Environ Geochem Health (2023) 45:2051–2063
https://doi.org/10.1007/s10653-022-01324-7

ORIGINAL PAPER

Seasonal variations and associated health risks of polychlorinated naphthalenes in Markman Canal, Eastern Cape Province, South Africa

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Received: 23 August 2021 / Accepted: 13 June 2022 / Published online: 1 July 2022

Abstract This study focused on evaluation of the levels, seasonal variations and human health risks associated with polychlorinated naphthalenes (PCNs) in water and sediment samples of Markman Canal using solid phase and soxhlet extraction methods respectively, followed by clean-up and quantification with gas chromatograph coupled with microelectron capture detector. The sum of eight PCNs congener's ($\sum_8$PCNs) in water and sediments varied from 0.035 to 0.699 μg/L and 0.260 to 6744.16 μg/kg dw, respectively. Highest PCNs concentrations were recorded in water during winter, while sediment samples collected during spring contained maximum levels. The estimated toxic equivalency (TEQ) for water and sediments was 1.19×10^{-7}–1.47×10^{-4} μg/L and 4.43×10^{-5}–4.19×10^{-1} μg/kg consecutively. The PCN levels and TEQ values revealed that this waterbody is polluted but constitutes no excess health risk. Efforts should be made to control all the activities contributing to pollution of this canal.

Keywords Persistent organic pollutant · Polychlorinated naphthalene · Markman Canal · Toxic equivalency

Introduction

Persistent organic pollutants (POPs) are group of carbonaceous compounds that exhibit toxic properties, withstand environmental disintegration and bioaccumulate in living things. They all have four key characteristics in common: environmental persistence, toxicity, long-range transportation in the atmosphere, and bioaccumulation in adipose tissues (Ashraf, 2017*)*. These include PCNs; they are a class of organochlorine chemical compounds made up of the naphthalene ring system, in which one to eight hydrogen atoms have been substituted with chlorine atoms, yielding 75 congeners (Agunbiade et al., 2020). They were industrially produced in the early 1900s to be applied in electronics industries as insulators and as

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Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10653-022-01324-7.

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dielectric fluids in transformers and capacitors, considering their good heat resistance, insulating properties, and low chemical reactivity (Park et al., 2010). They also serve as additives in wood preservation, dye, and plastic product manufacturing. The generic molecular formula is $C_{10}H_{8-n}$ Cl_n; where n ranges from 1 to 8.

PCNs were added to the list of banned POPs at the seventh meeting of the Conference of the Parties to the Stockholm Convention in May 2015 (UNEP, 2015). Some harmful health effects such as chloracne (severe skin reactions), liver disease, cirrhosis of the liver, irritation of the eyes, fatigue, headache, anemia, hematuria, and nausea have all been reported in human beings who were occupationally exposed to PCNs, with likelihood of such workers being in danger of different kinds of cancers (CICAD, 2001).

The bioaccumulation and persistence natures of organic pollutants have rendered them slow human killers. They are omnipresent in virtually all environmental media; air, water, humans, lands, flora and fauna, where they result in different unpleasant environmental situations and dangerous diseases. Certain environmental and health challenges such as cancer, diabetes, obesity, disruptions to cardiovascular, endocrine and reproductive systems have been linked to POPs (Alharbi et al., 2018).

The occurrence of PCNs has been widely studied in various matrices around the world (Lei et al., 2022; Li et al., 2020; Hu et al., 2019; Gewurtz et al., 2018; Kim et al., 2018; Fernandez et al., 2017; Mahmood et al., 2014), but studies relating to PCN distribution in Africa is very minimal. Also, studies have indicated Chatty River, Markman, and Motherwell Canal as the pollution sources in Swartkops estuary (SWE) caused by communal and industrial wastes (Adams et al., 2019; Olisah et al., 2019), but there are few published reports on the polluting rivers and canals (Ohoro et al., 2021). Markman Canal (MMC) is one of the major tributaries discharging into SWE; SWE is an important estuary in Port Elizabeth, Eastern Cape Province (ECP) of South Africa (Ohoro et al., 2021; Olisah et al., 2019; Adams et al., 2019; EFA, 2011). MMC infiltrates into the SWE at about 6.1 km from the estuary mouth. MMC originates from an industrial area called Markman, which housed many industries in Port Elizabeth (PE), from where liquid waste empties into the canal. The canal moves through a small community before accessing the SWE around a flyover (Adams et al., 2019) and eventually empties into SWE (EFA, 2011). Ohoro et al. (2021) reported certain polybrominated diphenyl ethers (PBDEs) in water and sediments of this canal.

The aim of this study was to determine the pollution status of the canal by evaluating levels, seasonal variations, and possible health risks associated with eight PCN congeners in its surface water and sediments. The relationship existing between certain water or sediments physicochemical parameters (PPs) and the pollutants are also evaluated. To the best of our knowledge, this is the first study to report PCNs occurrence in South Africa. The findings will provide benchmarks for future work on PCNs distribution and risk assessment in environmental matrices.

