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Quantitative analyses of selected polychlorinated biphenyl (PCB) congeners in water, soil, and sediment during winter and spring seasons from Msunduzi River, South Africa

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Abstract The lack of information and the need for knowledge on the organic pollutants within the area of KwaZulu-Natal together with the global problem of water supply have prompted our investigation into the analyses of eight polychlorinated biphenyl (PCB) congeners in the Msunduzi River of KwaZulu-Natal, South Africa. Soil, sediment, and water samples were collected at ten different sites along the river during winter and spring seasons. Soil and sediment samples were extracted using ultra sonication with dichloromethane while water samples were liquid-liquid extracted using dichloromethane. All sample extracts were cleaned-up using a multi-layer silica gel column and analyzed with gas chromatography-mass spectrometry. Quality assurance measures were also determined. The percentage recoveries for water were 53–128 for all the PCBs analyzed, while sediment recoveries ranged between 69 and 105%. The highest total concentrations of the PCBs in sediment were 214.21–610.45 ng/g dw at the Du Toit sampling site and 30.86–444.43 ng/g dw basis at the wastewater treatment inlet for winter and spring, respectively. Soil PCB concentrations were 76.53–397.75 ng/g dw at the Msunduzi Town sampling site and 20.84–443.49 ng/g (dry weight) at the Du Toit sampling site for winter and spring, respectively. In addition, high PCB concentrations were found in effluent of the wastewater treatment inlet compared to other sampling sites, which ranged between 0.68–22.37 and 2.53–35.69 ng/mL for winter and spring seasons, respectively. In all the sampling sites selected for this study, Du Toit afforded the highest PCB concentration levels and the lowest was after chlorination at the Darvill wastewater treatment plant. The results presented are new and it is the first study of organic pollutants such as PCBs that has been carried out on this river.

Keywords Organic pollutants · Polychlorinated biphenyls (PCBs) · Msunduzi River · Gas chromatography-mass spectrometry · Surface water · KwaZulu-Natal

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Introduction

Persistent organic pollutants (POPs) have been a serious environmental concern to both the local and the international community. This important class of organic pollutants, once released into the environment, persists and remains intact for a long period, due to their stability against chemical, photolytic, and biological degradation (Buccini 2003; Yenisoy-Karakas et al. 2012). POPs are lipophilic, have long-range transportation, are bio accumulating in the food chain, and are characterized as acutely toxic. POPs are found almost everywhere even where they have never been generated (Buccini 2003). They tend to travel from hotter regions towards colder areas and settle in the soil and sediment for very long periods because temperature and light do not encourage their degradation (Zhao et al. 2006).

Polychlorinated biphenyls (PCBs) are one of the 12 major organic pollutants known as the dirty dozen listed under the Stockholm Convention. They are a group of chlorinated synthetic organic chemicals that have relatively low water solubility and relatively long environmental and biological half-lives of 8–15 years (ATSDR 2000). PCBs are introduced into the environment by anthropogenic activities such as incineration of PCB-containing waste; burning of many materials that may contain chlorine; and wood treated with pentachlorophenol as well as uncontrolled landfills and hazardous waste sites (Safe 1994; Davis et al. 2007). PCBs were once widely used as dielectric and coolant fluids in electrical appliances such as transformers and capacitors. PCBs were also used as pesticide extenders, heat exchange fluids, and flame retardants but such applications of PCBs have since decreased (Fiedler 2001). Due to their environmental toxicity and classification as a POP, PCB production was banned in the USA in 1979 and by the Stockholm Convention (SC) on POPs in 2001 in which South Africa was a party to (Porta and Zumeta 2002; Bouwman 2004). However, because of their persistency and tendency to bioaccumulate in the sediment, they are still found in the environment today. In addition, they bioaccumulate in organisms and transfer to higher trophic levels and thus progress through the food chain posing serious health problems to animals and humans (Tanabe 2002; Chau 2005). PCBs are ubiquitous in the environment, and humans are primarily exposed to this organic pollutant via the ingestion of contaminated foods containing commercial mixtures of PCB congeners (Kreis 1985; Rose et al. 2001; Shadel et al. 2001). PCBs are endocrine disruptors and exposure to them has been linked to some health-related problems such as acne-like skin conditions in adults and neurobehavioral and immunological changes in infants (Klanova et al. 2007; ATSDR 2000). Other related health issues associated with PCB exposure are cancer-related illnesses, mental disorders, and toxicity problems such as endocrine and neurotoxicity effects in humans (Kimbrough 1995; ATSDR 2000; Klanova et al. 2007). In the South African context, there is limited information on the concentrations and distributions of POPs particularly in KwaZulu-Natal. Previous research on KwaZulu-Natal's rivers focused on inorganic pollutants and very little research has been carried out on POPs, which are just as toxic and accumulating as the inorganic pollutants. Any research that has been carried out on POPs was also undertaken many years ago which is now out dated and new studies are required to provide a more updated scenario of the state of the rivers. This, together with the global problem of water supply, has stimulated our investigation into the analysis of POPs most especially PCBs in the Msunduzi River of KwaZulu-Natal province, South Africa. This research investigated the presence and concentration of selected PCBs: PCB 28, PCB 77, PCB 101, PCB 52, PCB 153, PCB 105, PCB 138, and PCB 180 in soil, sediment, and surface water samples of the Msunduzi River during winter and spring seasons.

