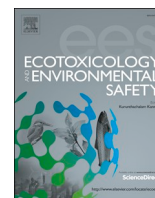


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Item Type	article
Authors	Yahaya, A;Okoh, O.O;Agunbiade, F.O;Okoh, A.I
Citation	Yahaya A, Okoh OO, Agunbiade FO, Okoh AI. Occurrence of phenolic derivatives in Buffalo River of Eastern Cape South Africa: Exposure risk evaluation. Ecotoxicology and Environmental Safety. 2019;171:887-93. DOI: https://doi.org/10.1016/j.ecoenv.2019.01.037 .
DOI	10.1016/j.ecoenv.2019.01.037
Publisher	Elsevier
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Download date	2026-05-15 14:32:10
Item License	https://www.elsevier.com/tdm/userlicense/1.0/
Link to Item	https://doi.org/10.1016/j.ecoenv.2019.01.037



Occurrence of phenolic derivatives in Buffalo River of Eastern Cape South Africa: Exposure risk evaluation

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ARTICLE INFO

Keywords:

Organic chemicals
Phenolic derivatives
Pollutants
Water
Half-lives

ABSTRACT

Phenolic derivatives are compounds used in the production of pesticides, pharmaceutical products and several other industrial applications. These compounds are discharged into freshwater from industrial effluents, domestic sewage, urban and agricultural run-offs which leads to pollution. Water at six sampling locations along the course of Buffalo River; namely Buffalo river estuary (BRE), Mdantsane (MSN), Zwelitsha (ZW), King William's Town (KWT), Izele Town (IZ) and Maden dam (MD) in the Eastern Cape Province, South Africa, were evaluated for phenolic contamination using eleven phenolic derivatives of United State Environmental Protection Agency (USEPA) priority pollutants. Samples were extracted using liquid-liquid extraction technique, derivatized with acetic anhydride and analyzed with gas chromatography mass spectrometry (GC-MS). The levels of the individual pollutants in the river water were higher in summer ($< \text{LOD}$ to 12246 ng/L) than in autumn ($< \text{LOD}$ to 713 ng/L). Their concentrations were found higher than the USEPA recommended limit (500 ng/L) in most of the sampling sites. The most prominent pollutant was 2-NP. However, the cancer risk assessment values and hazard quotient were below USEPA maximum limits of 10^{-6} and 1, respectively. Conclusively, the concentrations of these organic pollutants could be a threat to public health and should be managed to be below the recommended limit though the present levels are unlikely to cause cancer to both human and wildlife.

1. Introduction

Phenolic derivatives are chemical compounds used in textiles, pesticides, paper, dye, polymer and pharmaceuticals industries. Other phenols like Chlorophenols, are used as wood preservatives and disinfectants (Faludi and Záray, 2015). Phenolic derivatives are soluble in water. However, the less chlorinated phenols penetrate the aquatic environment easily while more chlorinated ones (e.g. pentachlorophenol), persist in sediments and soils in the environment for a longer period of time. Pentachlorophenol is less soluble in water but accumulates in the lipid stores of humans and animals (Ronald, 1988; Santana et al., 2009; Igbinsosa et al., 2013). These compounds penetrate the ecosystem through municipal and industrial wastes discharged into surface water (Debadatta and Rajdeep, 2012; Ruiz-Fernández et al., 2014). Other anthropogenic sources include wastes from agricultural farm land, pulp mills and wood treatment facilities, accidental spillage during loading and transportation, leachates from waste site and

landfills or even as a metabolite of benzene from publicly owned treatment works and sewerage (Vrsaljko and Haramija, 2012; Krastanov et al., 2013; Maral et al., 2017). Consumption of phenolic derivatives produces toxic effects in bone marrow (El-Shahawi et al., 2010; Nawawi et al., 2014), and induces cardiac depression, blood changes, as well as kidney and liver damage (Soliman and Koriem, 2014). Phenols have been reported to cause necrosis, defects in eyes and muscle and, irritation of the skin (Ronald, 1988; Michałowicz and Duda, 2007; Soliman and Koriem, 2014). Other toxicity issues associated with phenolic derivatives include malfunctioning of the biochemical system and reproductive impairment in domestic animals (Hammam et al., 2015). Chlorophenols for instance, have been identified as carcinogenic and capable of suppressing the immune system (Michałowicz and Duda, 2007; Soliman and Koriem, 2014). Several studies have established the occurrence of phenolic derivatives in South African freshwater resources. Studies conducted on seasonal variation and distribution of phenolic derivatives in surface water in South Africa