Materials and methods

Site description, sample collection, and storage

This study was carried out on MMC along the course of latitudes 33°47′57.7" S—33°50′35.7" S and 25°36′02.5" E—25°38′38.9" E longitudes, in PE, ECP, South Africa. Sampling point coordinates were measured with a global positioning system and selected based on the literature survey, proximity to pollution sources detected on the canal, and ease of sample collection. Five sampling points coded as MMC 1, 2, 3, 4, and 5 were selected. The points are at least 200 m apart from each other. The site map and description are shown in Fig. 1 and Table S1 respectively. Sampling was carried out once in each season from August until December 2020 to cover three seasons; winter (August), spring (October), and summer (December). Twenty-eight (28) surface water and 14 sediment samples were collected across the three seasons with 1000 mL amber glass bottles and stainless-steel grab respectively, enclosed in aluminum foil and properly labeled. The samples were transported inside an ice-parked cooler to the laboratory. The water was filtered and extracted on arrival in the laboratory, while the extracts were stored in the refrigerator until further analysis. Sediments were air-dried for several days in a well-ventilated drying room and sieved with 500-µm mesh.

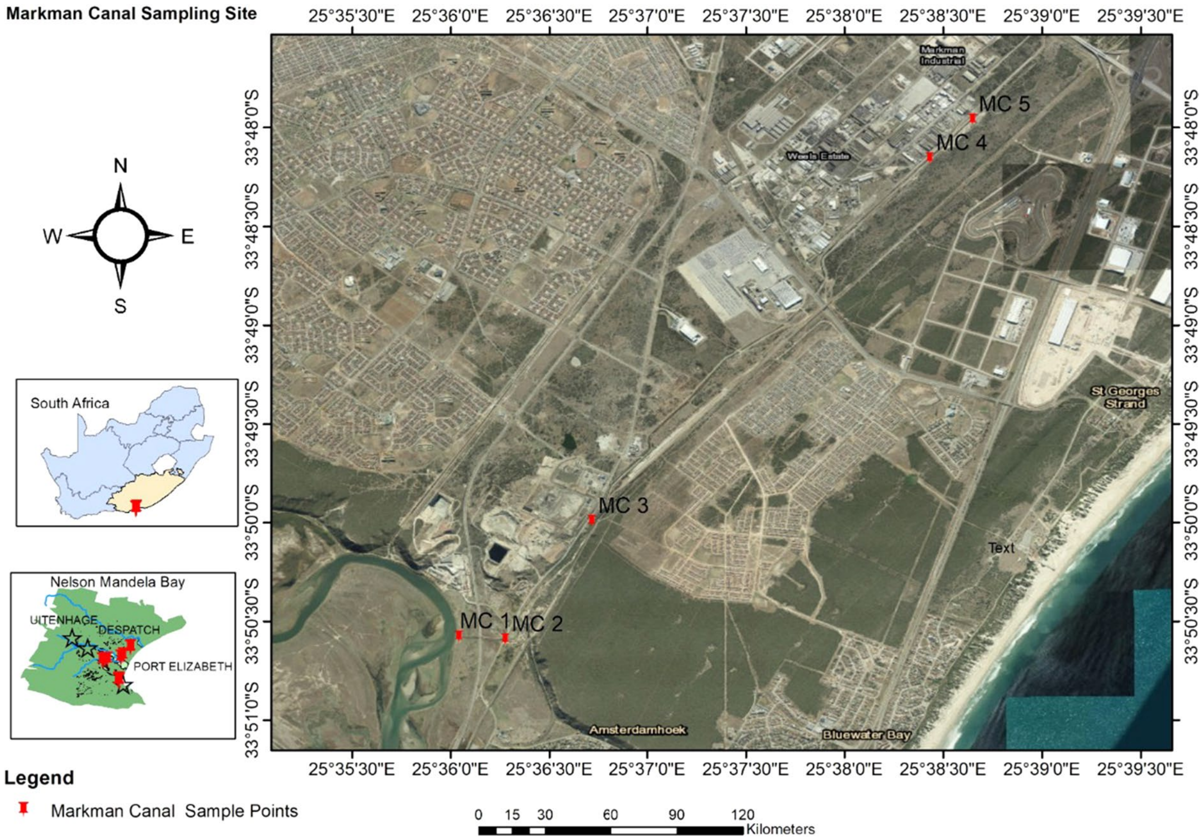


Fig. 1 Map of Markman canal

Solvents and other research consumables

GC grade solvents: acetone, ethyl acetate, dichloromethane (DCM), n-hexane, isooctane, and other materials such as alumina (70–290 mesh), anhydrous sodium sulfate, copper fine powder (> 230 mesh ASTM), silica gel (70–230 mesh), glass wool and pure sand (50–70 mesh) were supplied by Merck Pty Ltd, South Africa. Phenomenex—Strata C_{18} cartridges (Promolab Pty Ltd, South Africa); surrogate standard 2, 4, 5, 6-tetrachloro-m-xylene (TCMX) (Dr. Ehrenstorfer Laboratories, Augsburg, Germany), standard mixture of PCNs (PCN-MXA) (Wellington laboratories, Canada) were also procured. Afrox Pty Ltd, South Africa supplied nitrogen gas (99.9% pure). The standard PCN mixture was sold as 1.2 mL of 5000 µg/L in amber bottles and properly stored in the fridge at 4 °C until needed. PCN standard solutions were prepared by diluting stock in isooctane.

Samples analysis

Some water PP were measured on site using portable Hanna multiparameter instrument (HI 98,195 model). Total suspended solids (TSS) were measured with HACH DR 900 (HACH Company, USA) portable meter. PP of the sediments including moisture, organic carbon (OC), and organic matter (OM) contents were determined gravimetrically (Heiri et al., 2001).

PCNs were extracted from water using the method of Marti and Ventura (1997). Solid phase extraction (SPE) of samples was carried out using C_{18} (55 µm, 70A; 500 mg/6 mL) cartridges. SPE cartridges (C_{18}) were preconditioned with 10 mL of each methanol and deionized water. Five hundred milliliters (500 mL) of the filtered water were separately passed through the cartridges under vacuum at a flow speed of 10 mL/min. Two hundred microliter (200 µL) of 5000 µg/L 2, 4, 5, 6-tetrachloro-m-xylene (TCmX) was added as surrogate standard to a sample in every batch of 10 samples (Liu et al., 2018). Cartridges were dried with nitrogen gas (99.9% purity) to remove any drop of water. Extract was eluted with 20 mL of ethyl acetate, evaporated, and reconstituted with 1.5 mL of isooctane before instrumental analysis.