Materials and methods

Site selection

The Msunduzi River is one of the main tributaries of the uMgeni River, which is the main source of water to the greater region of KwaZulu-Natal. The Msunduzi River passes through highly industrialized areas as well as rural and agricultural areas, which all contribute to the levels of organic pollution in the river. This river is also used for various national water sports competitions (e.g., the Dusi canoe marathon) where people could possibly be exposed to these pollutants. Therefore, it is a suitable and important river for this type of study and the results will provide much needed information to a wide variety of stakeholders including the municipality and the scientific community. Winter and spring samples were collected in July 2013 and September 2013, respectively. Soil, sediment, and surface water samples were collected from ten different sites along the river course as indicated in Fig. 1 and Table 1. Global positioning system (GPS) was used to locate each sampling site along the river. Sampling sites WWT 1 and 2 had the same GPs coordinates as they were both inside the wastewater treatment plant but at different locations within the plant. Thus, only nine GPS sites are shown the map.

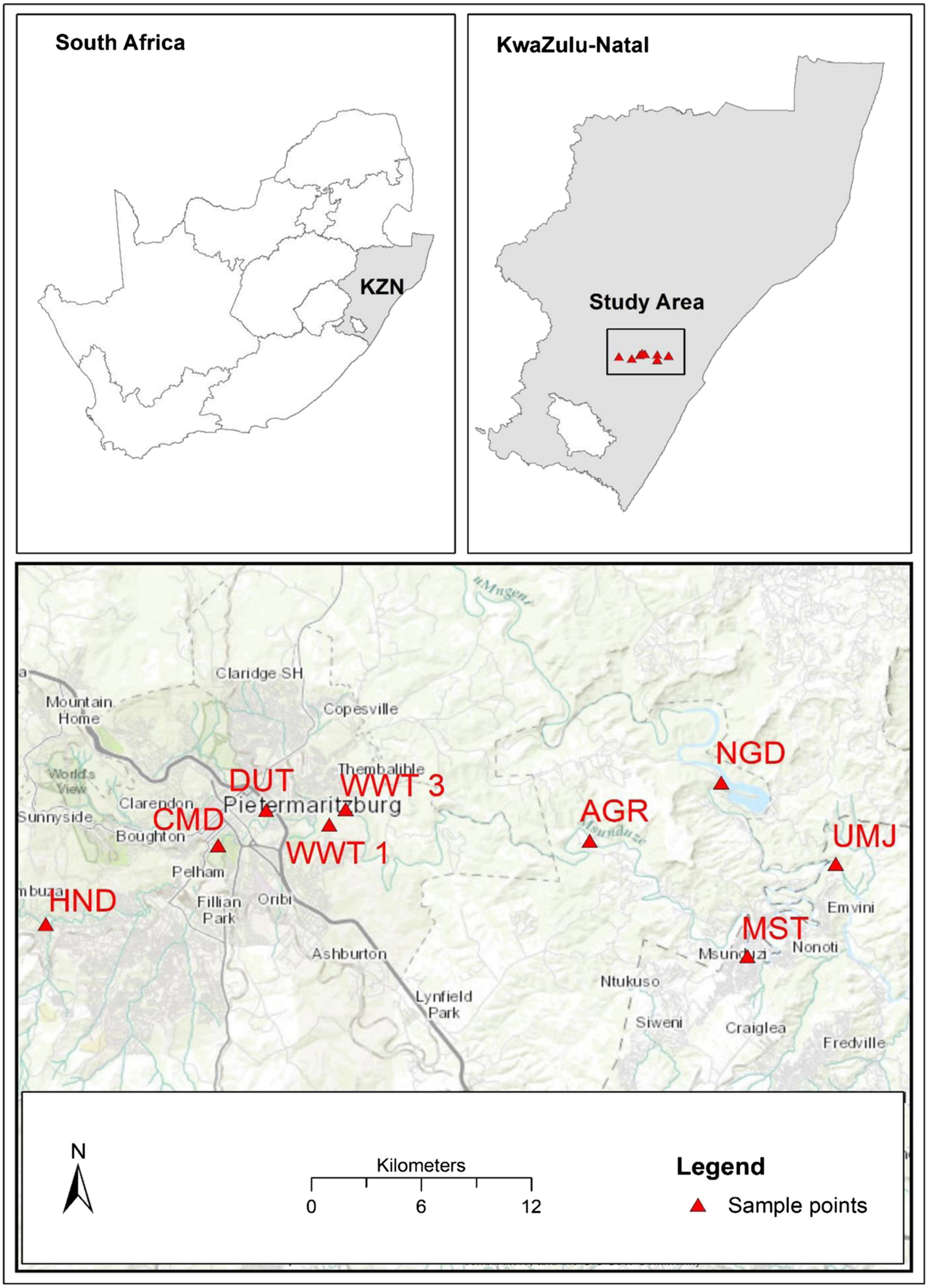

Fig. 1 Map showing the sampling sites for this study along the Msunduzi River, South Africa (created using ArcMap10.4 version)

Table 1 Sampling coordinates and physicochemical parameters of the Msunduzi River water during the winter and spring sampling seasons

Site	Location		pH		Temperature (°C, winter)		Temperature (°C, spring)	
Name	Latitude	Longitude	Winter	Spring	Ambient	Water	Ambient	Water
HND	29° 38′ 51″	30° 17′ 32″	6.21	7.52	21	14	22	19
CMD	29° 36′ 47″	30° 22′ 36″	5.15	8.05	16	21	24	21
DUT	29° 35′ 52″	30° 24′ 01″	7.20	7.49	23	15	25	18
WWT 1	29° 36′ 15″	30° 25′ 52″	5.31	7.24	25	19	29	22
WWT 2	29° 36′ 15″	30° 25′ 52″	5.54	7.85	24	19	25	22
WWT 3	29° 36′ 15″	30° 25′ 52″	*	7.70	*	*	28	22
AGR	29° 36′ 40″	30° 33′ 32″	5.12	8.72	19	14	28	24
MST	29° 39′ 40″	30° 38′ 10″	4.77	8.92	20	15	24	26
NGD	29° 37′ 08″	30° 09′ 30″	5.56	8.87	18	15	22	21
UMJ	29° 37′ 16″	30° 40′ 46″	5.07	7.60	15	15	26	25