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<https://doi.org/10.1016/j.ecoenv.2019.01.037>

Received 8 August 2018; Received in revised form 20 November 2018; Accepted 9 January 2019

Available online 25 January 2019

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and reported by Olujimi et al. (2012a) analyzed 11 priority phenols in five selected rivers in South Africa. Occurrence of endocrine disruptor chemicals such as phthalate esters, nonylphenols and bisphenol in the locations used for study have been documented in literature (Olujimi et al., 2012b; Salaudeen et al., 2018). High level of pollutants such as bacteria, heavy metals and other wastes which overflow due to anthropogenic activities like accidental spillage and clogging of ship, was reported at harbor side. The industries and waste treatment plants in the neighbourhood discharge final effluents containing many harmful chemicals into the water body (RHP, 2004; Dallas, 2008; Olujimi et al., 2012b; Yahaya et al., 2017). Previous studies have revealed the level of persistence organic pollutant (POPs) and physico-chemical indices in the river (Zamxaka et al., 2004; Dallas, 2008; Chigor et al., 2013). In recent time, Adeniji et al. (2017) and Yahaya et al. (2017, 2018) reported the levels of organochlorine pesticides, polychlorinated biphenyl (PCBs) and the total petroleum hydrocarbon in this water body. There is however, paucity of information on the occurrence and concentration of phenolic derivatives in this area.

The presence of phenolic derivatives in the river water is undesirable because of their adverse effects on the aquatic biota and humans. Previous studies revealed that industrial effluents discharged from textile industry in King William's Town into Buffalo River containing pollutants such as heavy metals and organic pollutants, can cause the death of aquatic biota like fishes, crustacean and could bioaccumulate in aquatic animals and pass to human being through food chain (RHP, 2004). Phenols cause unpleasant odours and taste of surface water and this leads to the reduction in the quality and quantity of water available for human consumption.

Buffalo River is important because it is considered a major water resource in the Eastern Cape Province. It discharges its content into the ocean and incidentally, available data on the levels of organic pollutants in the River appear limited aforementioned studies. Therefore, information regarding the exposure risk of human and aquatic life to the pollutants is insufficient. The Buffalo River passes through several regions and finally empties into Indian Ocean. Therefore, this regional investigation has a significant effect on the global scale because, the organic contaminant that affects people in the Eastern Cape Province could possibly have negative consequences on the other countries through which the water flows. For instance, in Southern Spain, the Coto de donana nature reserve was contaminated due to a burst dam owned by a mining company. This led to the pollution of Europe's biggest bird national Park, fisheries and agriculture (Hassaan et al., 2016). The release of Cadmium into Jinzu River basin, led to Itai-itai disease in Japan (Hassaan et al., 2016; Almeida and Stearns, 1998). It is evident from above instances, that the presence of organic contaminants in the Buffalo River could have significant global impact. The aim of this study was therefore to fill the gap of inadequate information about phenolic derivatives by determining the distribution of these phenolic derivatives along the course of Buffalo River and, to provide information on the possible health risk from exposure.

2. Materials and methods

2.1. Description of study sites

Buffalo River is of high economic value to the Eastern Cape Province. It feeds dams such as Maden (MD), Rooikrantz, Laing and Bridle Drift, c mainly to The dams were built as impoundments along the course of the river to provide water to communities within the

river's catchment Izele Town (IZ), King William's Town (KWT), Zwelitsha (ZW), Mdantsane (MSN), Berlin, Bhisho and East London (Yahaya et al., 2017). Buffalo River flows through these urban and suburban areas and the anthropogenic activities in these locations are predisposing factors to the discharge of agricultural, domestic and industrial wastes into the river. The river receives hazardous wastes from an old tannery textile mill and leached toxic wastes from the dump site close to Zwelitsha. The harbor located at the Buffalo River Estuary (BRE) receives the last freshwater before being discharged into the ocean. The river flows from Amathole Mountain and ends in Indian Ocean via the East London Creek. The sampling points in the locations were reported by Yahaya et al. (2017).

