

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

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Abstract

The accumulation of Polyaromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) was investigated in sediments of the Klip River wetland Johannesburg South Africa. The wetland serves as an important source of potable water to the Vaal Dam Johannesburg and purifier of contaminants from different anthropogenic activities at the Witwatersrand basin. In this study, PCBs and PAHs were found to be spatially distributed in surface and core sediments of the two major tributaries entering into the wetland. The total concentration of PAHs and PCBs found in the surface sediments ranged from 45–95 mg/kg and 0.2–5.3 mg/kg respectively. Highlights of the distribution of PAHs indicated the upstream sites of both tributaries to be more polluted and were attributed to the proximity of these sites to heavy traffic and industrial complexes. Conversely, the downstream sites were more polluted with residues of PCBs and were attributed to anthropogenic activities from the residential settlements of Soweto and Lenasia. The total amount of PAHs and PCBs found in the sediment core site were 2.4 – 6.3 mg/kg and 0.17–0.80 mg/kg respectively, which is significantly lower than the concentrations found in the surface sample sites. Risk characterization 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 investigation is therefore required for comprehensive ecotoxicological risk assessment.

1. Introduction

The negative repercussions associated with the long-standing use of Persistent Organic Pollutants (POPs) have been well documented (Jones and De Voogt, 1999). Some of these health-related issues include cancer (Karlsson and Viklander, 2008), gene mutation (Ghaeni et al., 2015), reproductive impairment, and endocrine disruption tendencies (Thomas et al., 2007). As a result of their environmental and human health challenges, there is a global effort through the Stockholm Convention to eliminate or reduce their production and use by 2025 (UNEP, 2001). Globally, their use for any purpose has been banned or severely restricted. Nonetheless, they are continuously detected in several environmental compartments such as fatty tissues (Buah-Kwofie et al., 2018; Gerber et al., 2016; Naigaga et al., 2011; Saldanha et al., 2010), breast milk (Bouwman et al., 2012), blood serum (Darnierud 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; Pheiffer et al., 2018; Rimayi et al., 2017). Of particular concern are the polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) which are sometimes produced unintentionally from incomplete combustion of fossil fuel, refuse incineration, sewage treatments, asphalt paving, vehicular exhaust, and other industrial activities (Arruti et al., 2012; Chen et al., 2003; Li et al., 2001). PCBs in particular were widely produced and used as dielectric fluid in electric transformers and capacitors, plasticizers etc. at the height of the 20th century industrialisation (El-Shahawi et al., 2010; O'Donovan et al., 2011; Rimayi et al., 2017). Globally, it is estimated that about 1.3 million tons of PCBs were produced at its production peak, with the most industrialised countries accounting for the highest usage proportion (Rimayi et al., 2017).

South Africa, as a country has numerous inland water bodies (Wetlands, Rivers, and Lakes) which hold a lot of global and economic value. One such system is the Klip River wetland located south of Johannesburg and is considered as one of the most economically significant wetlands in South Africa. The wetland initially served as a local source of water for adjoining communities and now functions as a purifier of contaminants from various anthropogenic activities occurring within the Witwatersrand Basin (Fig. 1) (McCarthy et al., 2007). Industrial activities are strategically sited within the basin to make use of the vast resource the wetland offers. The upper reaches of the wetland receive surface run-off from the Klipriver and Klipspruit tributaries, and also groundwater from the underlying dolomite aquifer. Thus, the wetland purifies the water entering the Vaal Dam, which serves as the main source of water to the over five million residents of 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, 2006a), 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). Soweto and Lenasia, two densely populated communities are situated downstream of the two tributaries. Additionally, a number of the industries that are dotted around the wetland rely heavily on coal as a source of fuel, while two major highways in Johannesburg are sited around the wetland, exacerbating the contaminant pressure of the wetland. Various studies have reported on different contaminants in sediments of the Klip River wetland catchments (Humphries et al., 2017; McCarthy and Venter, 2006b; Pheiffer et al., 2018). However, as important as this wetland is and the fact that several industries that potentially emit PCBs and PAHs are dotted around the basin, very limited studies reports on PCBs and PAHs and their potential impact on the ecology of the wetland. This study aims to provide useful information on contaminant status, potential sources, and possible ecotoxicological risks of PAHs and PCBs by assessing catchment and core sediment samples from the Klip River wetland.

2. Materials And Methods

2.1 Study area

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 (Fig. 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. The wetland is covered by reed swamps (*Phragmites australis*) and is filled by organic-rich sediment/peat. 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.

2.2 Sample collection

Surface sediment samples were collected from the two main tributaries (Klipriver and Klipspruit), which drain into the upper section of the Klip River wetland (Fig. 1). A sediment core from the upper section of the wetland was collected (site C₁) 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 the wetland. The pH, electrical conductivity, and redox potential were measured using a multipurpose electrode (ORION Thermo Scientific Star A3255) in the field. Sediment samples were kept on ice in the field and later at 4 °C in the laboratory. Sediment samples were air-dried at room temperature and milled. The samples were then kept in amber bottles and stored under -18°C until analysis. Total organic matter was estimated on each sub-sample as loss on ignition (LOI) at 500 °C temperature for 6 hours according to the method described by Byers et al. (1978).

2.3 Extraction and analysis

A modified QuEChERS method was adopted for the extraction of target PAH and PCB compounds (See Table 1 for the complete list) (Salem et al., 2016). In summary, 1 g of the sediment sample was accurately weighed into a 50 ml centrifuge tube and hydrated with 10 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 (MgSO₄), 0.7 g sodium acetate (C₂H₃NaO₂), and 0.7 g sodium acetate trihydrate (C₂H₃NaO₅) were added, followed by vigorous shaking to ensure complete dispersion. Samples were then centrifuged at 5000 rpm for 10 minutes. 7 ml of the organic extract was transferred into a centrifuge tube containing 0.5 g MgSO₄, 0.2 g C18, and 0.2 g primary secondary amine (PSA). This mixture was vortexed, then centrifuged to isolate the clean extract. A 4 mL aliquot of the extract was evaporated to dryness under vacuum at a temperature ≤ 40°C, reconstituted in hexane (1 mL) before transferring into a GC vial for analysis.

The analysis was performed by two-dimensional gas chromatography – time-of-flight mass spectrometry (GC X GC-TOFMS) using an Agilent 7890 GC coupled to a Leco Pegasus 4D TOF mass spectrometer. The separation was achieved using a

Restek Rxi-5Sil MS column with Integra-Guard (30 m × 0.25 mm i.d. × 0.25 μm film thickness) coupled to a Rxi-17Sil MS (1.1 m × 0.25 mm i.d. × 0.25 μm thickness) secondary column. A 2 μl sample was injected in splitless mode using ultra high-purity helium as the carrier gas at a constant flow rate of 1.4 ml min⁻¹. The transfer line and inlet temperatures were set at 260 and 250 °C, respectively. The ion source temperature was set at 250 °C, with an acquisition delay time of 180 seconds and an acquisition voltage of 1850 V. The initial oven temperature was set at 80 °C, held for 0.5 min, and then increased to 180 °C at a rate of 20 °C/min, and finally to 300 °C at 5 °C/min. The secondary oven and modulator temperatures were offset at 5 °C and 15 °C, respectively, relative to the primary oven temperature. 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.

2.4 Quality assurance and quality control

Quantification was performed using high purity (> 98%) reference standards purchased from Sigma Aldrich. Linear regressions derived from matrix-matched calibration curves for individual PAH and PCBs were ≥ 0.99. Sample extracts were analysed in triplicate with relative standard deviations typically < 12% for PAH and PCBs respectively. Quality control standards were run after every third sample to monitor and correct for variations in instrument response. Detection limits were in the range of 0.04–1.1 μg/kg (PAHs) and 0.03–0.39 μg/kg for PCBs, respectively. Analysis of data was conducted using the two-tailed student t-test to investigate the difference in mean concentrations of sediment samples from the Klipriver tributaries and Klipspruit. Descriptive data analyses were conducted using Microsoft excel 2018, all test was considered significant at p < 0.05.