*Samples were not collected due to major renovation at that particular sampling point during the sampling period

NGD Nagle dam, *UMJ* uMgeni, Msunduzi River joining point, *MST* Msunduzi Town, *AGA* agricultural area, *WWT1* the Darvill wastewater treatment plant 1 (inlet), *WWT2* the Darvill wastewater treatment plant 2 (after chlorination), *WWT3* the Darvill wastewater treatment plant 3 (discharge), *DUT* Du Toit, CMD Camps Drift, *HND* Henley dam outlet

Reagents and materials

All reagents and chemicals were of HPLC grade and the eight selected PCB standards were purchased from Sigma-Aldrich® (South Africa). PCB stock solutions of 200 mg/L of individual standards were prepared by dissolving about 0.02 g of the individual PCB standards in 100 mL of *n*-hexane and stored in the refrigerator at 4 °C. The lower working concentrations for the PCB standards were prepared by appropriate dilution in *n*-hexane. High purity anhydrous sodium sulfate (Gold line (CP) CAS No. 7757-82-6, Associated Chemical Enterprises (ACE)) was used as a desiccant throughout the study, while silica gel (grade 634, of 100- to 200-mesh size (0.063–0.2 mm)) purchased from Merck was used in preparation of both basic and acidic silica used for the clean-up of the extracts prior to analyses. Reagent grade sulfuric acid (specific gravity 1.84, Promark Chemicals) was used for acidification. All the glassware were baked in the oven at about 130 °C prior to use and the cotton wool was soaked in acetone and activated in the oven over night at 130 °C prior to use.

Sampling and sample treatment

Soil and sediment samples were collected using the same sampling method. A total of seven soil and eight sediment samples were collected for winter and spring seasons, respectively, while a total of nine and ten samples were collected for sediment and soil in winter and spring seasons, respectively. Bio-solids were collected as a sediment sample from the Darvill wastewater treatment plant. In addition, the point of discharge of treated wastewater back into the Msunduzi River was not accessible during the winter period due to major maintenance at that particular sampling site. Sediment samples were collected by scooping 0–10 cm of the sediment from the river bed with a stainless steel spade, while the soil samples were collected at a depth of 0–15 cm along the banks of the river close to the water using a grab sampler and stainless steel soil auger. The samples were stored in glass bottles. The lids of glass bottles were lined with acetone pre-washed aluminum foil to prevent sample reactions with phthalates possibly present in the plastic lining of the lid. Soil and sediment sample containers were kept cool under ice during transportation to the laboratory. Once in the laboratory, samples were kept at 4 °C prior to extraction to prevent break down and bio-degradation of the compounds of interest (Hilscherova et al. 2003). Soil and sediment samples were air dried in the fume hood for 5 days; the dried samples were sieved with 75 μm, 300 μm, and 450 μm stainless steel sieves and stored prior to extraction.

Surface water samples were collected in 2.5-L amber reagent bottles, which were washed with phosphate-free soap (dDyna Chem), rinsed with tap water, and distilled water prior to sampling. The bottles were also rinsed with HPLC grade acetone and *n*-hexane to eliminate both polar and non-polar contaminants. Bottles were rinsed with the river water to be sampled before the water sample from the river was collected. Grab sampling technique was used to collect water samples from a depth of 1–2 cm below the water surface. A 1-mL aliquot of 50% sulfuric acid was added to each of the samples immediately after collection to prevent microbial degradation of the samples. Sample bottle lids were also lined with acetone pre-washed aluminum foil to prevent the possibility of migration of plasticizers (such as phthalates) from the plastic bottle lids into the sample (Derek and Sverko 2006). Water samples were kept cool during transportation to the laboratory and stored at 4 °C prior to extraction. Glass and stainless steel were used throughout the sample preparation to prevent sample contamination with phthalates from plastic materials.

Sample extraction

Soil and sediment samples (20 g dw each) were dried, homogenized, and mixed with 10 g of anhydrous sodium sulfate to remove excess moisture from the sample. An ultrasonic bath (UMC 20, 90022112 Kenmare) was used for the extraction. Ultrasonication was the method of extraction, due to its efficiency for extracting organic pollutants as well as it requiring less solvent compared to the conventional soxhlet method, which requires much solvent and is time consuming (Adegbenro et al. 2011). Soil and sediment samples were extracted with three times 20 mL dichloromethane (DCM) at a temperature of 30 °C for 30 min each. Extracts were combined, filtered, and concentrated to 2 mL using rotary evaporation (Hei-Vap, Heidolph version, Germany).

Water extraction used liquid-liquid extraction because it offered better results (Fatoki and Awofolu 2003; Sibali et al. 2008) compared to the solid-phase extraction (SPE) method. SPE cartridges, during sample preparation, have been reported to introduce phthalate ester interferences, originating from the housing materials of the cartridges (Fatoki and Awofolu 2003). A 500-mL aliquot of water was extracted with three times 40 mL of DCM in a separating funnel. The combined extract fractions were reduced to 2 mL using rotary evaporation. Only the water sample collected from the wastewater treatment plant was filtered through a vacuum glass funnel prior to extraction, to remove the solids and suspended particles due to its high turbidity. Water samples from other sites were extracted without being filtered because the water samples were free of visible suspended particulate materials, although freely dissolved or dissolved particulate matter may be present which would contribute to the level of PCBs detected in water. In addition, the water used by the residents of the informal settlements and animals who use it as a source of water was used directly without filtration and the aim was to determine the PCB concentrations that humans and animals are exposed to. It is for these reasons that the river water samples were not filtered.