2.2. Sample preparation

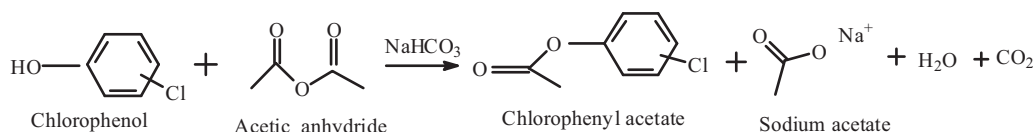
One litre amber glass bottles and vials were washed with soap, rinsed with distilled water, dried in oven at 105 °C for 24 h, cooled, and rinsed again with acetone, then drained in the oven at 105 °C for another one hour. The water samples were collected in triplicates into one litre amber glass bottle, followed by addition of 5 mL of hydrochloric acid (1:1), preserved in an ice-chest at 4 °C and transported to the laboratory for analysis. All samples were collected before 12 noon both in autumn and summer. Sampling could not be carried out in winter because of drought that resulted in the river water drying up at IZ and some parts of KWT and ZW.

2.3. Reagents

Phenolic derivatives (US EPA 11-priority pollutants): Phenol (P); 2-nitrophenol (2-NP); 2-chlorophenol (2-CP); 4-nitrophenol (4-NP); 2-methyl-4,6-dinitrophenol (2-M-4,6-DNP); 2,4-dimethylphenol (2,4-DMP); 4-chloro-3-methylphenol (4-C-3-MP); 2,4-dichlorophenol (2,4-DCP); 2,4,6-trichlorophenol (2,4,6-TCP); 2,4-dinitrophenol (2,4-DNP); Pentachlorophenol (PCP) and 2-fluorophenol (2-FP), were purchased from Ultra-Scientific Analytical Solution, USA, while the HPLC grade solvents (n-hexane, dichloromethane and methanol), were obtained from Sigma Aldrich (Czech Republic) and sulphuric acids (99% purity) from Merck (Germany). Ultra-pure nitrogen (99.99%) and helium gases were supplied by Afrox Limited, South Africa and were used as make-up and carrier gases respectively for the gas chromatography (GC) analysis.

2.4. Extraction of phenolic derivatives

The water samples (500 mL each) were spiked with 1 mL of 10 µg/mL surrogate standard (2-fluorophenol), extracted three times with 30 mL portions of dichloromethane in 1 L separating funnel. All samples extracts were concentrated to 4 mL with rotary evaporator at 37 °C, solvent exchanged with 40 mL methyl alcohol, and re-concentrated at 40 °C into 3–4 mL before derivatization (Kawaguchi et al., 2012; Al-Janabi et al., 2012). About 3 mL of the sample extract was transferred into a 4 mL vial, and 0.2 g of sodium hydrogen bicarbonate (NaHCO₃) and 0.2 mL of acetic anhydride were added for derivatization (Scheme 1). The mixture was shaken vigorously for about two minutes, left for another two minutes to settle before an aliquot of 1 mL was taken with a syringe into a 2 mL vial for GC-MS analysis (Kawaguchi et al., 2012; Al-Janabi et al., 2012).



Scheme 1. Equation of derivatization reaction.

2.5. Instrumental analysis for phenolic derivatives

Agilent gas chromatograph (7890B) coupled with 5977 mass selective detector (MSD) and an HP5 capillary column (30 m × 0.32 mm × 0.25 μm) were used for the separation of the sample components with helium used as a carrier gas flowing at 1 mL/min. A sample extract (1 μL) was injected in a splitless mode at 270 °C, with a purge flow of 50 mL/min at 1 min. The initial column temperature was set at 70 °C (1 min hold), conditioned at 14 °C/min to 150 °C and at 6 °C/min to 290 °C having a total runtime of 30 min. An auxiliary, ion source and quadruple temperatures were set at 280 °C, 230 °C and 150 °C, respectively (Cherta et al., 2012; Zhou et al., 2015).

2.6. Quantification of phenolic derivatives

A phenol standard mixture containing the 11 priority pollutants was prepared in acetone diluted into series of concentrations from 10 to 15 μg/mL. Exactly, 3 mL of each concentration was derivatized and analyzed with GC-MS as explained above and the calculation was done using the formula reported by Kumar et al. (2014). The instrument was re-calibrated whenever a shift in retention time was observed.