PCN congeners in sediments were extracted using the method of Mahmood et al. (2014). Ten grams (10 g) of the specimen and procedural blank were soxhlet-extracted in duplicate with 200 mL DCM for 24 h after adding fine copper powder to prevent interference from elemental Sulphur (Zhang et al., 2015) and 200 µL of 5000 µg/L TCmX to a sample in every batch of 10 samples. The sediment extract was passed through a glass chromatographic column (30 cm long × 10 mm I.D.) packed with glass wool, activated silica gel, sodium sulfate, and alumina. These chemical salts (silica gel, sodium sulfte, and alumina) were previously extracted with DCM, dried at 450 °C, and cooled before used for packing the glass column. The extracts were eluted with n-hexane, evaporated to dryness, dissolved in isooctane before instrumental analysis.

Instrumental analysis

Quantification of PCN congeners contained in the purified extracts was achieved with an Agilent 7820A gas chromatograph GC coupled with microelectron capture detector (µ-ECD) (model—G2397AE). This is fitted with an Agilent HP-5 column (30 m long × 0.32 mm ID × 0.25 µm film thickness), compounds were identified by comparing retention times of the individual congeners in the standards with those in the samples. Samples (1µL) were injected in splitless mode at inlet temperature of 300 °C. The carrier gas was helium at flow rate of 2 mL/min and the detector temperature was 325 °C. Initial oven temperature was fixed at 80 °C for 0.5 min, increased to 160 °C at a rate of 15 °C/min, then raised to 240 °C at a rate of 3 °C/min, and finally increased to 270 °C at a rate of 6 °C/min for 10 min, the total runtime was 47.5 min (Mahmood et al., 2014). PCNs were quantified using Agilent Chemstation software incorporated into the instrument.

Quality control and statistical analysis

Calibration standard solutions were prepared by diluting stock solution (5000 µg/L) in isooctane at concentrations between 5–120 µg/L (Castells et al., 2008) to obtain eight external calibration points. Linear calibration curves were obtained with correlation coefficients varying from 0.9984–0.9993 (Table S2). Recalibration of the instrument was performed at interval. The sensitivity of the instrument was estimated in terms of limit of detection (LOD) and limit of quantification (LOQ). LOD and LOQ were determined by running a known concentration (40 µg/L) of calibration solution on the instrument eight times. The LOD and LOQ were estimated using 3.3*(SD/S) and 10*(SD/S), where SD is the standard deviation of the instrument responses, S is the slope of the calibration curve for each congener and surrogate. RSD was calculated using this relation: RSD = 100*(SD/M); where M is the mean of the instrument responses (Babalola & Adeyi, 2018; Swartz & Krull, 2012). LOD, LOQ, and RSD values ranged from 0.007 to 0.214 µg/L, 0.020–0.647 µg/L, and 2.91–4.57% respectively for each congener (Table S2). The efficiency of the analytical method was appraised by analyzing surrogate standard (200 µL of 5000 µg/L TCmX) spiked samples alongside every batch of 10 samples and by performing recovery studies on procedural blanks (deionized water and pure sand). Recovery of the eight congeners in deionized water and pure sand ranged from 66.7–95.4% and 70.2–88.8% respectively, while surrogate standard recovery followed the same trend as 84.4% ± 0.25 (mean ± SD) and 77.7% ± 0.02 (Table S3). The reported pollutants levels in samples were not amended with blank nor surrogate recovery values, while those below LOD were assigned zero during data computation. Mean, minimum, maximum, and standard deviation of the parameters were calculated for their descriptive statistics using Microsoft Excel 2016. Pearson correlation of the parameters was deduced in SPSS 21 and the significance was defined at $p < 0.01–0.05$ (Liu et al., 2017).