Sample clean-up

All samples were subjected to clean-up after extraction. Clean-up is an important step after extraction, most especially for the removal of interferences from unwanted compounds and to prevent unambiguous results. Two major steps were needed to reduce interferences: lipids were removed by treating the extracts with concentrated sulfuric acid and elemental sulfur was removed by treating the extracts with activated copper powder set as a top layer on the silica column. In this study, a multilayer silica gel column was used as recommended by the United States Environmental Protection Agency (USEPA method 1668B 2008; Kumar et al. 2013) for anthropogenic PCB pollutants. The column (Quickfit D1/11 England 50 mL) was packed from bottom to top with 2.5 g silica gel, 1.5 g basic silica gel, 2.5 g silica gel, 5.0 g acidic silica gel, 2.5 g silica gel, 2 g activated copper powder, and 10 g anhydrous sodium sulfate (Na_2SO_4). The column was pre-eluted with 20 mL *n*-hexane before the extract was loaded; 50 mL of *n*-hexane:DCM:toluene solvent combination was used for the elution in the ratio 2.5:1.5:1. The eluent was reduced to 2 mL using rotary evaporation and thereafter evaporated to dryness at room temperature. Samples were reconstituted to 2 mL with *n*-hexane and filtered through a 0.45-μm acrodisc filter prior to GC-MS analysis.

Instrumental analyses and quality control

GC-MS analysis

Samples were analyzed using gas chromatography-mass spectrometry (GC-MS) (Shimadzu QP-2010 Ultra Japan), with a DB-5MS capillary column of length

Table 2 Percentage recoveries based on spiked sediment sampled from the agricultural area in winter and spring and spiked tap water, as well as limits of detection and quantification of PCB congeners in sediment and water

PCB congeners	Percentage recoveries		Limits of detection/limits of quantification				R^2 value ($n = 3$)	Retention times (minutes)
	Water (%)	Sediment (%)	Water (ng/L)		Sediment (ng/g dw)			
			LOD	LOQ	LOD	LOQ		
PCB 28	72.01	84.19	0.015	0.044	0.001	0.004	0.998	8.105
PCB 77	51.96	96.99	0.016	0.049	0.001	0.004	0.996	8.558
PCB 101	128.16	69.27	0.022	0.069	0.002	0.006	0.997	9.689
PCB 52	94.46	78.84	0.011	0.037	0.001	0.003	0.996	10.209
PCB 153	73.39	104.47	0.010	0.040	0.001	0.004	0.995	10.762
PCB 105	102.87	104.09	0.008	0.023	0.001	0.002	0.998	10.838
PCB 138	100.30	93.82	0.007	0.020	0.001	0.002	0.998	11.114
PCB 180	74.74	98.96	0.012	0.040	0.001	0.003	0.996	11.936

dw dry weight

30 m (0.25-μm internal diameter and 0.25-μm film thickness). Helium was the carrier gas with a flow rate of 0.72 mL/min and a total flow of 31.8 mL/s and a linear velocity of 32.2 cm/s at purge flow of 3.0 mL/min using splitless injection mode. The injection and detector temperatures were set at 220 °C and 320 °C, respectively. The oven temperature was set at 150 °C and held for 2 min, raised to 295 °C at 14 °C/min, and held for a further 2 min. A 1-μL injection volume was used. All the quality control steps were followed. Laboratory blanks for both water and sediment were subjected to the same analytical procedures as applied to the original samples but did not show any significant peaks for the analytes of interest. The laboratory blank used for water in this study was double-distilled water, and washed sand purchased from Sigma-Aldrich was used as the sediment laboratory blank. These were chosen because they were free of the targeted analytes of interest (PCBs). Triplicate linear range values (R^2) for all the analytes were not less than 0.995 and LOD and LOQ values were determined for the analytes (Table 2). The method recoveries were calculated by analyzing matrix spiked samples (USEPA method 1668B 2008). Sediment recoveries used the actual sediment samples that were then spiked, and for water recoveries, tap water was spiked. Matrix spiking was adopted in this study in order to replicate the field conditions and to determine the matrix interferences on the behavior of the selected analytes. To carry out matrix spiking, a real sample of sediment obtained from one of the sampling sites was divided into two subsamples of equal mass. One subsample was spiked and the other subsample was left unspiked. The amount of PCB obtained from the unspiked sample was subtracted from the amount determined in the spiked sample and divided by the amount the sample was spiked with. This gave the percentage recovered and is shown in Table 2. Routine analysis of blanks with every ten sample sets were carefully monitored to determine the possibility of any interferences from the column. Standards were run intermittently between samples to monitor changes in the instrument's sensitivity. Sample extracts were spiked with 80 μg/L of the mixed PCB standards and their concentrations were determined. An external calibration method was used for the quantification of eight PCB congeners based on the peak areas of the targeted compounds. Analytes were identified by comparing their retention times with those of the PCB standards.

Results and discussion

Temperature and pH

The pH, ambient, and water temperatures were measured during the sampling seasons as shown in Table 2. The pH values for all the sampling sites were shifted slightly towards acidic levels during the winter season except for the Du Toit sampling site which was