2.7. Quality assurance

All samples were spiked with surrogate standard (2-Fluorophenol) to monitor the extraction efficiency. Double distilled water was spiked with 2 μg/mL of phenolics standard mixture for recovery study (Kumar et al., 2014). Furthermore, a portion of 10 μg/mL standard mixture of phenolic compounds was run seven times for the estimation of limit of detection (LOD), limit of quantification (LOQ) and relative standard deviation (RSD) (Kumar et al., 2014).

2.8. Statistical analysis

The data were analyzed with one way analysis of variance (ANOVA), regression analysis, mean and standard deviation using MINITAB for windows version 12.11 (2014), Minitab Ltd., University City, PA, USA at a significant level of $p < 0.05$.

2.9. Risk assessment

Risk evaluation of the analytes was carried out using life average daily dose (LADD), average daily dose (ADD), cancer risk value and hazard quotient (HQ) in accordance with standard methods with application of Eqs. (1)–(4) as reported in some previous studies (Carafa et al., 2011; Pawelczyk, 2013; Megahed et al., 2015; ECETOC, 2016; Yahaya et al., 2017).

$$HQ = \frac{ADD}{RfD} \quad (1)$$

HQ = Hazard Quotient (Unit less); ADD = intake exposure level (mg/kg/day); RfD = Reference Dose (mg/kg/day); ADD = intake exposure level mg/kg/day (Zhou et al., 2017).

$$ADD = \frac{C \times FI \times IR \times EF \times ED}{BW \times AT} [mg/kg/d]. \quad (2)$$

$$LADD = \frac{C \times FI \times IR \times EF \times ED}{BW \times AT} [mg/kg/d] \quad (3)$$

where LADD = Life average daily dose (mg/kg/body weight); C = Average concentration of phenolic derivative (mg/L); FI = Fraction ingested (0.98); IR = Daily water intakes based on age group (which are Age 0–6 years = 0.3 L/day; Age 7–17 years = 1 L/day; Adult = 1.4 L/day); EF = Exposure Frequency = 365 days/year; ED = Exposure duration based on age group (which are expressed as Age 0–6 years = 6; Age 7–17 years = 11; Adult = 3); BW = Average body

weight (expressed as Age 0–6 years = 30 kg; Age 7–17 years = 46 kg; Adult = 70 kg); AT = Averaging times in days (values used being AT_{0–6} = 2190 days; AT_{7–17} = 4015 days; AT_{Adult} = 10950 days). Note: For LADD the AT = 70years × 365 = 25,550 days (the same for all age groups).

$$Cancer\ risk = \frac{C \times DI \times ED \times CSF \times CF}{BW \times AT} \quad (4)$$

where DI = daily input L day⁻¹: 2 L/day; BW = body weight (kg): 60 kg; ED = Exposure duration = 183 days; CSF = Cancer slope factor (mg/kg/day); CF = Conversion factor (Zhou et al., 2017).

3. Results and discussion

3.1. Quality assurance

The results of the recovery study of the phenolic derivatives and the surrogate (2-Fluorophenol) in the sample, showed the efficiency of the method. The generally acceptable recovery for analysis in ng/L is in the range of 60–120%. Thus, acceptable recovery in the range of 60–109%, was witnessed for eight out of the twelve analytes in this study. However, the recoveries for P, 2-CP, 2, 4-DMP and 2,4,6-TCP were below the acceptable limit which indicate significant errors in the extraction using the method adopted in this study. This may be attributable to the instability of these compounds, the effects of the derivatization process or loss during extraction. The precision of the recovery study was good at a relative standard deviation (RSD) level in the range of 1.99–10.9%. Notwithstanding, the error level and the method were found applicable to the analysis of the phenolics in the water samples examined in this study. Similar study on phenolic derivatives reported recoveries in the range of 67.1–101.3% and RSD of 2.2–6.1% (Al-Janabi et al., 2012). Moreover, the results of the method's limit of detection applied to this study showed that it was sensitive at a limit of detection (LOD) range of 10–70 ng/L and limit of quantification (LOQ) in the range of 33–222 ng/L. Our study method proved more sensitive than the ones reported by Zhou et al. (2015) which reported LOD of 100 – 1390 ng/L for volatile phenols in wines using GC-MS and Al-Janabi et al. (2012) who reported LOD of 1 – 5 μg/L for chlorophenols in real water samples with GC-ECD. Other analytical parameters, for instance retention time and linearity (0.9987) were comparable with those reported in other similar studies (Al-Janabi et al., 2012; Zhou et al., 2015).