Human health risk due to PCNs estimation

PCN congeners showed comparable toxicities with dioxins; hence, possible health risk due to these congeners are calculated by converting their concentrations to toxic equivalent factor corresponding to 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) using Eq. (1) below (Li et al., 2020). TCDD has a reference value of one (van den Berg et al., 2013).

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

where *TEQ* Toxic equivalency, *C* Concentration of congeners (μg/L or μg/kg), *REPs* Relative potencies for each congener.

REPs for the studied congeners in water and sediments are listed in Table S4.

Results and discussion

Physicochemical parameters of water samples

The average water PP is displayed in Fig. 2, while the details are provided in the supplementary (Table S5).

The temperature ranged from 15.6–16.4 °C during winter, 22.8–24.5 °C (spring), and 20.4–22.5 °C (summer). The temperature was least in winter; this is expected as the coldest season of the year (Awe et al., 2020), while temperature in spring was comparable to that of summer. The values are all within South African guideline range of 15–35 °C for potable waters (DEA, 2012). The mean temperature from this study compares well with 14.0–24.2 °C recorded from Diep River water by Awe et al. (2020). Changes in water temperature are influenced by seasons of the year, time of the day, latitude, air movement, water flow direction, and depth (Chapman & Kimstach, 1996).

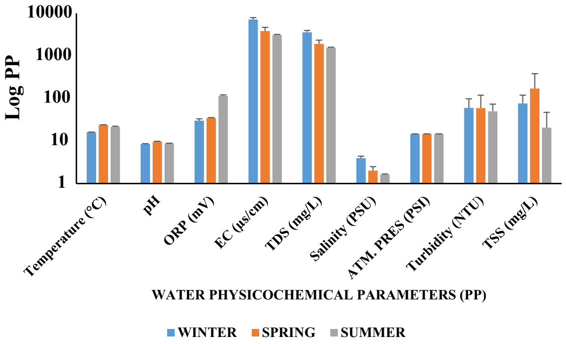


Fig. 2 Seasonal variations in MMC water physicochemical parameters

The pH varied from 8.4–8.8 in winter, 9.0–10.2 (spring), and 8.6–9.1 (summer). The values exceeded "6–9" set limits of the Department of Water Affairs and Forestry, South Africa (DWAF, 1996) at few points during spring. All these values exceeded 7.16–7.98 reported from Diep River in South Africa (Awe et al., 2020). pH measurement is important in any water analysis as it influences both biological and chemical reaction occurring in the water and provides substantial information on the extent of environmental pollution (Carr & Neary, 2008).

Oxidation–reduction potential (ORP) varied as 7.8–49.2 mV in winter, 9.0–50.7 mV (spring) and 103.1–130 mV (summer), the ORP was highest in summer at all sampling points. ORP measurements are equally important as pH in evaluating water quality and extent of water pollution (Copeland & Lytle, 2014). Electrical conductivity (EC) across the three seasons ranged from 6755 to 8004 μS/cm in winter, 3043–4815 μS/cm (spring), and 1885–4025 μS/cm (summer). The reported values for the three seasons were greater than 1700 μS/cm permissible limit for potable water by the South African National Standards (SANS 241:2015). The high EC values could be attributed to the dissolved ions emanating from the industrial wastes into the water (Edokpayi et al., 2015). EC was reported to have a direct relationship with salinity, considering its capacity to allow electrical current to flow through at 25 °C (Al Dahaan et al., 2016). All the EC results in this study are below 2200–51,300 μS/cm obtained by Olisah et al. (2019) in their study on Sundays and Swartkops Estuaries, ECP, South Africa.

Total dissolved solids (TDS) ranged from 3378–4002 mg/L in winter, 1522–2407 mg/L (spring), and 943–2012 mg/L (summer). The minimum and maximum values were measured at the same point (MMC 5) but at different seasons; MMC 5 had the least value during summer but TDS was maximum at this same point in winter. All the points except MMC 5 during summer exceeded 1200 mg/L set standard specified for clean water by the South African National Standards (SANS 241:2015). Elevated TDS values were linked with stunted growth in animals, bad odor, and color in water (Sharma et al., 2017).