3. Results

3.1 PAH and PCB concentrations

The PAH and PCB concentrations measured were normalized using total organic matter (TOM) estimates to account for the variability in the organic content of the samples and are quoted as dry weight (dw) concentration. 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 (10.5 ± 0.2 mg kg⁻¹) and PAH (274 ± 4.9 mg kg⁻¹) concentrations in surface sediments collected from Klipspruit tributary was significantly higher than the ∑PCBs (6.4 ± 0.2 mg kg⁻¹) and ∑PAHs (156 ± 3.6 mg kg⁻¹) detected in sediments from Klipriver tributary. Chrysene (21 %), benzo [a] anthracene and pyrene (13 % respectively), and phenanthrene (9 %) were the four dominant PAH congeners detected at both tributaries and they accounted for > 55 % of ∑PAH concentration at both tributaries. While PCB 180 and PCB 195 (15 % respectively), PCB 118 (13 %) and PCB 101 (9 %) accounted for > 50 % of ∑PCB concentrations at both Klipriver and Klipspruit tributaries (Table 1). The least detected PAH congener (acenaphthylene) contributed ~ 2 % to ∑PAH concentration while PCB 52 contributed ~ 3 % ∑PCB concentrations (Table 1).

Spatially, there was an inconsistent variation in ∑PAH and ∑PCB concentrations at both tributaries (Fig. 2). The highest ∑PAH concentrations were detected at site S1B of the Klipspruit tributary, with a total mean concentration of 95 ± 6.7 mg/kg, while site S3A of the Klipriver tributary recorded the lowest mean concentration of 44 ± 2.6 mg/kg across all the sites investigated (Fig. 2). ∑PAH concentrations decreased downstream towards the wetland at both tributaries; however, the decrease was not significant and was inconsistent. On average, the Klipspruit tributary (69 ± 4.6 mg/kg) showed a higher level of contamination of ∑PAH compared to the Klipriver tributary (52 ± 3.6) (Fig. 2, Supplementary Table S1). The total mean concentration of PAHs at both tributaries is significantly different at a 95% confidence level.

The highest and the lowest mean ∑PCB concentrations were recorded at Sites S3B located on the Klipspruit (5.3 ± 0.2 mg/kg) and S1A on the Klip River (1.1 ± 0.07 mg/kg) respectively. Additionally, site S4B (lower reach of the tributary) on the Klipspruit (2.4 ± 0.08 mg/kg) recorded a higher residual concentration of ∑PCB compared to site S3A the lower reach on the Klip River (1.2 ± 0.06 mg/kg), which is a similar trend of observation made for ∑PAH concentrations. Generally, average

Σ PCB concentrations along the Klipspruit (2.6 ± 0.2) were higher than that detected along the Klip River (2.1 ± 0.09) (Fig. 2, Table S1). There is no significant difference in the total mean concentration of PCBs at both tributaries.

Table 1

Average concentration (mg/k \pm SD, n = 3), percentage contribution, and potential source identification ratio of individual congeners and physico-chemical parameters present in the surface sediments from the Klip River and Klipspruit tributaries.

Concentration(mg/k g) dw							
Congeners	Klipriver Tributary	Klipspruit Tributary	%Contr ibution	Congeners	Klipriver Tributary	Klipspruit Tributary	%Contribution
Naphthalene	10 \pm 0.6	7.6 \pm 0.2	4.1	PCB 18	0.56 \pm 0.013	0.81 \pm 0.022	8.4
Acenaphthylene	2.2 \pm 0.1	5.1 \pm 0.1	2.1	PCB 31	0.38 \pm 0.05	0.66 \pm 0.008	6.4
Acenaphthene	1.4 \pm 0.06	3.6 \pm 0.2	1.4	PCB 44	0.62 \pm 0.03	0.56 \pm 0.014	7.0
Fluorene	2.2 \pm 0.04	9.8 \pm 0.2	2.7	PCB 52	0.2 \pm 0.003	0.32 \pm 0.004	3.1
Phenanthrene	22 \pm 0.4	17 \pm 0.2	9.1	PCB 101	0.7 \pm 0.01	0.82 \pm 0.02	8.7
Anthracene	5.2 \pm 0.3	7.2 \pm 0.6	3	PCB 118	0.86 \pm 0.02	1.4 \pm 0.06	13
Fluoranthene	12 \pm 0.2	19 \pm 0.2	7	PCB 153	0.47 \pm 0.02	0.95 \pm 0.02	8.5
Pyrene	25 \pm 0.4	30 \pm 0.5	13	PCB 138	0.37 \pm 0.008	0.73 \pm 0.02	6.5
Chrysene	35 \pm 0.8	54 \pm 0.6	21	PCB 149	0.41 \pm 0.06	1.0 \pm 0.008	8.4
Benzo[a]anthracene	14 \pm 0.2	43 \pm 0.7	13	PCB 180	0.87 \pm 0.006	1.7 \pm 0.01	15
Benzo[k]fluoranthene	9.4 \pm 0.1	29 \pm 0.6	8.8	PCB 195	0.92 \pm 0.02	1.6 \pm 0.03	15
Benzo[b]fluoranthene	6.8 \pm 0.2	24 \pm 0.4	7.2	Σ PCBs	6.4 \pm 0.2	10.5 \pm 0.2	
Benzo[a]pyrene	11 \pm 0.2	25 \pm 0.4	8.3	Organic (%)	21	19.8	
Σ PAHs	156 \pm 3.6	274 \pm 4.9		pH	7.1	6.8	
Fla/(Fla + Pyr)	0.97	1.53					
Ant/(Ant + Phe)	1.65	2.78					
BaA/(BaA + Chr)	0.85	1.97					

3.4 Downcore variation in the distribution of PAHs and PCBs

There was an inconsistent but gradual increase in mean Σ PAH concentrations with increasing depth to \sim 160 cm where the highest concentration of 6.3 ± 0.49 mg/kg was detected. THE Lowest Σ PAH concentrations (2.4 ± 0.22 mg/kg) were detected in the wetland (Fig. 3a; Supplementary Table S2). The distribution

of PAHs varied according to the number of aromatic rings. Four-membered ring compounds contributed the highest of 37 % followed by the two-membered ring compounds (30%). The three- and five-membered rings recorded approximately 23% and 9%, respectively (Supplementary Table S2). 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 the highest concentrations measured between 40–60 cm and 150–180 cm respectively (Fig. 3b).

Total PCB concentrations through the sediment core showed substantial variations, with concentrations ranging between 0.17 mg/kg and 0.8 mg/kg (Fig. 3c, Supplementary Table S3). The highest concentrations (0.8 ± 0.028 mg/kg) were detected at 160 cm but were lower than the measured concentrations in surface sediment samples (1.1–5.3 mg/kg). The distribution of PCBs according to the number of chlorine atoms revealed 4–6 chlorinated PCB compounds to be the dominant group. This group contributed 64% to \sum PCB concentrations followed by the 7–8 chlorinated PCBs at ~25%. The 3 chlorinated PCBs contributed the least with about 10% (Fig. 3d, Supplementary Table S3). All three classes of PCBs showed similar patterns down the core with gradual increases in concentration from the surface to 180–200 cm (Fig. 3d).

4 Discussion

4.1 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 Klipriver and the Klipspruit tributaries. This is consistent with a recent study that 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. The distribution of \sum PAHs within the study area indicates that the Klipspruit tributary is more contaminated compared to the Klipriver tributary (Fig. 2, Table 1). The highest PAH concentrations were recorded at the most upstream sites along the Klipspruit and Klipriver tributaries, with concentrations decreasing downstream towards the wetland (Fig. 2).

The upstream sites of the Klipspruit are proximal to several major highways including N1, R41, and to a lesser extent R12. In the case of Klipriver, the R41 is the only major highway 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 Klipriver tributary. According to Caricchia et al. (1999), 90% of the total PAH emissions worldwide are from stationary sources, but this may not be true in urban settlements where mobile sources from vehicular exhaust are dominant. Sibiya, (2012) reported a 5% increase in the amount of PAHs released from vehicular emissions in the city of Johannesburg from 2005 to 2011. This likely results from 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 contribute to the high levels of PAHs at these sites compared to the Klipriver tributary.