3.2. Seasonal occurrence and concentrations of phenolic derivatives in Buffalo River

This section presents the results of the occurrence and concentrations of phenolic derivatives in six locations in Buffalo River in two seasons, summer and autumn (Tables 1–6). The results are presented and discussed on site basis, but a general trend was observed across all the sites: the individual and total concentrations of the analytes were higher in the summer than the autumn. This is attributable to higher atmospheric precipitation in the summer resulting in increased agricultural activities, higher washing of the soil and increase in urban storm water discharge into the river. These are predisposing factors to increase in pollutant concentrations in summer. Likewise, phenol and 2-chlorophenol were below the limit of detection in all summer samples but were detected in the samples collected in autumn except for 2-CP and phenol detected in MSN and IZ respectively. There may be possibility of biogeochemical decomposition or transformation of the higher molecular weight derivatives into the phenol and 2-CP based on temperature variation that can affect the biogeochemistry of the area and the compounds (Debadatta, and Rajdeep, 2012; Jennifer et al., 2017; Zhou et al., 2017).

Table 1
Seasonal Occurrence and total concentrations of phenolics in BRE.

Analytes in BRE	Summer		Autumn	
	Concentration (ng/L)	FD (%)	Concentration (ng/L)	FD (%)
P	< LOD	0	140 ± 0.08	100
2-CP	< LOD	0	295 ± 0.21	100
2-NP	1224 ± 0.02	33	540 ± 0.45	67
2,4-DMP	809 ± 0.01	33	56 ± 0.05	100
2,4-DCP	885 ± 0.02	100	215 ± 0.10	67
4-C-3-MP	155 ± 0.72	100	93 ± 0.01	100
2,4,6-TCP	416 ± 0.34	67	164 ± 0.01	67
2,4-DNP	774 ± 0.05	67	< LOD	0
4-NP	< LOD	0	< LOD	0
2-M4,6-DNP	< LOD	0	< LOD	0
PCP	629 ± 0.01	33	< LOD	0
ΣPhenolics	4892 ± 1.17		1293 ± 0.91	

Values are means ± SD; N = 3. FD – Frequency of detection.

Table 2
Seasonal Occurrence and total concentrations of phenolics in MSN.

Analytes in MSN	Summer		Autumn	
	Concentration (ng/L)	FD (%)	Concentration (ng/L)	FD (%)
P	< LOD	0	59 ± 0.01	100
2-CP	< LOD	0	< LOD	0
2-NP	1205 ± 0.08	100	713 ± 0.07	100
2,4-DMP	815 ± 0.01	100	< LOD	0
2,4-DCP	759 ± 0.05	100	< LOD	0
4-C-3-MP	676 ± 0.29	100	< LOD	0
2,4,6-TCP	569 ± 0.09	100	410 ± 0.02	100
2,4-DNP	< LOD	0	< LOD	0
4-NP	1212 ± 0.01	33	< LOD	0
2-M4,6-DNP	< LOD	0	< LOD	0
PCP	632 ± 0.02	100	< LOD	0
ΣPhenolics	5868 ± 0.55		1182 ± 0.11	

Values are means ± SD; N = 3. FD – Frequency of detection.

Table 3
Seasonal Occurrence and total concentrations of phenolics in ZW.

Analytes in ZW	Summer		Autumn	
	Concentration (ng/L)	FD (%)	Concentration (ng/L)	FD (%)
P	< LOD	0	36 ± 0.01	100
2-CP	< LOD	0	95 ± 0.02	100
2-NP	182 ± 0.02	100	84 ± 0.04	100
2,4-DMP	163 ± 0.04	100	< LOD	0
2,4-DCP	87 ± 0.02	100	< LOD	0
4-C-3-MP	< LOD	0	< LOD	0
2,4,6-TCP	71 ± 0.01	100	< LOD	0
2,4-DNP	< LOD	0	< LOD	0
4-NP	< LOD	0	< LOD	0
2-M4,6-DNP	< LOD	0	< LOD	0
PCP	77 ± 0.01	100	< LOD	0
ΣPhenolics	579 ± 0.1	–	215 ± 0.07	

Values are means ± SD; N = 3. FD – Frequency of detection.

