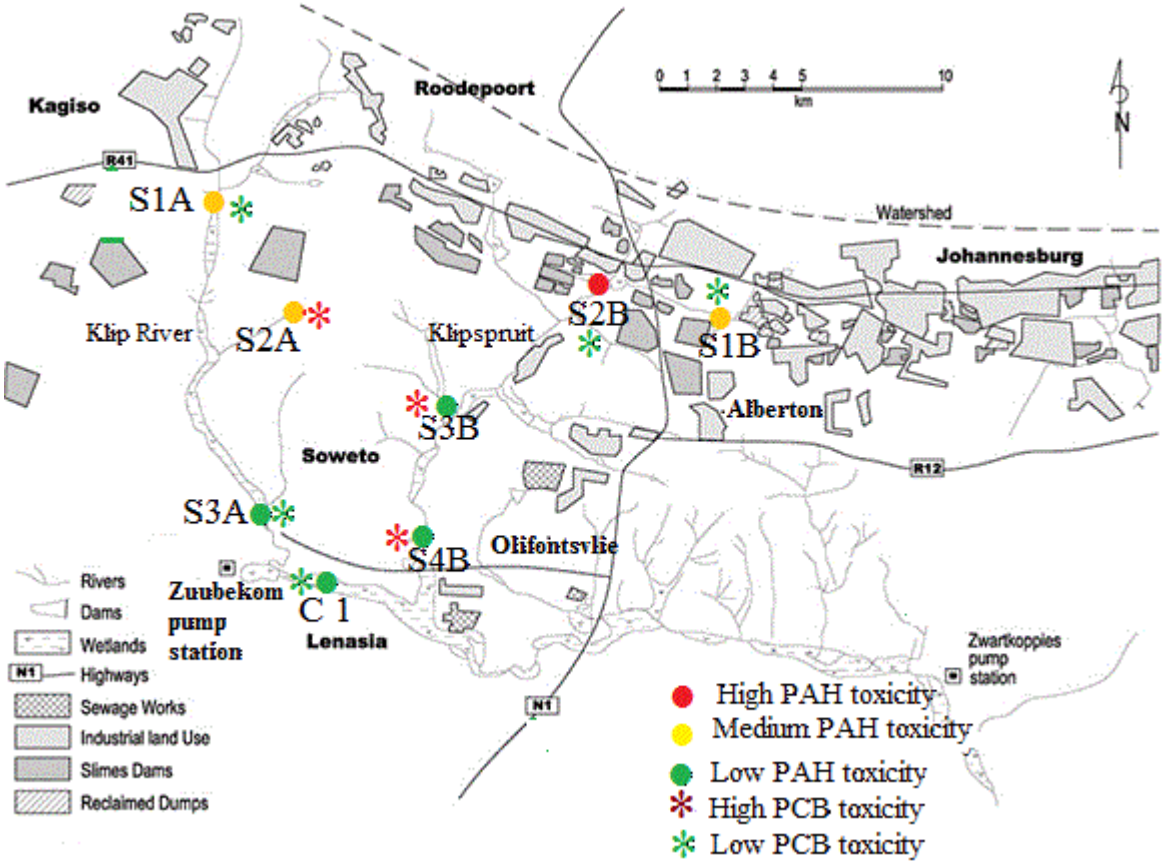


Figure 6.2 Ecotoxicological risk assessment of PAHs and PCBs, showing investigated sites of high and low toxicity

The overall assessment of all sites in the study area indicates PAHs and PCBs have the potential to cause acute toxicity such as carcinogenic and mutagenic effect to biota. PCBs like PAHs can bioaccumulate in benthic invertebrate, which later biomagnifies in the food chain through fish predators (Clements et al., 1994). Aquatic life is susceptible to chronic effects of PAHs upstream of both river tributaries, and magnified PCB concentrations could affect the diversity and population of these organisms (Pheiffer et al., 2018). Further investigations into the acute toxicity effects of PAHs and PCBs are required at the study site in order to better predict other effects to human health.