Turbidity value was 2.9–142 NTU for winter, 15–154.2 NTU (spring), and 12.2–118.1 NTU (summer). Turbidity was higher at all points during spring than in the other two seasons. TSS varied from 7–168 mg/L (winter), 26–491 mg/L (spring), and 4–54 mg/L (summer). The TSS values were highest in spring. The runoff from heavy rainfall during wet season convey more wastes from various sources into the canal, thereby resulting in elevated turbidity and TSS levels. There is a strong relationship between TSS and turbidity; suspended solids can inhibit light conduction in water samples (Daphne et al., 2011). Water with a turbidity of below 5 NTU is considered satisfactory for consumption (WHO, 2008), while high turbidity is associated with microbial poisoning (Fatoki et al., 2003). MMC has salinity in the range of 3.73–4.47 PSU (winter), 1.58–2.58 PSU (spring), 0.96–2.14 PSU (summer). Most of the reported salinity values exceeded 1 PSU, which is the permissible value for aquatic life protection (Kaushal et al., 2005). Salinity is the measurement of total soluble salts (NaCl, KCl, MgCl$_2$) in water (Hussain et al., 2017). Salinity level beyond the standard range may alter dissolved oxygen levels and osmosis control (Abou Anni et al., 2016), which can lead to death of living organisms (Hussain et al., 2017).

Seasonal variations and spatial distribution of PCNs in MMC water samples

POPs such as PBDEs, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), among others have been widely reported (Cappelletti et al., 2019; Ohoro et al., 2021; Olisah et al., 2019; Selvaraj et al., 2021), but studies on PCNs are still insufficient. One of the limitations of PCN evaluation is lack of quantification standards for the available 75 congeners (Kucklick & Helm, 2006); hence, only eight CNs (CN-2, 6, 13, 28, 52, 66, 73, 75) were analyzed in this study. The total PCNs concentrations ($\sum_8$PCNs) for winter, spring, and summer were 0.192–0.699 μg/L, 0.035–0.553 μg/L, and 0.076–0.368 μg/L respectively (Table S5). The levels decreased across the three seasons as; winter > spring > summer. The concentrations were highest during dry (winter) season when compared with the two other wet seasons. This is in disparity with the usual occurrence of more PCNs during wet season than dry period due to surplus surface flow caused by rainwater (Li et al., 2017). During winter, there is usually no rainfall; the pollutants are accumulated more on soil surface (Li et al., 2012). Point source pollution, suspended particulate matters, flow rate, or distance traveled, among other factors could be responsible for the high PCNs levels during winter (Li et al., 2017).

The sum of individual CNs and the spatial distributions of the $\sum_8$PCNs across the three seasons are shown in Figs. 3a and b respectively.

According to Fig. 3a, CN 2 had the highest concentrations during winter. CN 52 was below LOD during spring and summer, while CN 66 was below LOD only in spring. CN 73 had the least concentrations across the three seasons. Percentage distribution follows: CN 2 (64.9%) > CN 6 (20.5%) > CN 13 (10.1%) > CN 28 (2.9%) > CN 66 (0.7%) > CN 52 (0.4%) > CN 75 (0.3%) > CN 73 (0.2%). CN 2, the least chlorinated congener in this study was the prevalent congener in the water samples across the three seasons. Our results were comparable with those of Lei et al. (2022) in which low-chlorinated congeners (mono- and di-CNs) were more abundant in water samples than high-chlorinated congeners due to the former high water solubilities and volatilities.

For the spatial distributions (Fig. 3b), the $\sum_8$PCNs were appreciable at all points on the canal but elevated levels were recorded at MMC 1. MMC 1 is

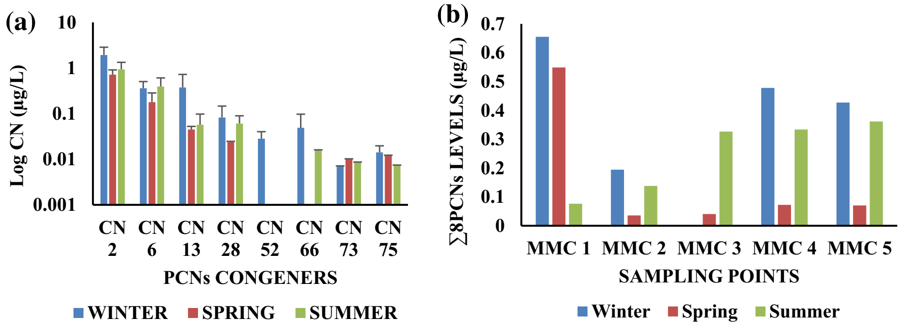


Fig. 3 Seasonal variations and spatial distributions of PCNs in MMC water samples

the entry point where Markman canal empties into Swartkops estuary; thus, confirming pollution of the estuary by influx from this canal. MMC 4 and 5 are two other notable points with higher $\sum_8$PCNs; they are both located within a manufacturing zone from where raw industrial effluents are discharged into the canal (Adams et al., 2019).