The downstream sites of both tributaries are in close proximity to the residential settlements of Soweto and Lenasia (Fig. 2). 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 Klipriver and Klipspruit tributaries could be attributed to the domestic combustion of coal/wood for cooking and heating in and around the densely populated areas of Soweto and Lenasia (Fig. 2).

Similar to PAHs, \sum PCB concentrations revealed a similar pattern downstream with site S3B decreasing downstream toward the wetland (Fig. 2). Alberton is an industrial town 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. The concentrations of PCBs detected in the Klipriver and Klipspruit tributaries could be as a result of the industrial complex of Alberton, such as the incineration of PCB

equipment, coal combustion, and leakages from transformer oil (Rimayi et al., 2017; Samara et al., 2006), municipal solid waste incineration, hospital waste, sewage waste, domestic coal combustion, and effluents from sewage plants located within proximity of the downstream sites (Brent and Rogers, 2002; Rimayi et al., 2016). Additionally, the National Energy Regulation of South Africa (NERSA) reported leakages of transformer oil (which is a major distributor of PCBs) as a common occurrence at electricity substations in Gauteng and other provinces (NERSA, 2015). Furthermore, due to a lack of air pollution regulations that were non-existent before April 2015 in South Africa, most industries located downstream were under no obligation to control air pollutions and resulted in the uncontrolled and unregulated release of incomplete combustible gasses into the environment (Brent and Rogers, 2002).

4.2 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). Some sewage treatment plants are situated at the Olifontsvlie which is located along the upper reaches of the wetland system (Fig. 2). According to McCarthy et al. (2007), the 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. Besides, Naiker et al. (2012) reported groundwater contamination through leakage and subsequent seepage of one of these wastewater treatment plants at the Klip River wetland.

The high level of \sum PAHs and \sum PCBs at the lower end of the core could be attributed to the 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 levels of \sum PAHs and \sum PCBs recorded at the upper sections of the core compared to the bottom could be attributed to the Klip River wetland's inability to retain contaminants for a long period hence their downward migration (McCarthy et al., 2007).

4.3 Identification of potential sources of PAHs and PCBs

Overall, four- and three-member rings were the most dominant PAH congeners detected within the study area (Fig. 4a), this is similar to what was reported by Pheiffer et al. (2018). The Klipspruit tributary recorded higher contaminant burdens compared to the Klipriver tributary, with two membered-ring congeners dominating the wetland site (Fig. 4a). 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 often signature to pyrogenic sources (combustion of biomass) (Culotta et al., 2006). Both tributaries and wetland indicated a mix of petrogenic and pyrogenic sources of contamination.

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. 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; Yunker et al., 2002). 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).

The Ant/(Ant + Phe) values for all sites across both tributaries were \approx 0.1, which suggests a pyrogenic source of contamination from the combustion of coal and biomass (Fig. 4c; Table 1). Fla/(Fla + Pyr) values suggest approximately 63% of the site's pollution to be from dominantly petrogenic sources (incomplete combustion of petroleum), while the remaining 37% is from the combustion of biomass (Fig. 4c&d). The BaA/(BaA + Chr) values also suggest approximately 63% of all site contamination was from petrogenic sources while the remaining 37% from mixed petrogenic and pyrogenic sources (Fig. 4c&d; Supplementary Table S2).

Hence, 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, Lenasia and to a lesser degree Alberton (Fig. 2).

At all catchment sampling sites, PCB congeners with 4–6 chlorine substituents (PCBs 101, 118, 153, 138, and 149) were the most dominant contributing ~ 45% to \sum PCB concentration, followed by congeners with 7–8 chlorine atoms (PCBs 180 and 195) ~ 30 %. The percentage of 4–6 chlorinated PCBs were fairly evenly distributed across all sites (Fig. 4b). 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 (PCBs 18, 31, 44, and 52) 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 (Fig. 4b). The 7–8 chlorinated PCBs were more dominant upstream of both tributary sites, followed by a decrease downstream towards the wetland (Figs. 2 & 4b). The 2–3 chlorinated PCBs were the least dominant at all sites (Fig. 4b), which is consistent with previous studies conducted on the Klipriver and Jukskei tributaries (Rimayi et al., 2017). The distribution of PCBs in the environment can be influenced by the loss of the less chlorinated PCB congeners through volatilization, 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 volatilization, and microbial degradation. Despite transformer oil leakages reported by NERSA (2015) in Gauteng province including areas surrounding Klipriver and its tributaries, Aroclor 1242 (a mixture of low chlorinated PCBs) were found in relatively low concentrations in this study.

4.4 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 analyzed, analytical methods used, storage conditions, and the number of congeners investigated, this nonetheless allows data from the current study to be placed within context. Compared to a study conducted by Pheiffer et al. (2018) within the same study area (Klip River system), \sum PAH concentrations reported in this study are three times higher. Other regional studies conducted within the Jukskei River (Sibiya, 2012) and the Vaal triangle (Nieuwoudt et al., 2011) report \sum PAH concentrations in sediments that are >2–3 times higher than the concentrations detected in the current study (Supplementary Table 2). The levels of \sum 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). An exception is Shi et al., (2005) where \sum PAH was found to be about 100 folds more than was detected in the current study (Table 2).

Table 2

Comparison of \sum PAH dry weight concentrations in sediments at different locations around the world

Research area	No of PAHs	\sum PAH (mg/kg)	Reference
Klip River, Johannesburg	13	8–15	Current study
Regional Studies	16	0.06-45	(Sibiya, 2012)
Jukskei River, Johannesburg			
Vaal triangle, South Africa	16	4–39	(Nieuwoudt et al., 2011)
Klip River, Johannesburg	16	0.3-5	(Pheiffer et al., 2018)
International Studies	16	0.4–11	(Mai et al., 2002)
Pearl River Delta, China			
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 Brahmaputra 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 the 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)

Generally, \sum 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). Similarly, studies from the Americas (Alonso-Hernandez et al., 2014; Combi et al., 2013) and Yamuna River in Delhi, India (Kumar et al., 2008) had \sum PCB concentrations that were significantly lower than what was detected from the current study (Table 3). Conversely, the levels of \sum PCBs detected in other studies did not differ substantially from the current study, except for a study conducted by Li et al. (2005) on sediments from Sheboygan River, Wisconsin USA, where \sum PCB levels were more than 100 times the levels of the current study (Table 3).

Table 3
Comparison of Σ PCB dry weight concentrations in sediments at different locations around the world, n.d = not detected

Research area	Σ 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	(Kanzari et al., 2014)
Naple Harbour, Italy	0.001–0.9	(Sprovieri et al., 2007)
Sheboygan River, Wisconsin in the 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)

4.5 Ecological Risk assessment

A congener-based approach of analyzing PAH toxicity using effect range median (ER-M) and effect range low (ER-L) guideline values were used for all the investigated sites. According to Long and MacDonald, (1998), congener concentrations exceeding ER-M guideline values pose 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 ER-M guideline values at one site each (Table 4). Of concern is the classification of benzo(a)anthracene and benzo(k)fluoranthene, particularly as human carcinogens by the US-EPA (2002).

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

$$M - ERM - Q = \frac{\sum (C_i / ERM_i)}{n}$$

Where C_i is the concentration of congener i in the sediment, ERM_i 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. 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 (Fig. 5). The only site identified to display a high level of PAH toxicity was located

ed by heavy industrial activities and motorways. The other

upstream site of the Klipspruit tributary (S1B) and the two upstream sites of the Klipriver tributary (S1A and S2A) all showed medium levels of toxicity (Fig. 5).

All sites investigated exceeded the ERL guideline values for \sum PCBs with three of the sites exceeding the ERM guideline values (Table 4). The toxic \sum 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 Klipriver tributary (S2A) was located further upstream of the Klip River tributary (Figs. 5 & 6).

The direct environmental impact 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. 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 effects to biota. PCBs like PAHs can bioaccumulate in benthic invertebrates, 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 and understand the potential effects on human health.