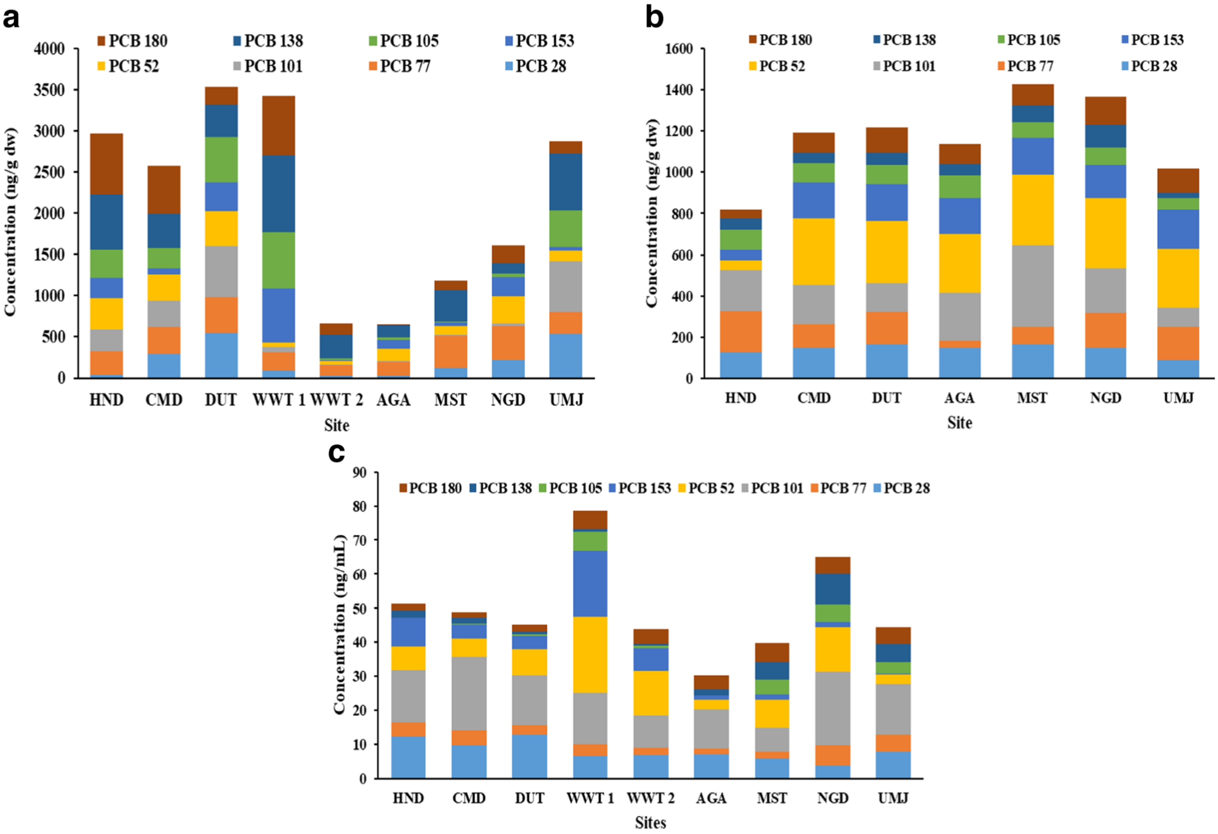

Fig. 2 Concentrations of PCBs at different sites of **a** sediment, **b** soil, and **c** surface water during winter

within the neutral to slightly alkaline range. The pH values for all the sampling sites were within the alkaline range during the spring season but during the winter season, a low river flow rate was expected due to decreased rainfall which would result in higher accumulation of particulate matter in the water thus leading to low pH. Furthermore, during the spring period, the slightly higher temperature reduces the solubility of CO_2 which in turn leads to a more alkaline pH. Both water flow rate and current velocity affect adsorption and sediment transportation of pollutants (Yang et al. 2009) which in turn affect the pH of the water. Pollutant dilution and diffusion as well as distribution of organic pollutants in the surface sediments are greatly influenced by temperature as well as hydrodynamic conditions (Tang et al. 2000; Zhang et al. 2007).

Concentrations of PCB in sediment, soil, and water samples

Concentrations of PCBs in sediment, soil, and water during the winter and spring seasons are presented in Figs. 2a–c and 3a–c, respectively. Concentrations of PCBs were found to be higher in sediment samples compared to soil in both winter and spring seasons. The concentrations of PCBs in water samples were also higher in winter than the spring season except for the WWT 1, which was higher in the spring season. The higher concentrations in the sediment and soil were expected because these pollutants are lipophilic and hydrophobic and tend to prefer to interact with organic surfaces and fatty tissues of organisms (WSPMP 1996). Sediments and soils tend to be a “sink” for these organic pollutants and are a measure of their concentrations over times (Aydin and Yurdun 1999).

Lower PCB concentrations were observed for the samples collected during the spring season as compared to the winter period for all matrices sampled. This is possibly due to the increase in temperature in spring, which would have caused snow, which fell during the winter season in high lying areas, to melt. This in turn leads to an increase in water flow, thereby increasing the dispersion and dilution of pollutants, resulting in lower detectable concentrations of PCB during the spring