3.3. Buffalo River Estuary (BRE)

The results of the frequency of detection of the analytes and their concentration in BRE for the two seasons are presented in Table 1. The highest concentration was observed for 2-NP: 1224 ng/L and 540 ng/L in summer and autumn respectively. The most detected (FD - 100%) analytes were 2,4-DCP and 4-C-3-MP in summer. In the autumn samples, four phenolics were most detected: P, 2-CP, 2,4-DMP and 4-C-3-

Table 4
Seasonal Occurrence and total concentrations of phenolics in KWT.

Analytes in KWT	Summer		Autumn	
	Concentration (ng/L)	FD (%)	Concentration (ng/L)	FD (%)
P	< LOD	0	22 ± 0.01	100
2-CP	< LOD	0	120 ± 0.04	100
2-NP	1143 ± 0.58	100	< LOD	0
2,4-DMP	630 ± 0.40	100	< LOD	0
2,4-DCP	608 ± 0.27	100	< LOD	0
4-C-3-MP	610 ± 0.44	100	< LOD	0
2,4,6-TCP	482 ± 0.36	100	< LOD	0
2,4-DNP	693 ± 0.01	33	< LOD	0
4-NP	< LOD	0	< LOD	0
2-M4,6-DNP	< LOD	0	< LOD	0
PCP	574 ± 0.25	100	< LOD	0
ΣPhenolics	4740 ± 2.31	–	142 ± 0.05	

Values are means ± SD; N = 3. FD – Frequency of detection.

Table 5
Seasonal Occurrence and total concentrations of phenolics in IZ.

Analytes in IZ	Summer		Autumn	
	Concentration (ng/L)	FD (%)	Concentration (ng/L)	FD (%)
P	< LOD	0	< LOD	0
2-CP	< LOD	0	136 ± 0.01	100
2-NP	1109 ± 0.32	100	< LOD	0
2,4-DMP	713 ± 0.16	100	301 ± 0.05	100
2,4-DCP	570 ± 0.21	100	< LOD	0
4-C-3-MP	313 ± 0.18	100	< LOD	0
2,4,6-TCP	723 ± 0.08	100	< LOD	0
2,4-DNP	< LOD	0	< LOD	0
4-NP	< LOD	0	< LOD	0
2-M4,6-DNP	680 ± 0.01	33	< LOD	0
PCP	635 ± 0.04	100	< LOD	0
ΣPhenolics	4743 ± 1.00	–	437 ± 0.06	

Values are means ± SD; N = 3. FD – Frequency of detection.

Table 6
Seasonal Occurrence and total concentrations of phenolics in MD.

Analytes in MD	Summer		Autumn	
	Concentration (ng/L)	FD (%)	Concentration (ng/L)	FD (%)
P	< LOD	0	52 ± 0.01	100
2-CP	< LOD	0	41 ± 0.01	100
2-NP	1149 ± 0.32	67	55 ± 0.01	67
2,4-DMP	484 ± 0.36	100	37 ± 0.01	100
2,4-DCP	657 ± 0.05	100	< LOD	0
4-C-3-MP	538 ± 0.36	100	< LOD	0
2,4,6-TCP	632 ± 0.05	100	34 ± 0.05	100
2,4-DNP	< LOD	0	< LOD	0
4-NP	< LOD	0	< LOD	0
2-M4,6-DNP	< LOD	0	< LOD	0
PCP	528 ± 0.05	100	< LOD	0
ΣPhenolics	3988 ± 1.19	–	219 ± 0.09	100

Values are means ± SD; N = 3. FD – Frequency of detection.