Despite variations in number of analyzed congeners and sampling period, results obtained in this study (0.035– 0.699 µg/L) were above the findings of Lei et al. (2022) from Yangtze River Delta, China, Ishaq et al. (2009) in Norway, Mahmood et al. (2014) in Pakistan, but below the highest PCN concentration recorded until date by Marti and Ventura (1997) from Llobregat groundwater in Spain (Table 1).

Seasonal levels of sediment physicochemical parameters

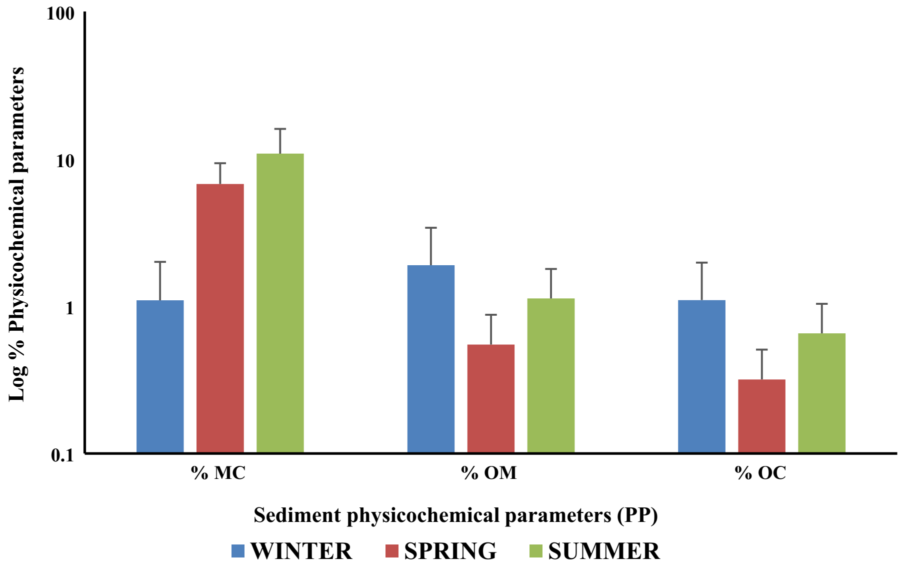
The average moisture content (MC), OM, and OC contents of MMC sediments are shown in Fig. 4.

The MC during winter, spring and summer are 0.4–2.6%, 3.2–9.5% and 4.3–18.9% sequentially, while the OM and OC contents followed the same trend as 0.4–4.5%, 0.2–1.1%, 0.4–2.0% and 0.2–2.6%, 0.1–0.6%, 0.2–1.2% in winter, spring and summer respectively (Table S6). It was observed that the MC was highest in summer but least in winter. This can be explained by the drought peculiar to dry (winter) period (Archer et al., 2019). OC composition is an important feature that regulates POPs partitioning in sediment (Wang et al., 2016). The highest average OC from this study was 1.1 ± 0.8%, this value was lower than those recorded from Lake Shihwa, Korea (4.5 ± 5.1%, Moon et al., 2012), seven major river basins in China (2.03 ± 1.00%, Wang et al., 2016)

Table 1 Comparison of MMC PCN water concentrations with other studies around the world

Country	Sampling year	Concentration (µg/L)	Prevalent homologue (s)	References
South Africa	2020	0.035–0.699	Mono- and Di-CNs	This study
China	2019	0.000022–0.00031	Di-CNs	Lei et al. (2022)
Pakistan	2013	0.178–0.489	Octa-CN	Mahmood et al. (2014)
Spain	1995–1996	0.0005–79.1	Tetra-CNs	Marti and Ventura (1997)
Norway	1999–2000	1.4×10^{-5}–4.1×10^{-4}	Penta-CNs	Ishaq et al. (2009)

Fig. 4 Seasonal variations in MMC sediments physicochemical parameters



and Beijiang River, China (1.29 ± 0.82%, Chen et al., 2009).

Seasonal and spatial variations in sediment PCNs levels

According to Table S6, the $\sum_8$PCNs in sediments varied from 9.54–1054.67 µg/kg, 11.09–6744.16 µg/kg, and 0.26–34.30 µg/kg. It follows the order: spring > winter > summer. The changes in PCNs concentrations across the three seasons are depicted in Fig. 5a and b.