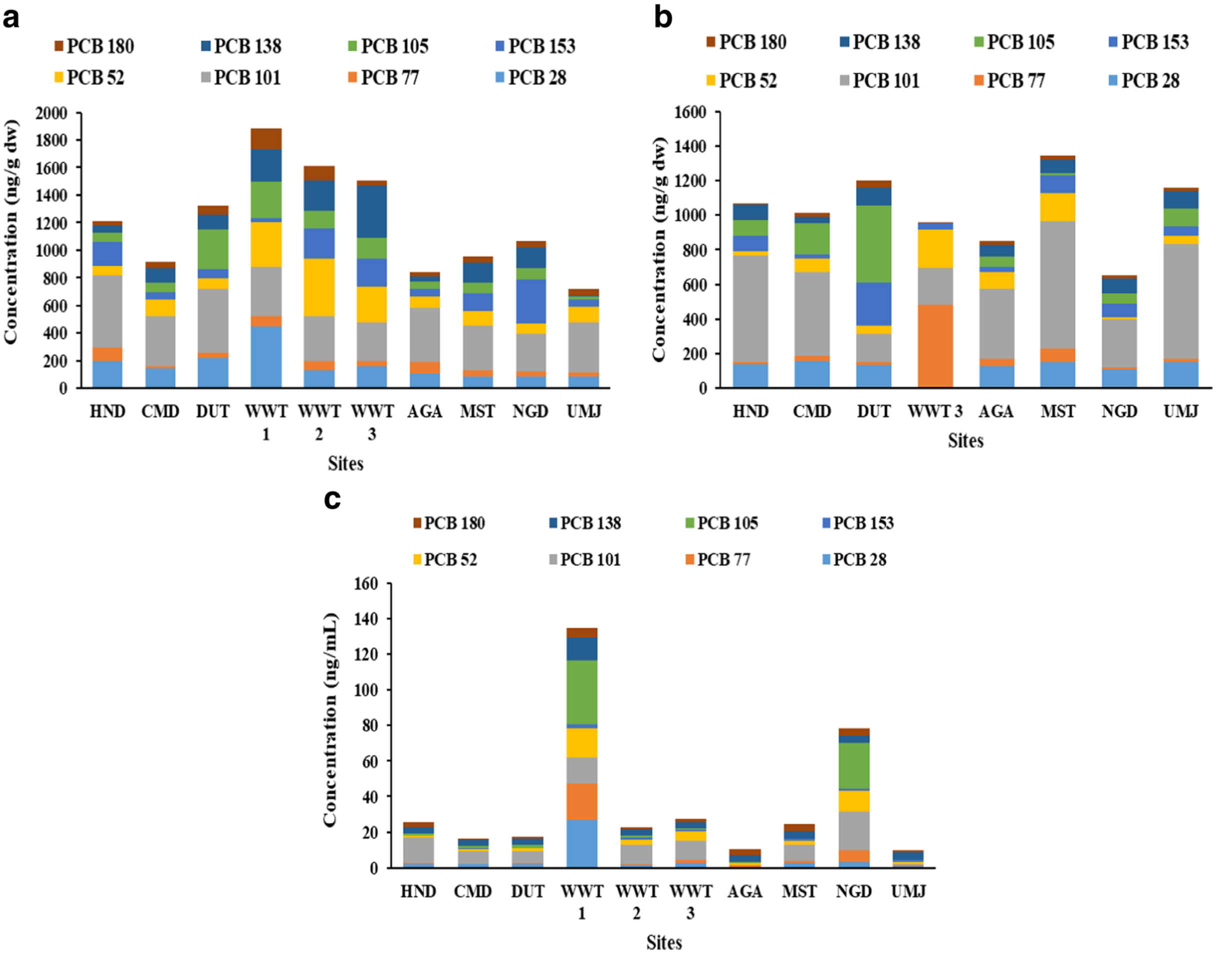

Fig. 3 Concentrations of PCBs at different sites of **a** sediment, **b** soil, and **c** surface water during spring

Table 3 Total PCB concentrations and the percentage contribution of the analytes at sampling sites for sediment (ng/g dw), soil (ng/g dw), and surface water (ng/mL) during winter and spring seasons

Site code	Sediment		Soil		Water		Percentage (%)
	Winter (ng/g dw)	Spring (ng/g dw)	Winter (ng/g dw)	Spring (ng/g dw)	Winter (ng/mL)	Spring (ng/mL)	
HND	2972.79	1179.48	817.13	1063.75	51.30	22.87	12.74
CMD	2569.74	868.60	1191.78	991.83	48.88	15.57	11.86
DUT	3530.62	1255.50	1216.72	1161.37	45.34	16.31	15.07
WWT 1	3424.07	1734.27	Nil*	Nil*	78.71	129.32	11.19
WWT 2	669.18	1506.21	Nil*	Nil*	43.82	21.64	4.67
WWT 3	Nil	1468.05	Nil*	955.77	Nil*	25.84	5.11
AGA	644.63	808.81	1136.05	827.30	30.26	6.90	7.20
MST	1181.19	907.26	1427.22	1323.94	39.75	20.19	10.22
NGD	1603.83	1023.77	1365.54	634.35	64.94	74.40	9.94
UMJ	2874.84	673.71	1016.28	1142.21	44.39	8.74	12.01

dw dry weight

Table 4 PCB congener concentrations in sediment, soil (ng/g dw) and surface water (ng/mL) during the winter (a) and spring seasons (b) in the Msunduzi River, South Africa

PCB congeners	Sediment ($n = 9$, ng/g)			Soil ($n = 7$, ng/g)			Water ($n = 9$, ng/mL)		
	Min–max	Mean	SD	Min–max	Mean	SD	Min–max	Mean	SD
(a) Winter season									
PCB 28	21.93–549.19	209.36	208.55	86.33–165.54	140.25	27.44	3.90–12.97	8.24	2.97
PCB 77	130.80–438.18	295.08	108.55	36.78–200.66	132.72	56.90	1.45–5.80	3.40	1.50
PCB 101	8.87–611.92	216.60	252.63	90.88–397.75	209.52	96.24	6.86–21.77	14.55	4.89
PCB 52	38.86–422.55	214.13	146.84	46.82–343.44	275.20	103.37	2.84–22.37	9.19	6.16
PCB 153	15.05–656.86	196.21	207.84	49.18–190.80	157.17	48.48	0.20–19.33	5.22	5.92
PCB 105	11.92–683.77	264.58	256.79	54.67–110.14	88.14	18.31	0.09–5.73	2.21	2.37
PCB 138	127.75–933.34	447.59	266.50	25.64–111.42	62.07	27.08	0.50–9.00	3.04	2.86
PCB 180	6.52–745.88	319.89	280.17	42.73–134.51	101.87	29.52	1.66–5.54	3.85	1.56
∑PCB	361.70–5041.69	2163.43	1727.36	433.03–1654.26	1167.25	407.64	17.56–102.51	49.71	28.24
(b) Spring season									
PCB 28	82.32–444.43	166.68	108.53	108.76–156.73	136.47	17.34	0.53–27.01	4.52	7.95
PCB 77	13.63–101.92	53.27	27.01	10.86–482.45	86.87	161.24	0.11–20.13	3.32	6.17
PCB 101	271.40–519.35	365.84	76.45	161.87–741.73	444.22	217.69	0.34–21.77	9.45	6.52
PCB 52	64.47–418.34	162.84	124.20	15.12–222.36	87.09	71.60	0.99–16.40	4.50	5.30
PCB 153	30.86–314.22	130.47	95.00	26.64–249.61	85.03	72.20	0.14–2.53	0.88	0.68
PCB 1O5	26.93–285.36	119.47	89.14	13.75–443.49	135.04	144.84	0.18–35.67	6.81	12.77
PCB 138	05.72–377.04	144.00	110.71	41.11–107.68	22.06	23.23	3.39–12.67	4.70	2.82
PCB 180	32.41–145.59	59.88	37.30	1.85–38.13	19.93	11.71	0.81–5.50	2.55	1.73
∑PCB	528.24–2606.25	1202.45	668.34	379.96–2442.18	1076.69	719.84	6.49–141.68	36.73	43.93