Table 4

Toxicity risk assessment of PAHs and PCBs based on the guidelines of (Long and MacDonald, 1998), in sediments ($\mu\text{g}/\text{kg}$ dw) of the Klip River catchments and wetland.

Compounds	ERL ($\mu\text{g}/\text{kg}$)	ERM ($\mu\text{g}/\text{kg}$)	PAH range in the study sites ($\mu\text{g}/\text{kg}$)	Number of sites	
				☒ ERL	☒ 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
\sum PCB	50	400	183–692	5	3

5 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 residents in the city of Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js 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 pollutants 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, including a) in-depth investigation to better understand the accumulation of these compounds in different environmental compartments and their implication on the food chain within the study area and b) assess impact of these compounds on the health of residents of Soweto and Lenasia. Finally, the study highlights the need for a more regular and formal monitoring program in the area to help in management decisions regarding the wetland.

Declarations

1 Ethics approval and consent to participate

Response: Not applicable

2 Consent for publication

Response: Not applicable

3 Availability of data and materials

Response: Not applicable

4 Competing interests

Response: The authors declare that they have no competing interests

5 Funding

Response: Not applicable

6 Authors' contributions

Response: First author (Ayo Olasupo) conceptualised the idea, collected the samples from the field, did the experiment, started the writeup and completed it.

Second author (Archibold Buah-Kwofie) conceptualised the idea, proof-read the writeup and gave correction for the final draft of the manuscript.

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References

Alonso-Hernandez, C., Mesa-Albernas, M., and Tolosa, I. (2014). Organochlorine pesticides (OCPs) and polychlorinated
Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js, Cuba. *Chemosphere* 94, 36–41.

- Anderson, J.W., Newton, F., Hardin, J., Tukey, R.H., and Richter, K.E. (1996). Chemistry and toxicity of sediments from San Diego Bay, including a biomarker (P450 RGS) response. In *Environmental Toxicology and Risk Assessment: Biomarkers and Risk Assessment: Fifth Volume*, (ASTM International), p.
- Arruti, A., Fernández-Olmo, I., and Irabien, Á. (2012). Evaluation of the urban/rural particle-bound PAH and PCB levels in the northern Spain (Cantabria region). *Environ. Monit. Assess.* *184*, 6513–6526.
- Balmer, M. (2017). Household coal use in an urban township in South Africa. *J. Energy South. Afr.* *18*, 27–32.
- Baumard, P., Budzinski, H., and Garrigues, P. (1998). PAHs in Arcachon Bay, France: origin and biomonitoring with caged organisms. *Mar. Pollut. Bull.* *36*, 577–586.
- Borja, J., Taleon, D.M., Auresenia, J., and Gallardo, S. (2005). Polychlorinated biphenyls and their biodegradation. *Process Biochem.* *40*, 1999–2013.
- Bouwman, H., Kylin, H., Sereda, B., and Bornman, R. (2012). High levels of DDT in breast milk: intake, risk, lactation duration, and involvement of gender. *Environ. Pollut.* *170*, 63–70.
- Brent, A.C., and Rogers, D.E. (2002). Establishing the propensity for dioxin formation using a plume temperature model for medical waste incinerator emissions in developing countries. *J. Air Waste Manag. Assoc.* *52*, 811–821.
- Buah-Kwofie, A., and Humphries, M.S. (2017). The distribution of organochlorine pesticides in sediments from iSimangaliso Wetland Park: Ecological risks and implications for conservation in a biodiversity hotspot. *Environ. Pollut.* *229*, 715–723.
- Buah-Kwofie, A., Humphries, M.S., Combrink, X., and Myburgh, J.G. (2018). Accumulation of organochlorine pesticides in fat tissue of wild Nile crocodiles (*Crocodylus niloticus*) from iSimangaliso Wetland Park, South Africa. *Chemosphere* *195*, 463–471.
- Budzinski, H., Jones, I., Bellocq, J., Pierard, C., and Garrigues, P. (1997). Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Mar. Chem.* *58*, 85–97.
- Byers, S.C., Mills, E.L., and Stewart, P.L. (1978). A comparison of methods of determining organic carbon in marine sediments, with suggestions for a standard method. *Hydrobiologia* *58*, 43–47.
- Caricchia, A.M., Chiavarini, S., and Pezza, M. (1999). Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy). *Atmos. Environ.* *33*, 3731–3738.
- Chen, S.-J., Hsieh, L.-T., and Chiu, S.-C. (2003). Characteristics of the PAH emissions from the incineration of livestock wastes with/without APCD. *Environ. Int.* *28*, 659–668.
- Chen, Y., Jia, R., and Yang, S. (2015). Distribution and Source of Polycyclic Aromatic Hydrocarbons (PAHs) in Water Dissolved Phase, Suspended Particulate Matter and Sediment from Weihe River in Northwest China. *Int. J. Environ. Res. Public Health* *12*, 14148–14163.
- Clements, W., Oris, J., and Wissing, T. (1994). Accumulation and food chain transfer of fluoranthene and benzo [a] pyrene in *Chironomus riparius* and *Lepomis macrochirus*. *Arch. Environ. Contam. Toxicol.* *26*, 261–266.
- Combi, T., Taniguchi, S., Figueira, R.C.L., de Mahiques, M.M., and Martins, C.C. (2013). Spatial distribution and historical input of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in sediments from a subtropical estuary (Guaratuba Bay, SW Atlantic). *Mar. Pollut. Bull.* *70*, 247–252.
- Culotta, L., De Stefano, C., Gianguzza, A., Mannino, M.R., and Orecchio, S. (2006). The PAH composition of surface sediments from the Sicilian Channel (Mediterranean Sea). *Environ. Monit. Assess.* *117*, 117–127.

- Darnerud, P., Lignell, S., Glynn, A., Aune, M., Törnkvist, A., and Stridsberg, M. (2010). POP levels in breast milk and maternal serum and thyroid hormone levels in mother–child pairs from Uppsala, Sweden. *Environ. Int.* *36*, 180–187.
- De, S., Perkins, M., and Dutta, S.K. (2006). Nitrate reductase gene involvement in hexachlorobiphenyl dechlorination by *Phanerochaete chrysosporium*. *J. Hazard. Mater.* *135*, 350–354.
- Dickhut, R., Canuel, E., Gustafson, K., Liu, K., Arzayus, K., Walker, S., Edgecombe, G., Gaylor, M., and MacDonald, E. (2000). Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. *Environ. Sci. Technol.* *34*, 4635–4640.
- Dimitriou, E., Karaouzas, I., Sarantakos, K., Zacharias, I., Bogdanos, K., and Diapoulis, A. (2008). Groundwater risk assessment at a heavily industrialised catchment and the associated impacts on a peri-urban wetland. *J. Environ. Manage.* *88*, 526–538.
- Dragan, D., Cucu-Man, S., Dirtu, A.C., Mocanu, R., Vaeck, L.V., and Covaci, A. (2006). Occurrence of organochlorine pesticides and polychlorinated biphenyls in soils and sediments from Eastern Romania. *Int. J. Environ. Anal. Chem.* *86*, 833–842.
- El-Shahawi, M., Hamza, A., Bashammakh, A., and Al-Saggaf, W. (2010). An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants. *Talanta* *80*, 1587–1597.
- Gakuba, E., Moodley, B., Ndungu, P., and Birungi, G. (2015). Occurrence and significance of polychlorinated biphenyls in water, sediment pore water and surface sediments of Umgeni River, KwaZulu-Natal, South Africa. *Environ. Monit. Assess.* *187*, 568.
- Gao, S., Chen, J., Shen, Z., Liu, H., and Chen, Y. (2013). Seasonal and spatial distributions and possible sources of polychlorinated biphenyls in surface sediments of Yangtze Estuary, China. *Chemosphere* *91*, 809–816.
- Gerber, R., Smit, N.J., Van Vuren, J.H., Nakayama, S.M., Yohannes, Y.B., Ikenaka, Y., Ishizuka, M., and Wepener, V. (2016). Bioaccumulation and human health risk assessment of DDT and other organochlorine pesticides in an apex aquatic predator from a premier conservation area. *Sci. Total Environ.* *550*, 522–533.
- Ghaeni, M., Pour, N.A., and Hosseini, M. (2015). Bioaccumulation of polychlorinated biphenyl (PCB), polycyclic aromatic hydrocarbon (PAH), mercury, methyl mercury, and arsenic in blue crab *Portunus segnis* from Persian Gulf. *Environ. Monit. Assess.* *187*, 253.
- Gray, I.A.R. (2004). Guide for Polychlorinated Biphenyl (PCB) Management of Insulating oil in South Africa (wearcheck.co.za).
- Han, B., Lin, F., Ding, Y., and Zheng, L. (2018). Distribution characteristics, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons in sediments from Haizhou Bay, China. *Hum. Ecol. Risk Assess. Int. J.* *1–12*.
- Hu, D., Martinez, A., and Hornbuckle, K.C. (2011). Sedimentary records of non-Aroclor and Aroclor PCB mixtures in the Great Lakes. *J. Gt. Lakes Res.* *37*, 359–364.
- Humphries, M.S., McCarthy, T.S., and Pillay, L. (2017). Attenuation of pollution arising from acid mine drainage by a natural wetland on the Witwatersrand. *South Afr. J. Sci.* *113*, 1–9.
- Jeffrey, L. (2005). Characterization of the coal resources of South Africa. *J. South. Afr. Inst. Min. Metall.* *105*, 95–102.
- Jones, K.C., and De Voogt, P. (1999). Persistent organic pollutants (POPs): state of the science. *Environ. Pollut.* *100*, 209–221.
- Jooste, S., Bollmohr, S., and Thwala, M. (2008). National Toxicity Monitoring Program: Report on Phase 3: Pilot implementation and testing of the design (Report No. N/0000/REQ1008. Resource Quality Services, Department of Water Affairs and Forestry, Pretoria. URL: https://www.dwa.gov.za/iwqs/water_quality/ntmp/NTMPphase3ReportV2.pdf).