According to Fig. 5a, the concentrations of individual PCN congeners during spring were above other two seasons: while Fig. 5b revealed that more $\sum_8$PCNs were measured at MMC 4 and 5 sediments when compared with other points during the three seasons. Both points are situated within the manufacturing area of the Markman community from where untreated industrial effluents are discharged into the canal (Adams et al., 2019). Liu et al. (2018) linked PCN levels in aqueous environment to industrial and municipal wastes. CN 2 (63.7%) was the prevalent congener across the three seasons, followed by CN 52 (14.6%), CN 13 (10.5%), CN 6 (4.7%), CN 66 (3.4%), CN 28 (2.8%), CN 73 and 75 (0.1% each). It can be inferred that environmental degradation of higher-chlorinated congeners was responsible for the prevalence of lower congeners in this study (Mahmood et al., 2014).

When compared PCNs levels in this study with other sediment reports from around the world (Table 2), the values measured here were below those recorded in Detroit River, USA (Marvin et al., 2002) and near chlor-alkali plant, Georgia, USA (Kannan et al., 1998). However, the findings here were far above the published reports from Laojie River, Northern Taiwan (Dat et al., 2019), Yellow River, China (Li et al., 2017), Liaohe River Basin, China (Li et al., 2016), and Lake Ontario, Canada (Helm et al., 2008).

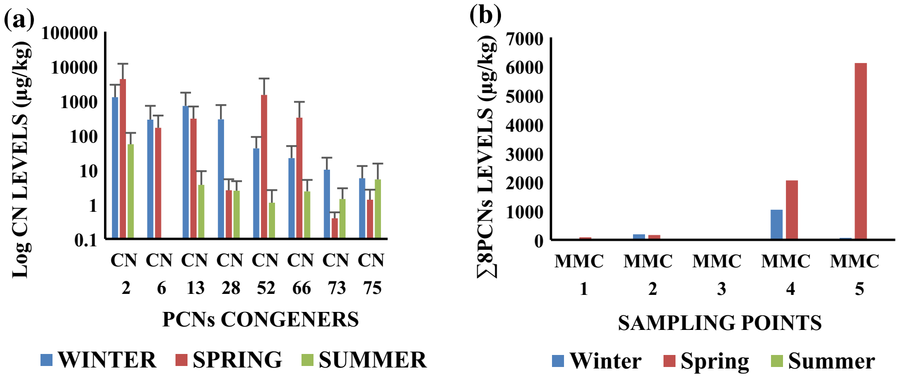


Fig. 5 Seasonal and spatial variations of MMC sediment samples PCNs levels

Table 2 Comparison of MMC PCN sediment concentrations with other studies around the world

Location/country	Sampling year	Concentration (µg/kg)	Prevalent homologue (s)	References
Markman canal, South Africa	2020	0.26–6744.16	Mono-CN	This study
Yangtze River Delta, China	2019	0.01–1.59	Di-CNs	Lei et al. (2022)
River Chenab, Pakistan	2013	8.94–414	Tetra-CNs	Mahmood et al. (2014)
Taiwan	2017	0.408–1.47	Tetra- and Penta-CNs	Dat et al. (2019)
Liaohe River Basin, China	2010	0.33–12.49	Tri- and Tetra-CNs	Li et al. (2016)
Yellow River, North China	2014	0.618–130	Tri-CNs	Li et al. (2017)
Yangtze River, East China	2009	0.60–4600	Hexa- to Octa-CNs	Zhang, Zhang, et al. (2015)
Michigan, USA	1998	0.08–187	Penta- and Hexa-CNs	Kannan et al. (2001)
Georgia, USA	1996	23,000	Hepta- and Octa-CNs	Kannan et al. (1998)
Lake Ontario	1998	21–38	Hexa- to Octa-CNs	Helm et al. (2008)
Detroit River, USA	1999–2000	1.23–8200	Hexa- and Hepta-CNs	Marvin et al. (2002)

In contrast to related studies from around the world, we reported mono-CN as the dominant homolog. Lower-chlorinated congeners (mono- to tetra-CNs) were mostly produced from waste combustion (Hu et al., 2013), while higher homologs were linked with industrial manufacturing of chloralkali (Brack et al., 2003; Kannan et al., 1998) and chlorinated methane (Zhang, Yang, et al., 2015). The predominance of lower CNs at this site could result from waste incineration; suggesting that human socio-economical activities around this catchment influence PCN concentrations (Lei et al., 2022).

Correlation of PCNs with water and sediment PPs

The relationship of PCNs with water PPs was examined using Pearson correlation matrix analysis in SPSS 21 as shown in Table S7. The Table summarizes the correlation coefficients of PCNs with water PPs while the p-values are in italics. PCN (average of the CNs) and CN 13 were selected to represent PCNs homolog. The analysis shows that CN 13 had a positive correlation with water salinity, TDS, turbidity, and EC; the implication is that the relationship of these variables is directly proportional with the pollutant and it is a function of molecular mass. CN 13 was negatively correlated with temperature ($p\text{-value} < 0.05$). ORP, TSS, pH, and atmospheric pressure showed no significant relationship with the PCNs ($p\text{-value} > 0.05$).