season. The increase in PCB concentration during the winter period could also possibly be due to low photochemical degradation, because of a decrease in temperature, shorter periods of available sunlight, and lower UV index values, which in turn could lead to high pollutant accumulation on particulate matter in the environmental media (Brunciak et al. 2001; Yeo et al. 2003; Cheng et al. 2007).

Concentrations trends of PCBs along the sampling sites

Table 3 shows the total concentrations and percentage contribution of PCBs in sediment, soil, and water along the course of the river during the sampling seasons. The study area Du Toit (DUT) had the highest total PCB concentration for both sediment and soil during the winter season (3530.62 ng/g and 1216.72 ng/g, respectively) with a total percentage of 15.31% followed by Henley dam outlet (HND) in all the sampling media with a percentage of 12.94%. Du Toit is located in the city center of Pietermaritzburg, and high concentrations of PCBs found at this site are probably because it receives a high pollution load from its surrounding environment, such as open dumping and high vehicular activities (including heavy-duty vehicles, and the site is near an exit onto a national highway) as well as uncontrolled industrial effluents that could possibly seep into the river environment. Previous studies have shown that these activities lead to PCB contamination of the environment (Zhang et al. 2003; Rissato et al. 2006; Nasir et al. 2014). Other sites that were shown to have high levels of the pollutants were the joining point of the Msunduzi tributary (UMJ) with the uMgeni River, Camps drift (CMD), and the wastewater treatment plant inlet (WWT1) with total PCB percentages of 12.20, 12.05, and 11.37%, respectively. The UMJ sampling site is located within a rural area with various agricultural activities. The higher PCB concentrations in this area could be attributed to the unintentional release of agricultural by-products into the water body and

Table 5 Comparison of polychlorinated biphenyl concentrations in sediment (ng/g), soil (ng/g), and water (ng/mL) from different studies around the world

Location	ΣPCBs	Sediment (ng/g)	Soil (ng/g)	Water (ng/mL)	References
Msunduzi River, South Africa	Σ^8PCBs	361.9–5041.7^a	433.0–1654.3^a	17.56–102.5^a	This study
		528.2–2606.3^b	379.9–2442.7^b	6.49–141.7^b	This study
Soil and sediment of central South Africa	Σ^{12}PCBs	0.12–1.80	0.3–4.70		Nieuwoudt et al. (2009)
Alexandria Harbor, Egypt	Σ^{96}PCBs	0.9–1211			Barakat et al. (2002)
Bizerte Lagoon, Tunisia	Σ^{10}PCBs	0.8–14.6			Barhoumi et al. (2013)
Jinzhou Bay, China	Σ^{28}PCBs			0.2–3.2	Yao et al. (2013)
Minjiang River, China	Σ^{21}PCBs	15.1–57.9		0.2–2.5	Zhang et al. (2003)
Northeastern Region, Brazil	Σ^7PCBs	2×10^{-2}–2.5×10^{-1}	2×10^{-5}–5×10^{-4}		Rissato et al. (2006)
Coast of Korea	2xΣ^{18}PCBs	0.2–371			Hong et al. (2006)
Rhone Prodelta, France	Σ^{12}PCBs	38.3–228.5			Tolosa et al. (1995)
Venice Lagoon, Italy	Σ^{18}PCBs	2×10^{-3}–2.1×10^3			Bellucci et al. (2000)
Coast, Spain	Σ^{18}PCBs	2.2×10^{-2}–30.1			Eljarrat et al. (2005)

^{a} winter, ^{b} spring

uncontrolled burning in the area, because the main source of power for cooking is through burning of biomass. Higher levels of burning are also expected to occur in winter as a means of keeping homes warm. In addition, this site might be receiving the accumulated pollutant load from the uMgeni River (upstream of the joining point), Nagle Dam, and the Msunduzi River passing through the Msunduzi town, which is only a few kilometers away. Thus, there is an accumulated effect of PCBs that would contribute to this site's overall high PCB concentration. Camps drift (CMD) site was also determined to be relatively polluted. This area is known for its annual Dusi Canoe Race and is located in the city center where vehicular activity is predominantly high. Since PCBs are trans-boundary, there is a high tendency for them to be transported from the upper course of the river downstream.

The wastewater treatment plant collected its waste from different locations, such as domestic, industrial, and agricultural runoff. The total pollution level was therefore expected to be higher at this site due to the accumulation of various components of the waste from different locations, but it should be noted that soil samples were not available for this site and biosolids were collected as a representation of sediment samples.