- Kanzari, F., Syakti, A., Asia, L., Malleret, L., Piram, A., Mille, G., and Doumenq, P. (2014). Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments of an industrialized urban river (Huveaune), France. *Sci. Total Environ.* *478*, 141–151.
- Karlsson, K., and Viklander, M. (2008). Polycyclic aromatic hydrocarbons (PAH) in water and sediment from gully pots. *Water. Air. Soil Pollut.* *188*, 271–282.
- Khim, J.S., Kannan, K., Villeneuve, D.L., Koh, C.H., and Giesy, J.P. (1999). Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 1. Instrumental analysis. *Environ. Sci. Technol.* *33*, 4199–4205.
- Kumar, B., Kumar, S., and Sharma, C.S. (2013). Ecotoxicological risk assessment of polychlorinated biphenyls (PCBs) in bank sediments from along the Yamuna River in Delhi, India. *Hum. Ecol. Risk Assess. Int. J.* *19*, 1477–1487.
- Kumar, K.S., Sajwan, K.S., Richardson, J.P., and Kannan, K. (2008). Contamination profiles of heavy metals, organochlorine pesticides, polycyclic aromatic hydrocarbons and alkylphenols in sediment and oyster collected from marsh/estuarine Savannah GA, USA. *Mar. Pollut. Bull.* *56*, 136–149.
- Li, C.-T., Zhuang, H.-K., Hsieh, L.-T., Lee, W.-J., and Tsao, M.-C. (2001). PAH emission from the incineration of three plastic wastes. *Environ. Int.* *27*, 61–67.
- Li, J., Mgonella, M.K., Bzdusek, P.A., and Christensen, E.R. (2005). PCB congeners and dechlorination in sediments of Upper Sheboygan River, Wisconsin. *J. Gt. Lakes Res.* *31*, 174–186.
- Long, E., and MacDonald, D. (1998). Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. *Hum. Ecol. Risk Assess.* *4*, 1019–1039.
- Lv, J., Zhang, Y., Zhao, X., Zhou, C., Guo, C., Luo, Y., Meng, W., Zou, G., and Xu, J. (2015). Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in sediments of Liaohe River: levels, spatial and temporal distribution, possible sources, and inventory. *Environ. Sci. Pollut. Res.* *22*, 4256–4264.
- Mai, B.-X., Fu, J.-M., Sheng, G.-Y., Kang, Y.-H., Lin, Z., Zhang, G., Min, Y.-S., and Zeng, E.Y. (2002). Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. *Environ. Pollut.* *117*, 457–474.
- McCarthy, T., and Venter, J. (2006a). Increasing pollution levels on the Witwatersrand recorded in the peat deposits of the Klip River wetland. *South Afr. J. Sci.* *102*.
- McCarthy, T., and Venter, J. (2006b). Increasing pollution levels on the Witwatersrand recorded in the peat deposits of the Klip River wetland. *South Afr. J. Sci.* *102*, 27–34.
- McCarthy, T., Arnold, V., Venter, J., and Ellery, W. (2007). The collapse of Johannesburg's Klip River wetland. *South Afr. J. Sci.* *103*, 391–397.
- Mohammed, A., Peterman, P., Echols, K., Feltz, K., Tegerdine, G., Manoo, A., Maraj, D., Agard, J., and Orazio, C. (2011). Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in harbor sediments from Sea Lots, Port-of-Spain, Trinidad and Tobago. *Mar. Pollut. Bull.* *62*, 1324–1332.
- Naigaga, I., Kaiser, H., Muller, W., Ojok, L., Mbabazi, D., Magezi, G., and Muhumuza, E. (2011). Fish as bioindicators in aquatic environmental pollution assessment: a case study in Lake Victoria wetlands, Uganda. *Phys. Chem. Earth Parts ABC* *36*, 918–928.
- Naiker, Y., Diab, R., Zunckel, M., and Hayes, E.T. (2012). Introduction of local Air Quality Management in South Africa: overview and challenges. *Environ. Sci. Policy* *17*, 62–71.

- Nascimento, R.A., de Almeida, M., Escobar, N.C., Ferreira, S.L., Mortatti, J., and Queiroz, A.F. (2017). Sources and distribution of polycyclic aromatic hydrocarbons (PAHs) and organic matter in surface sediments of an estuary under petroleum activity influence, Todos os Santos Bay, Brazil. *Mar. Pollut. Bull.* *119*, 223–230.
- Nieuwoudt, C., Pieters, R., Quinn, L.P., Kylin, H., Borgen, A.R., and Bouwman, H. (2011). Polycyclic aromatic hydrocarbons (PAHs) in soil and sediment from industrial, residential, and agricultural areas in central South Africa: An initial assessment. *Soil Sediment Contam.* *20*, 188–204.
- O'Donovan, J.V., O'Farrell, K.J., O'Mahony, P., and Buckley, J.F. (2011). Temporal trends in dioxin, furan and polychlorinated biphenyl concentrations in bovine milk from farms adjacent to industrial and chemical installations over a 15 year period. *Vet. J.* *190*, e117–e121.
- Pereira, W.E., Hostettler, F.D., and Rapp, J.B. (1996). Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California. *Mar. Environ. Res.* *41*, 299–314.
- Pheiffer, W., Quinn, L.P., Bouwman, H., Smit, N.J., and Pieters, R. (2018). Polycyclic aromatic hydrocarbons (PAHs) in sediments from a typical urban impacted river: application of a comprehensive risk assessment. *Ecotoxicology* *27*, 336–351.
- Polder, A., Venter, B., Skaare, J., and Bouwman, H. (2008). Polybrominated diphenyl ethers and HBCD in bird eggs of South Africa. *Chemosphere* *73*, 148–154.
- Rainbow, P.S. (2002). Trace metal concentrations in aquatic invertebrates: why and so what? *Environ. Pollut.* *120*, 497–507.
- Rimayi, C., Chimuka, L., Odusanya, D., de Boer, J., and Weiss, J. (2016). Distribution of 2, 3, 7, 8-substituted polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofurans in the Jukskei and Klip/Vaal catchment areas in South Africa. *Chemosphere* *145*, 314–321.
- Rimayi, C., Chimuka, L., Odusanya, D., de Boer, J., and Weiss, J.M. (2017). Source characterisation and distribution of selected PCBs, PAHs and alkyl PAHs in sediments from the Klip and Jukskei Rivers, South Africa. *Environ. Monit. Assess.* *189*, 327.
- Saldanha, G.C., Bastos, W.R., Torres, J.P.M., and Malm, O. (2010). DDT in fishes and soils of lakes from Brazilian Amazon: case study of Puruzinho Lake (Amazon, Brazil). *J. Braz. Chem. Soc.* *21*, 306–311.
- Samara, F., Tsai, C.W., and Aga, D.S. (2006). Determination of potential sources of PCBs and PBDEs in sediments of the Niagara River. *Environ. Pollut.* *139*, 489–497.
- Shi, Z., Tao, S., Pan, B., Fan, W., He, X., Zuo, Q., Wu, S., Li, B., Cao, J., and Liu, W. (2005). Contamination of rivers in Tianjin, China by polycyclic aromatic hydrocarbons. *Environ. Pollut.* *134*, 97–111.
- Shoeib, M., and Harner, T. (2002). Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* *36*, 4142–4151.
- Sibiya, P.N. (2012). Modification, development and application of extraction methods for PAHs in sediments and water.
- Sprovieri, M., Feo, M.L., Prevedello, L., Manta, D.S., Sammartino, S., Tamburrino, S., and Marsella, E. (2007). Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere* *67*, 998–1009.
- Thomas, P., Rahman, M.S., Khan, I.A., and Kummer, J.A. (2007). Widespread endocrine disruption and reproductive impairment in an estuarine fish population exposed to seasonal hypoxia. *Proc. R. Soc. Lond. B Biol. Sci.* *274*, 2693–2702.