CHAPTER 7: CONCLUSION AND RECOMMENDATIONS

7.1 Conclusions

This study was designed to investigate the bioaccumulation of PAH and PCB contaminants within the tributaries and wetlands of the Klip River. This is an important asset that protects and supplies water to over five million residents in the city of Johannesburg, South Africa. Residues of PAHs and PCBs were found to be widely distributed in sediments of the Klip River wetland and tributaries. Residual concentrations reported here were among the highest found in South Africa, including those from an earlier study that was conducted within a similar area to this study

Discharge of industrial effluent, proximity to busy highways, and possible leakage of oils from electrical transformers and capacitors were identified as potential sources of pollutant to the Klip River system. Furthermore, some sites were identified as posing moderate to high levels of risk, with the majority of congeners investigated in this study exceeding critical soil guideline values. This study highlights the importance of the Klip River system in filtering and sequestering pollutants that would otherwise likely enter the Vaal Dam further downstream and potentially affect the supply of potable water in the region.

Findings from this study raise some pertinent questions and present opportunities for future research. These include:

- The need for further studies to investigate accumulation of PAHs and PCBs in other environmental compartments including biota, air and water at the study site to determine the amount of PAHs and PCBs that are accumulated in those environmental compartments.
- The need to assess the potential of bioaccumulation within the aquatic food chain.
- The need to investigate and assess the exposure of residents from Soweto and Lenasia, especially in relation to the concentrations potentially accumulating in breast milk of breast feeding mothers, as babies are likely to be more susceptible to the effect of organic pollutants.
- Finally, the study area should be considered a potential hotspot for organic pollutants and regular environmental monitoring should be carried out to identify and reduce the sources of organic pollutants, in order to minimise effects on aquatic and human health.

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APPENDICES

Supplementary Table 1. Normalised concentration (mg/kg, n=3) of individual PAH congeners in the core samples, nd = not detected.

Depth (cm)	Nap	Acey	Acea	Flu	Phe	Ant	Fla	Pyr	Chr	BaA	BkF	BbF	BaP
0	0.71	0.12	0.04	0.05	0.27	0.03	0.07	0.08	0.59	0.22	0.06	0.08	0.05
10	0.96	0.16	0.03	0.09	0.31	0.03	0.07	0.17	0.7	0.27	0.07	0.09	0.1
20	1.1	0.22	0.07	0.18	0.10	0.14	0.16	0.37	0.93	0.18	0.09	0.07	0.15
30	1.7	0.11	0.09	0.25	0.24	0.22	0.12	0.11	1.14	0.3	0.09	0.4	0.21
40	1.1	0.07	0.07	0.37	0.39	0.05	0.03	0.43	1.25	0.19	0.06	0.35	0.11
50	1.1	0.15	0.06	0.04	0.25	0.02	0.06	0.07	0.29	0.21	0.08	0.08	0.03
60	1.1	0.15	0.07	0.06	0.32	0.03	0.12	2.07	0.32	0.22	0.07	0.1	0.05
70	1.0	0.06	0.08	0.07	0.28	0.08	0.04	0.21	0.86	0.21	0.05	0.3	0.1
90	1.0	0.07	0.06	0.04	0.14	0.06	0.06	0.05	0.74	0.22	0.06	0.18	0.03
100	1.3	0.1	0.11	0.05	0.29	0.08	0.16	0.13	1.02	0.26	0.07	0.25	0.08
110	1.5	0.14	0.1	0.06	0.05	0.05	0.18	0.28	0.8	0.29	0.09	0.22	0.06
120	1.6	0.21	0.14	0.09	0.28	0.08	0.21	0.23	0.84	0.34	0.11	0.23	0.07
130	1.3	0.19	0.16	0.07	0.31	0.13	0.17	0.3	0.83	0.32	0.11	0.27	0.09
140	1.5	0.13	0.19	0.09	0.39	0.17	0.22	0.28	0.96	0.32	0.16	0.36	0.1
150	1.8	0.2	0.23	0.14	0.52	0.21	0.29	0.31	1.04	0.37	0.16	0.36	0.12
160	1.9	0.19	0.18	0.24	0.53	0.19	0.41	0.44	1.13	0.41	0.19	0.38	0.14
170	1.8	0.18	0.17	0.25	0.47	0.22	0.46	0.36	1	0.47	0.18	0.23	0.12
180	1.7	0.2	0.19	0.27	0.52	0.25	0.47	0.35	0.96	0.45	0.21	0.23	0.14
190	1.6	0.16	0.2	0.24	0.51	0.28	0.32	0.41	0.82	0.41	0.21	0.24	0.15
200	1.1	0.1	0.11	0.15	0.39	0.19	0.2	0.26	0.63	0.26	nd	0.16	0.12
210	0.83	0.04	0.06	0.07	0.1	0.09	0.12	0.2	0.62	0.18	nd	0.11	0.11