Other areas with relatively high total PCB concentrations were the agricultural area (AGR), Nagle dam (NGD), and Msunduzi town (MST) with the total PCB percentages of 10.38, 10.10, and 7.32%, respectively. The AGR sampling site is located in a rural area with relatively low population density that has some small-scale to subsistence farming activity. High PCB levels in the area could be possibly due to open burning, most especially during the winter period, as preparation for the next planting season or to the use of sewage sludge, containing minor quantities of PCBs, applied to agricultural land (Gan and Berthouex 1994). The presence of PCBs at the Nagle dam (NGD) sampling site could be because the dam possibly serves as a "sink" for the PCB pollutants received into the water ecosystem over long periods through water transportation from different locations. The presence of PCB concentrations at the Msunduzi town (MST) sampling site could probably be due to incineration of PCB-containing wastes (burning is a common practice in rural areas), improper dumping or spillage, and deposition from vehicular emissions (MST sampling site was next to a taxi rank). The two sampling sites with the lowest PCB concentrations were the wastewater treatment after chlorination (WWT2) and the point of discharge back into the Msunduzi River (WWT3) with a total percentage of 4.75% and 5.19%, respectively.

This suggests that the wastewater treatment process could possibly be removing substantial quantities of PCB-containing pollutants before discharging the effluent back into the water ecosystem.

Table 4 a, b shows the concentrations of each PCB congeners in the sediment, soil, and surface water of the Msunduzi River during the winter and spring seasons. The ∑PCB (sum of eight congeners) concentrations (ng/

g) in the winter and spring seasons of sediment samples at all the sampling sites were 361.70–5041.69 (mean 2163.43) and 528.24–2606.25 (mean 1202.45), respectively, while the corresponding concentrations (ng/g dw) of ∑PCB (sum of eight congeners) in the soil samples for the two seasons were 433.03–1654.24 (mean 1167.25) and 379.96–2442.18 (mean 1076.69), respectively. However, the ∑PCB (sum of eight congeners) concentrations (ng/mL) in water samples for winter and spring seasons were 17.56–102.51 (mean 49.71) and 6.49–141.68 (mean 36.73), respectively. This study is in agreement with Zhou et al. (2006) and Zhang et al. (2008), who suggested that less desorption of organic carbon from soil and sediment in water occurs in winter which may be attributed to the low temperature and low dilution rate of organic pollutants which largely depends on water flow. As a result, there is a higher rate of sediment deposition in winter which leads to higher concentrations of pollutants. The trend of the PCB concentrations in the environmental media in this study also agreed with previous research carried out by Aydin and Yurdun, which showed that organic pollutants are more lipophilic and hydrophobic in nature and therefore bioaccumulate more in the organic matter than in surface water which is a possible reason for the high concentrations of pollutants observed in the sediment and soil than in the water (Aydin and Yurdun 1999). Among the PCB congeners shown in Table 4a, b, PCB 138 (hexa CB) was the dominant congener in the winter sediment followed by PCB 180 (hepta CB) and PCB 77. The lowest PCB congeners in winter sediment were PCB 153 and PCB 28 (hexa and tri CBs), while the dominant congeners in the winter soil and water were PCB 101 and PCB 52 (penta and tetra CB), respectively. However, in terms of individual PCB congeners across the river (Table 4a, b), the dominant congeners in both winter and spring seasons were PCB 101, PCB 138, PCB 52, PCB 28, and PCB 105. The PCB with the lowest concentration in the two seasons was PCB 180 which accounts for about 16.7% on an average of the total PCBs followed by PCB 77 and PCB 153 about 19.0% and 20.0%, respectively. PCB 105 (penta CB) which is a dioxin-type PCB was detected in the sediment samples having the concentrations (ng/g) of 11.92–683.77 (mean 264.58) and 26.93–285.36 (mean 119.47) in both winter and spring, respectively. The high total concentrations of PCB 28, PCB 52, PCB 101, PCB 105 (dioxin like), and PCB 138 could be attributed to fluids used in transformers, various electrical appliances, and paint industries (Barakat et al. 2002).

Comparison of PCB concentrations

The total PCB concentration obtained in this study was compared with the results reported by various authors from different parts of the world as shown in Table 5. Total PCB concentrations obtained in this work was higher compared to the results obtained in the study on Alexandria Harbor in Egypt, Bizerte Lagoon in Tunisia, and the Coast of Korea in 2002, 2013, and 2006, respectively (Barakat et al. 2002; Hong et al. 2006; Barhoumi et al. 2013). The results obtained in this study for water were also higher than the results obtained by Zhang et al. 2003 and 2013 on the Minjiang River and Jinzhou Bay in China. Overall, Table 5 shows that the results obtained in this study are higher than that obtained in most other similar studies undertaken on river environments around the world except results obtained on soil and sediment samples from central South Africa (Nieuwoudt et al. 2009).

Conclusion

The concentrations of eight PCB congeners were determined during the winter and spring seasons along the Msunduzi River in Pietermaritzburg, South Africa. Pollutant dilution in the environmental matrices was dependent upon temperature and hydrodynamic conditions based on seasonal changes. Surface water contained a lower concentration of PCBs (winter 0.68–22.37 ng/mL and spring 2.53–35.69 ng/mL) compared to sediment (winter 76.53–397.75 ng/g and spring 20.84–443.49 ng/g) and the winter samples showed higher total concentrations of PCBs (214.21–610.45 ng/g) compared to the spring season (30.86–444.43 ng/g). In all the sampling sites selected for this study, Du Toit was found to have the highest PCB concentration levels and the lowest was found to be after chlorination at the Darvill wastewater treatment plant. The results obtained for the total of eight PCB concentrations in this study were compared to that obtained from previous studies on the soil and sediment samples of Gauteng in Central South Africa, as well as to some studies done in other parts of the world. It could be possible that our studied area is more polluted with the selected PCB congeners as compared to other areas studied in previous studies. This finding suggests that the pollution sources needed to be investigated and urgent attention is needed to protect the aquatic life and health of the people consuming this water.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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