MP. Four other phenolics: 2,4-DNP, 4-NP, 2-M4,6-DNP and PCP, were below detection limits in all the autumn samples from this location. Generally, there are some indications that the individual and total concentrations of the phenolics in BRE surpass that of other sites except in few cases. This is attributable to the fact that it is an estuary and a discharge point into the ocean. The pollutants from the catchment of the river are washed down into this region before discharge into the ocean but the observed concentrations are governed by many

biogeochemical factors that can affect their fate. Furthermore, East London is a city near BRE. It is an industrial and urban city that generates significant levels of wastes. High concentration of the organic pollutants entering the river in summer (El-Naas et al., 2010; Debadatta and Rajdeep, 2012; Jennifer et al., 2017). However, the low level in autumn could be attributed to microbial transformation into carboxylic acids by the activities of *Comamonas* and *Pseudomonas* species from the pollutants entering the aquatic environment (Owicz and Duda, 2007; Zhou et al., 2017). **Mdantsane (MSN)**

Table 2 presents the results of the occurrence and concentrations of the eleven phenolics in MSN. The higher concentration of the analytes was observed for 4-NP and 2-NP in summer (1212 and 1205 ng/L respectively) and 2-NP (713 ng/L) in the autumn seasons which is similar to the trend observed in BRE. Six analytes had 100% frequency of detection while four were below detection limits in the summer samples (Table 2) which is much higher than the frequency observed in BRE. The total concentration of the phenolics during the summer season in MSN was also higher than at the estuary. This trend is attributable to the higher degree of anthropogenic activities in MSN. MSN hosts Potsdam wastewater treatment plant and may be responsible for the release phenolics from wastewater treatment plant's effluent from domestic sources and the since phenolic compounds are reportedly used for waste treatment and as home disinfectants (Debadatta and Rajdeep, 2012; Olujimi et al., 2012a). In the autumn sample only three analytes: phenol, 2-NP and 2,4,6-TCP were detected.

3.4. Zwelitsha (ZW)

The results of the pollutants' seasonal occurrence and concentrations in the sites are presented in Table 3. Similar to the first two sites presented, 2-NP is the most prominent phenolic derivative at ZW during the summer study followed by 2,4-DMP. The para isomer, 4-NP, was not detected in ZW unlike MSN where it was most prominent. Generally, ZW is less polluted with these compounds than the other two sites earlier presented. ZW has much lower total phenolic concentration in the summer and only five compounds were detected in ZW as against seven detected in BRE and MS. In the autumn samples, only phenol, 2-chlorophenol and 2-nitrophenol were detected with 2-chlorophenol being the most prominent closely followed by 2-nitrophenol. The other compounds were below the limit of detection. This may also be attributable to the degree of activities and the rate of wastes discharge from saw mills, agricultural farm land and aerated treatment plant in the area (Olujimi et al., 2012b; Saber et al., 2016). The understanding of the biogeochemistry of these sites will be essential to understand the fate of these compound and the factors responsible for the trend observed in each season.

3.5. King William's Town (KWT)

Table 4 presents the results of phenolic derivatives in KWT. The compound with highest concentration was 2-NP (1143 ng/L). There is high total concentration of the phenolics (4740 ng/L) witnessed in the summer samples from KWT similar to the concentrations witnessed in BRE and MSN. This high concentration of the derivatives at KWT could be ascribed to the proximity of the river to the industrial effluents point source (Eljarrat et al., 2004; Olujimi et al., 2012a). Four analytes were not detected in this site during the summer and only two analytes were detected in the autumn season. There was a remarkable drop in the total concentration of the phenolics from the summer to the autumn. It can be inferred that the observed variation in concentration between the summer and the autumn season is not likely to be discharge related but fate based.

3.6. Izele Town (IZ)

The results of the concentrations of the analytes studied in IZ are

presented in Table 5. Similar to other sites 2-NP was the most abundant analyte in the summer but was not detected in the autumn samples. It may therefore, be essential that source apportionment be done for 2-NP in this study area. This will assist in the management of and significant reduction in the phenolic pollution load of the area. The trend of the total concentration or pollution load across the sites was MSN > BRE > IZ ≈ KWT > MD > > ZW. 2-M4,6-DNP was not detected in other sites but was detected in IZ. The detection of the analytes at high concentration in summer at IZ might be related to the application of phenolic herbicides on the irrigated Amadalakufa Cooperative Farm and agricultural waste released from the suburb (Daassi et al., 2014; Musa, 2014).