UNEP (2001). United Nations Environmental Program, 2001. Final Act of the Conference of Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants. (UNEP/POPS/CONF/4UNEP Stockholm, Sweden/Geneva, Switzerland), p.

Xing, Y., Lu, Y., Dawson, R.W., Shi, Y., Zhang, H., Wang, T., Liu, W., and Ren, H. (2005). A spatial temporal assessment of pollution from PCBs in China. *Chemosphere* 60, 731–739.

Yan, W., Chi, J., Wang, Z., Huang, W., and Zhang, G. (2009). Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Daya Bay, South China. *Environ. Pollut.* 157, 1823–1830.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., and Sylvestre, S. (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33, 489–515.

Zhang, Z., Hong, H., Zhou, J., Huang, J., and Yu, G. (2003). Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. *Chemosphere* 52, 1423–1430.

Zhao, L., Hou, H., Zhou, Y., Xue, N., Li, H., and Li, F. (2010). Distribution and ecological risk of polychlorinated biphenyls and organochlorine pesticides in surficial sediments from Haihe River and Haihe Estuary Area, China. *Chemosphere* 78, 1285–1293.

Figures

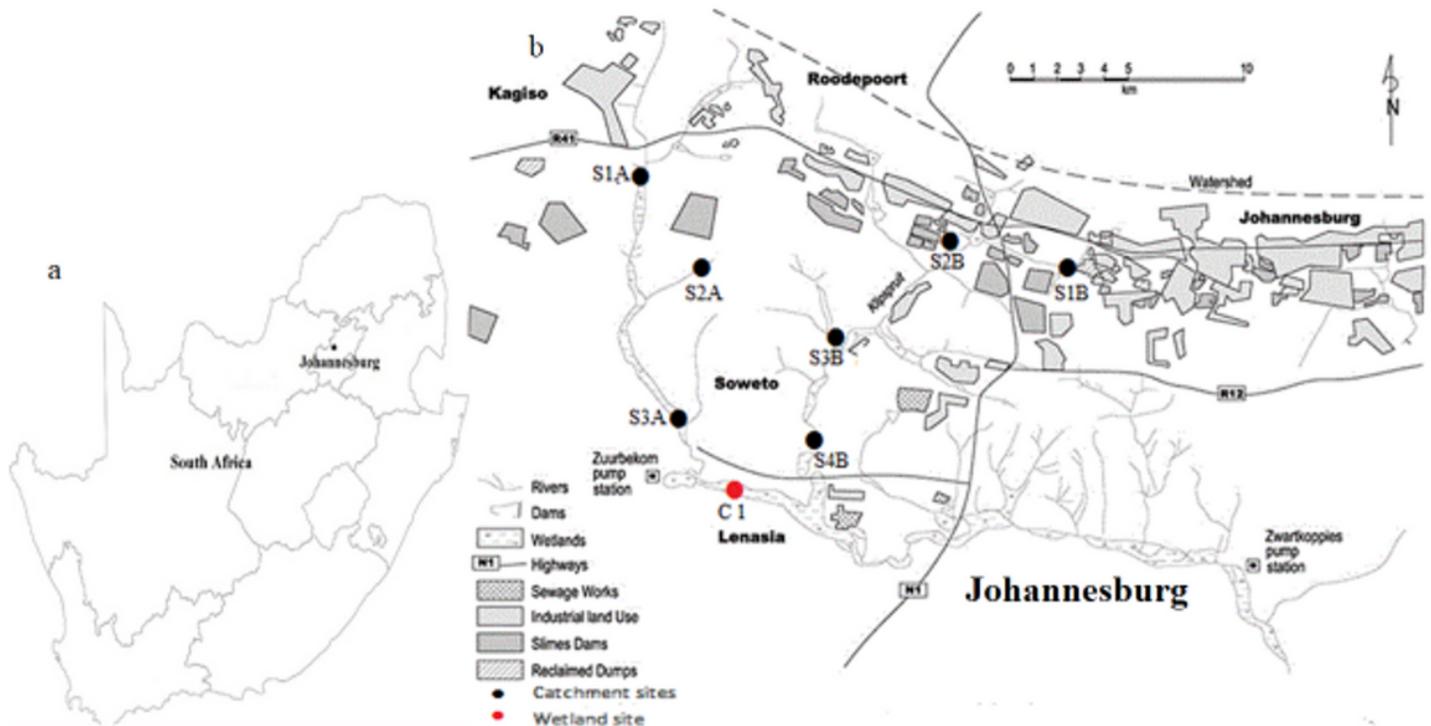


Figure 1

Map of the Klip River system showing the location of sediment sampling sites relative to industrial activities.