220	0.99	0.07	0.09	0.16	0.06	0.14	0.14	0.23	0.7	0.15	nd	0.14	0.14
230	1.2	0.07	0.12	0.12	1.57	0.13	0.17	0.21	0.87	0.14	nd	0.07	0.17
240	0.88	0.05	0.09	0.08	1.18	0.09	0.12	0.16	0.75	0.13	nd	0.06	0.14
250	0.69	nd	0.07	0.02	1.01	0.06	0.09	0.11	0.59	0.12	nd	0.04	0.1
260	0.73	nd	0.07	0.01	0.94	0.04	0.09	0.07	0.68	0.07	nd	0.03	0.08
270	1.0	nd	0.08	0.01	0.93	0.07	0.22	nd	0.86	0.07	nd	0.03	0.08
280	1.8	nd	0.09	nd	1.1	0.05	0.21	nd	1.2	0.09	nd	0.03	0.07

Supplementary Table 2. Normalised concentrations (mg/kg, n=3) of individual PCB congeners in core samples (nd = not detected)

Depth (cm)	PCB 18	PCB 31	PCB 44	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 149	PCB 180	PCB 195
0	0.007	0.009	0.030	0.011	0.026	0.045	0.020	0.021	0.015	0.027	0.032
10	0.014	0.013	0.038	0.008	0.017	0.050	0.015	0.022	0.027	0.022	0.038
20	0.021	0.018	0.014	0.014	0.013	0.034	0.014	0.040	0.040	0.021	0.041
30	0.032	0.030	0.066	0.014	0.029	0.055	0.024	0.028	0.047	0.040	0.069
40	0.035	0.018	0.069	0.012	0.031	0.056	0.025	0.024	0.017	0.035	0.059
50	0.032	0.016	0.074	0.015	0.033	0.070	0.031	0.033	0.029	0.043	0.060
60	0.039	0.017	0.077	0.017	0.038	0.082	0.022	0.042	0.034	0.047	0.051
70	0.041	0.013	0.040	0.010	0.026	0.085	0.020	0.022	0.018	0.044	0.053
90	0.038	0.020	0.030	0.022	0.026	0.081	0.026	0.017	0.018	0.032	0.042
100	0.049	0.031	0.050	0.037	0.042	0.076	0.041	0.036	0.032	0.050	0.060
110	0.048	0.034	0.069	0.041	0.079	0.084	0.038	0.065	0.024	0.080	0.081
120	0.053	0.035	0.097	0.031	0.062	0.080	0.038	0.027	0.024	0.069	0.098
130	0.059	0.027	0.106	0.029	0.068	0.093	0.050	0.033	0.034	0.068	0.096
140	0.052	0.029	0.121	0.032	0.065	0.105	0.071	0.043	0.041	0.083	0.070
150	0.047	0.028	0.104	0.039	0.059	0.095	0.094	0.058	0.046	0.051	0.119
160	0.057	0.030	0.109	0.047	0.061	0.087	0.107	0.080	0.048	0.062	0.109
170	0.033	0.038	0.097	0.046	0.059	0.060	0.043	0.045	0.029	0.047	0.076
180	0.036	0.031	0.093	0.054	0.119	0.034	0.037	0.052	0.021	0.092	0.154
190	0.027	0.009	0.089	0.058	0.114	0.021	0.033	0.042	0.033	0.096	0.108
200	0.008	nd	0.069	0.041	0.100	0.012	0.035	nd	0.036	0.088	0.075
210	0.009	nd	0.062	0.033	0.080	0.006	0.023	nd	0.027	0.066	0.048
220	0.010	nd	0.065	0.037	0.092	0.009	0.027	nd	0.023	0.079	0.015
230	0.014	nd	0.050	0.038	0.088	0.010	0.015	nd	0.034	0.066	0.017
240	0.008	nd	0.030	0.029	0.080	0.009	0.007	nd	0.026	0.072	0.012
250	0.001	nd	0.032	0.019	0.073	0.110	0.001	nd	0.015	0.049	0.003
260	nd	nd	0.033	0.017	0.062	nd	nd	nd	0.017	0.049	0.003
270	nd	nd	nd	0.020	0.065	nd	0.005	nd	0.026	0.049	nd
280	nd	nd	nd	0.024	0.091	nd	0.004	nd	0.016	0.074	0.001