A regression analysis was employed to determine the association between PCN congeners and sediments PPs as illustrated in Tables S8. The result showed that PCNs have no correlation with any of the parameters.

Estimation of risks due to PCNs

With the application of relative potencies of each PCNs, the estimated TEQs for MMC water and sediments are presented in Table S9. Water TEQ results varied from 1.19×10^{-7}-1.47×10^{-4} μg TEQ/L; the values were above 4.43×10^{-10}–8.45×10^{-9} μg TEQ/L obtained from Yangtze River Delta, China (Lei et al., 2022), but below 0.0001–0.211 μg TEQ/L recorded from River Chenab, Pakistan (Mahmood et al., 2014). The highest TEQ was due to CN 66, the results obtained were all less than one and this implies that the selected water constitute low risk to human. However, their usage would only be possible after strict compliance with other microbiological, physical, and chemical water qualities.

The TEQ values for sediments varied as 4.43×10^{-5}—4.19×10^{-1} μg TEQ/kg (Table 3), the maximum value is attributed to CN 66. TEQ recorded in MMC exceeded those from Daliao River Estuary, China (Zhao et al., 2011), East China Sea, China (Liu et al., 2018), Upper Danube catchment, Czech Republic (Kukucka et al., 2015), Canada (Helm et al., 2008), Feitsui Reservoir and Laojie river, northern Taiwan (Dat et al., 2019). Nevertheless, the results here are below that obtained from Yangtze River, China (Zhang, Zhang, et al., 2015). Liu et al. (2018) attributed the high TEQ recorded in the East China Sea to influents from industrial and municipal wastes being discharged into the sea. In the same vein, one can conclude that the elevated TEQ reported in this study originates from surrounding companies' effluents.

In order to ascertain the probable toxic effects these polluted sediments may have on aquatic creatures, TEQ value was compared with interim

Table 3 Comparison of TEQ levels of PCNs in MMC sediments with worldwide reports

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

sediment quality guidelines (ISQGs) and probable effect levels (PELs) from Canada for dioxins and furans (Dat et al., 2019). The ISQGs and PELs set standards are 0.00085 and 0.0215 μg TEQ/kg respectively (CCME, 1999). Although, it should be pointed out that 0.00085 μg TEQ/kg dw TEQ represents the summation of TEQ concentrations of all dioxins and dioxin-like compounds (PCDDs/Fs, PCBs, and PCNs) in environmental samples including sediment (Zhao et al., 2011). The maximum TEQ recorded in this study is 0.419 μg TEQ/kg TEQ, it exceeded 0.00085 μg TEQ/kg dw TEQ (ISQGs) and 0.0215 μg TEQ/kg dw TEQ (PELs) approved by Canada. This result revealed that the waterbody is not safe for aquatic creatures (Zhao et al., 2011).

Conclusions

Pollution reports due to PCNs in Africa and mostly in aqueous matrices are still scarce in the literature. To this end, this study evaluated for the first time PCNs concentrations in water and sediments collected from Markman canal, located in PE, ECP, South Africa. Published reports have indicated this canal as one of the tributaries discharging into Swarkops estuary; this study has substantiated this assertion. Pearson correlation analysis showed that the interrelationship between PCNs and certain water physicochemical parameters is dependent on their molecular mass. PCNs concentrations in both surface water and sediments were above some related global studies, with CN 2 as the predominating congener. Seasonal evaluations showed that water PCN concentrations were higher in winter than in the remaining two seasons, while sediments samples composed of elevated PCNs during wet seasons. Even though PCNs were never produced in South Africa, the results from this study have established the ubiquitous nature of these pollutants and pollution state of this waterbody in relation to PCN levels and TEQ values. Studies have indicated waste as major route through which these pollutants get into our environment; hence, the Management of surrounding companies should be compelled to properly treat and discard their effluents rather than discharging them into the canal.

Acknowledgements The authors show a special appreciation to the South African Medical Research Council (SAMRC) for their financial support.

Authors Contributions IVA: Conceptualization, methodology, validation, investigation, literature reviewing, writing, and editing of the manuscript. AOA, AIO, and OOO: Conceptualization, visualization, editing, and revision of the final manuscript. AIO and OOO: Research supervision and funding acquisition.

Funding This research was funded by South African Medical Research Council (Grant No. UFH/SAMRC/P790).

Declarations

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

Human and animal rights statement The present study does not involve animal.

Consent to participate Permission was obtained from all individuals involved in this study.

Consent to publish All the authors gave their consent for the submission of this article to Environmental Geochemistry and Health Journal.

Data availability Available data from this study are supplied in the supplementary materials; others can be obtained on request from the corresponding author.

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