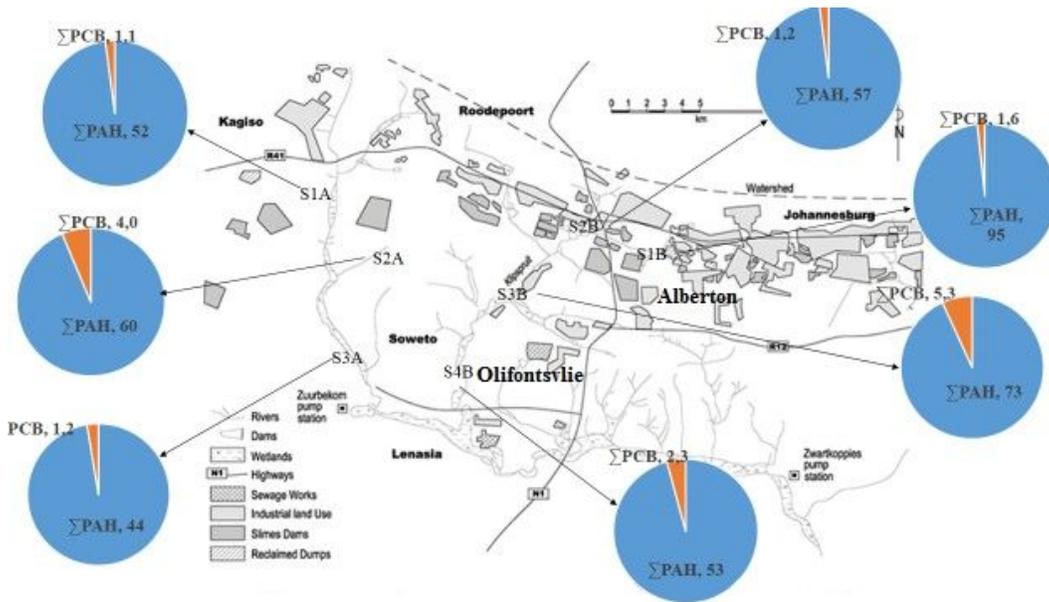
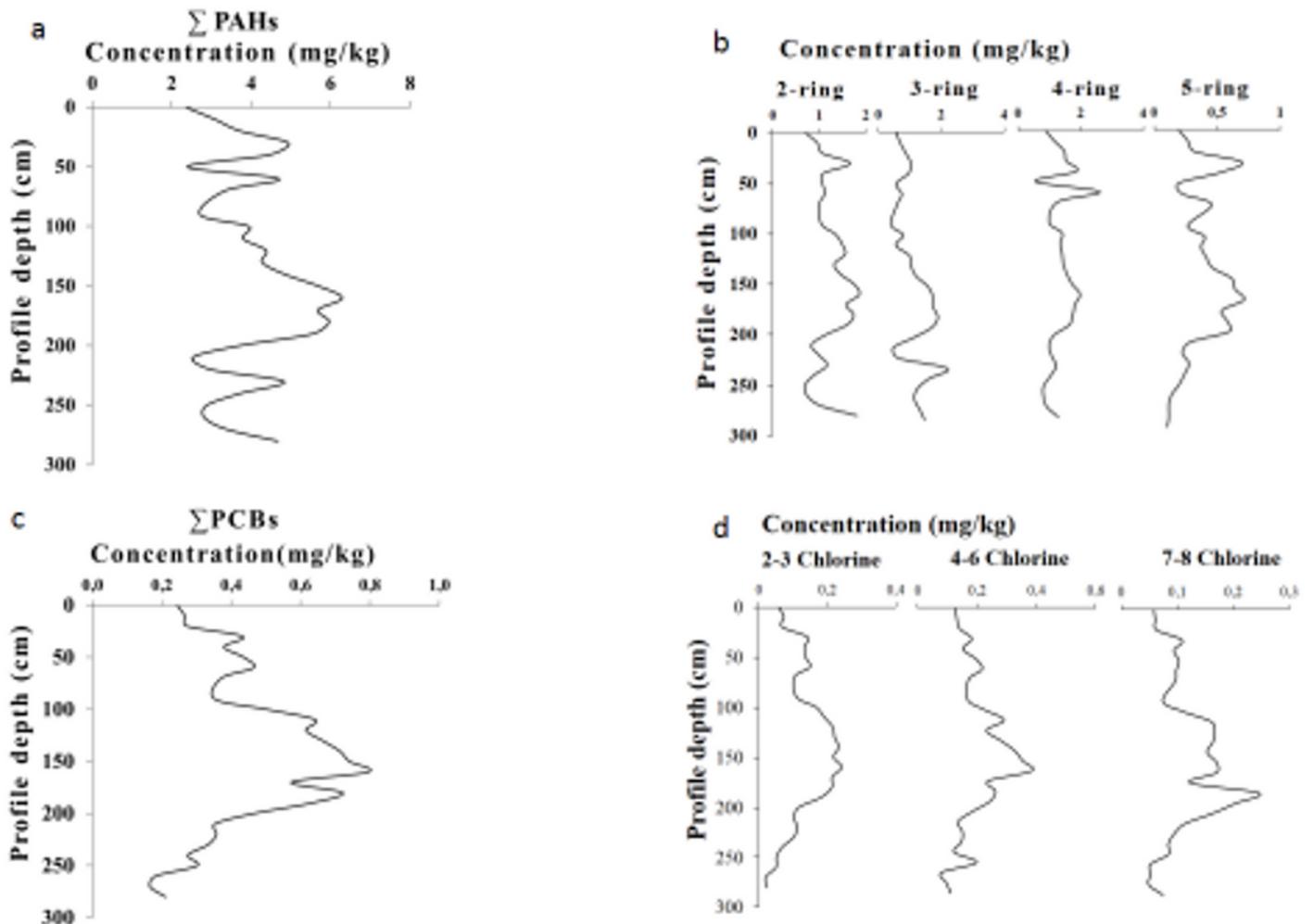


Figure 2

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



Vertical distribution of (a) \sum PAHs (mg/kg), (b) PAH congeners according to membered rings, (c) \sum PCBs (mg/kg), and (d) PCB congeners according to chlorine atoms at the core sampling site of the wetland.

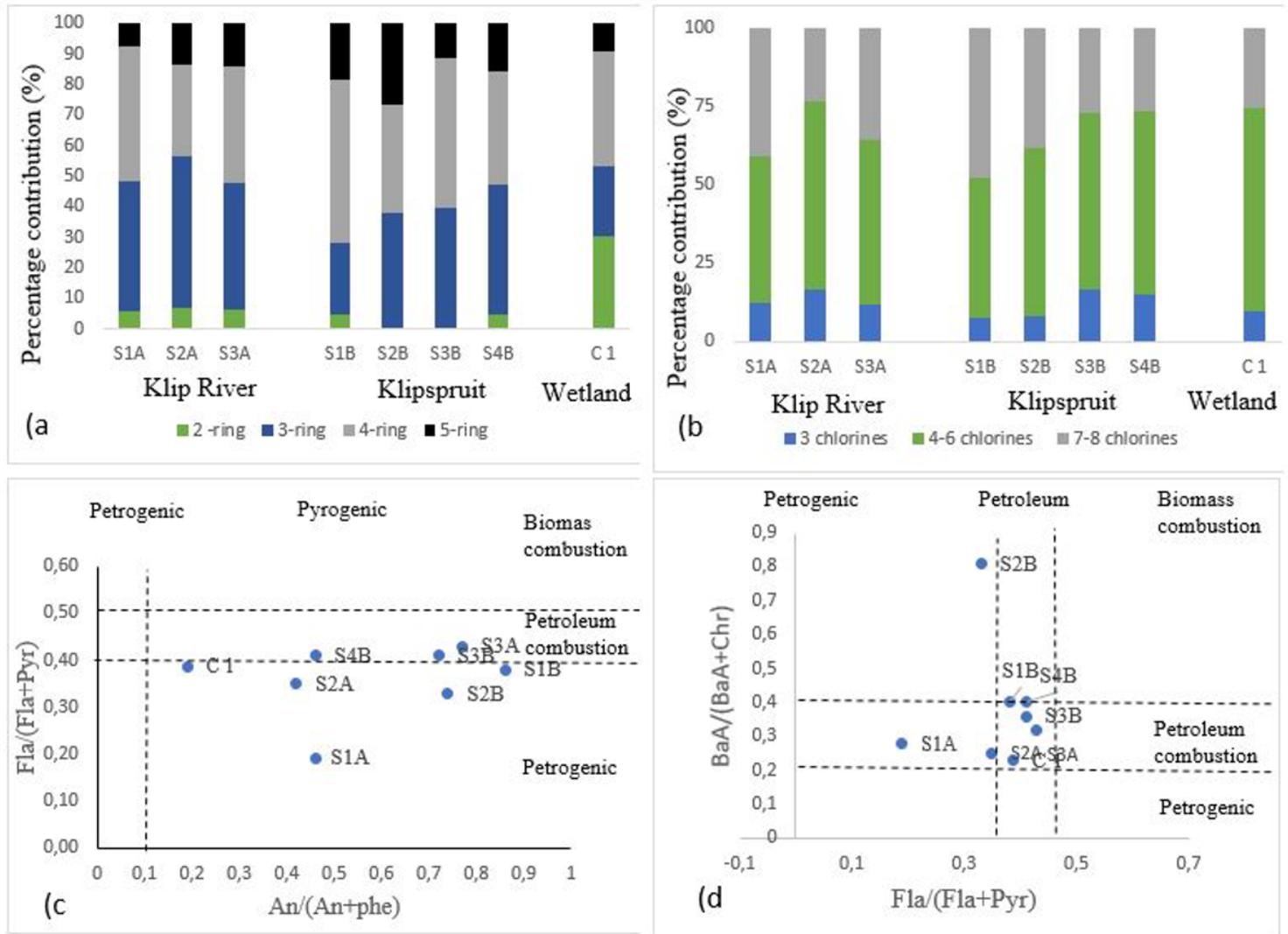


Figure 4

Graph showing (a) percentage distribution of PAHs according to rings, (b) percentage distribution of PCBs according to the chlorine atoms, (c) & (d) potential sources of PAHs.

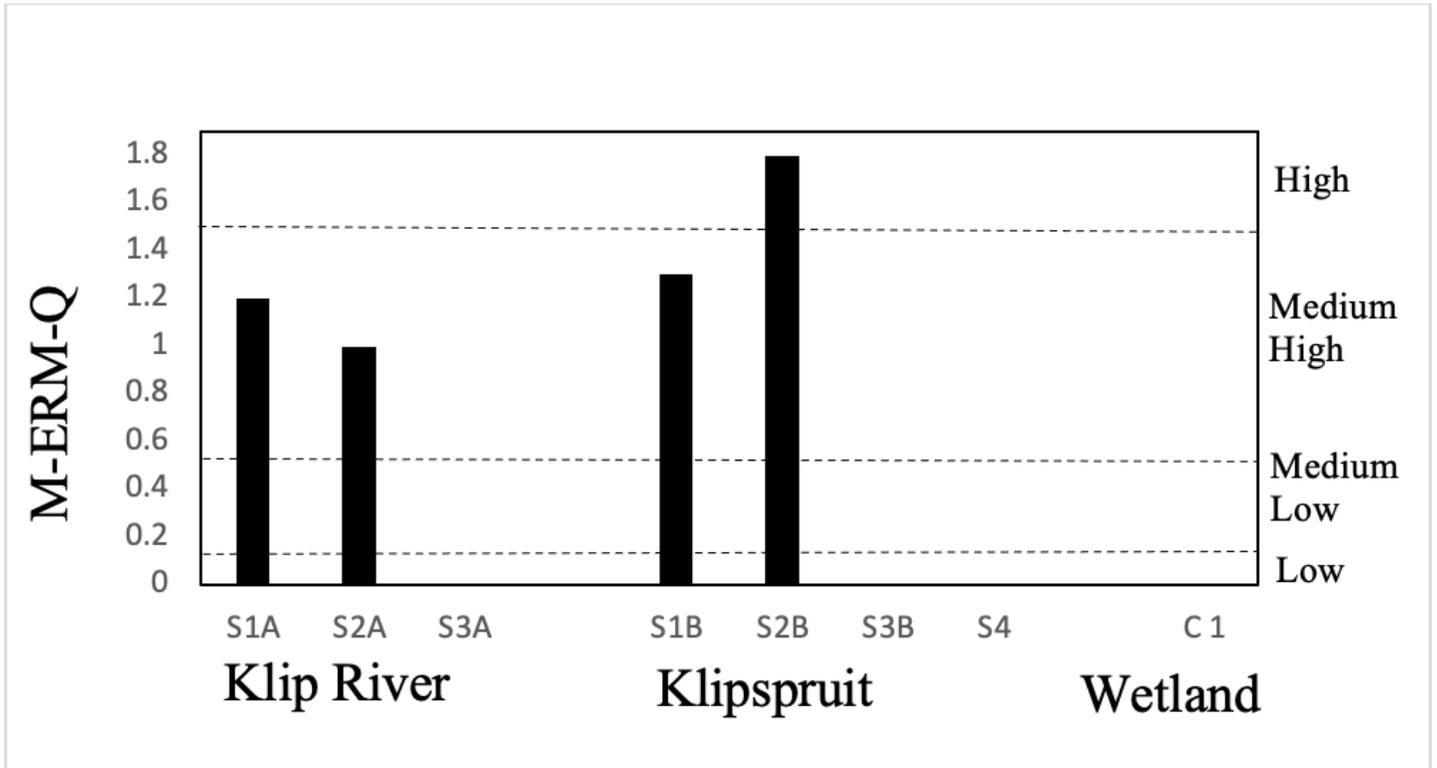


Figure 5

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

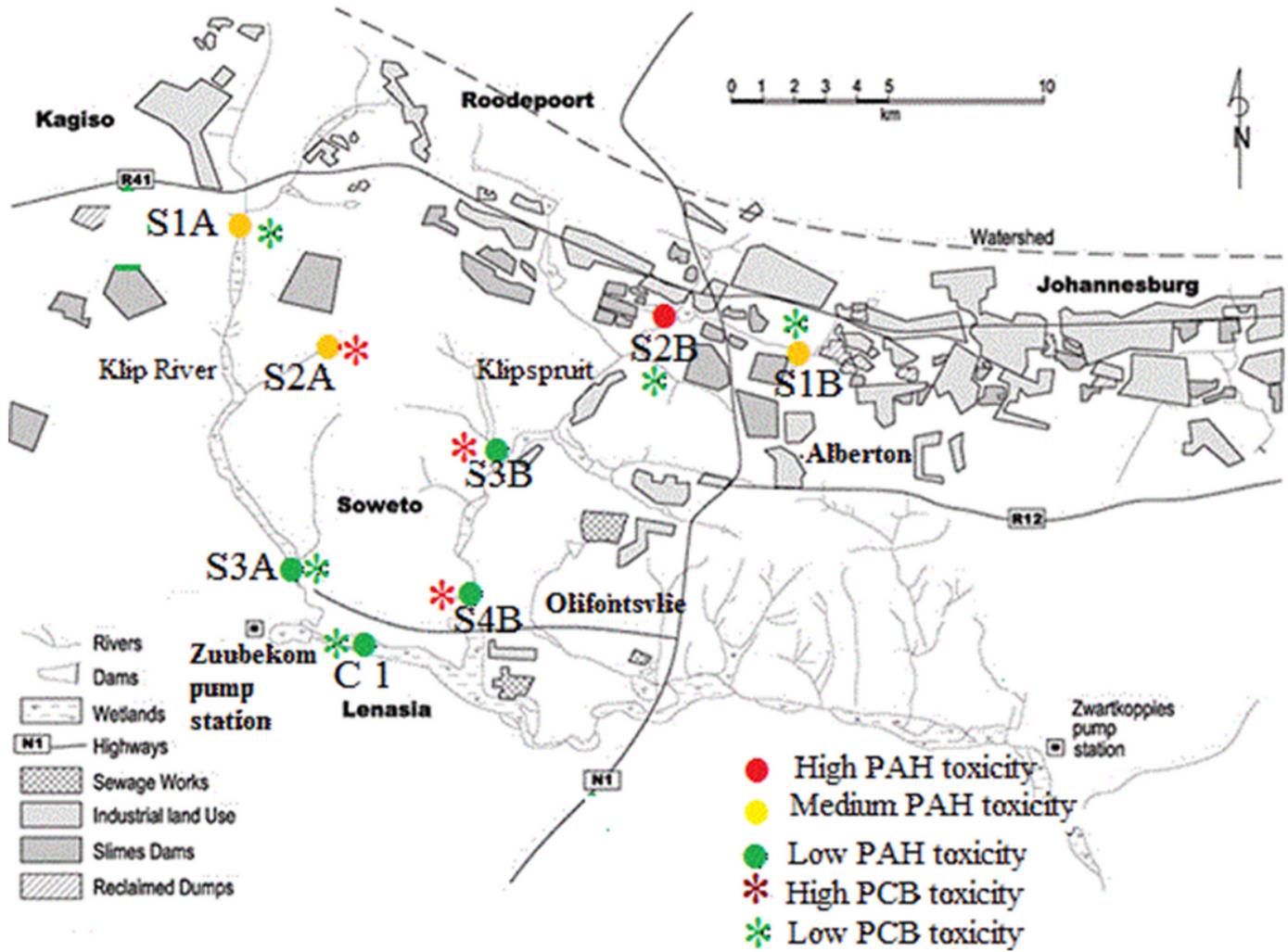


Figure 6

A map showing the ecotoxicological risk assessment of the investigated sites.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [APPENDICES.docx](#)