3.7. Maden dam

The results of the concentrations of the phenolics in the last sampling site studied (Maden dam) is presented in Table 6. The same trend of 2-NP being the most abundant analyte was witnessed in this site. The management of the source of input of 2-NP and its remediation is recommended. Similarly, more of the compounds were detected in summer at the Maden dam. There was however, high frequency of detection of more compounds in the autumn similar to what was observed in BRE but a remarkable drop in total concentration from 3988 ng/L in summer to 219 ng/L in autumn was witnessed just like the trend witnessed in KWT. There are strong indications that increased agricultural soil runoff contributes most significantly to the phenolic pollution load than domestic and industrial waste discharge. The mobility and the impact of the phenolic appear more seasonally based which associates the source to agricultural activities than other anthropogenic activities. The presence of these compounds in the dam water which is presumed to be less polluted because of minimal anthropogenic activities within its surroundings, could be attributed to biodegradation of vegetation and other organic matters that may have accumulated these compound or to low temperatures that are often recorded in the area which are favourable to the reduced rate of the compound's degradation process (Gnudi, 1999; Huang et al., 2010). 2,4,6-TCP was detected in MD at autumn, BRE and MSN but not in other site. This may be discharge associate and not based on the biogeochemical transformations.

Overall, the total concentrations of the phenolic derivatives were remarkably higher than the regulatory standard (USEPA) of 500 ng/L in all the sites during summer and in sites BRE and MSN during autumn study. Most of the individual compounds were also higher than the regulatory standard in the summer study. European Commission has identified phenolics as priority pollutants including various groups of heterogeneous contaminants which are common in the environment such as polychlorinated biphenyls, selected pesticides, triclosan, and phthalates (Snyder et al., 2003; EU European Union Commission, 2008; Olaniyan et al., 2016; Yahaya et al., 2017; Salaudeen et al., 2018). These endocrine disruptor chemicals, including phenolics, have exogenous and xenobiotic characteristic obstructing the normal activities of the endocrine system such as, metabolism, reproduction and behavior of living kinds in human and animals (Crisp et al., 1998; Snyder et al., 2003; Zgheib et al., 2012). Because of the adverse effects to humans, the toxicity needs to be studied and absolute regulation needs to be reviewed as research continues (Ahel et al., 1994; Xuemin et al., 2016)

The results of this study compared favorably with those from Danube river in Hungary (6.5–30.8 ng/L) and Tama river in Germany (< LOD - 814 ng/L), where fewer industrial and domestic wastes are discharged (Faludi and Záray, 2015). However, the results are in contrast with the data for Veldwatcher River in South Africa where upstream and downstream levels were reported as < LOD–1.063 × 10⁶ ng/L and < LOD–8.28 × 10⁶ ng/L respectively (Olujimi et al., 2012a). This may be due to increase in the anthropogenic activities hence there is need for strict regulation.

Table 7
HQ, ADD, LADD and Cancer risk.

PD	HQ × 10 ⁻⁴			ADD × 10 ⁻⁵			RfD	CSF × 10 ⁻²	LADD × 10 ⁻⁵		Cancer Risk × 10 ⁻¹⁴
	0–6	7–17	Adt	0–6	7–17	Adt			0–6 & Adt	7–17	
P	1.23	73	25	3.7	2.2	0.7	0.3	NR	3.2	0.3	NR
2CP	164	97	33	8.2	4.8	1.6	0.005	NR	7.0	0.7	NR
2,4DCP	814	78	161	24	14.3	4.8	0.003	NR	2.1	2.3	NR
PCP	61	24	8.2	31	12.1	4.1	0.05	4	1.7	1.9	34.2
TCP	NR	NR	NR	20	18.2	6.1	NR	1.1	2.6	2.9	6.27

Phenolics Derivatives (PD), Hazard Quotient (HQ); 0–6: Age group 0–6 years, 7–17: Age 7–17 years, Adt: Adult. Not Recorded (NR).

3.8. Risk evaluation

The results of Average daily dose (ADD), Life average daily dose (LADD), ADD and LADD are presented in mg/kg/d. The values for the HQ, ADD, LADD for ages 0–6, 7–17 and adult as well as cancer risk value in this study are reported in Table 7. Hazard quotient was evaluated as the ratio between predicted environmental concentration (PEC) and predicted no-effect concentration (PNEC) (Bouissou-schurtz et al., 2014; Jennifer et al., 2017). Value greater than unity, implies a harmful effect but below 1 suggest likelihood of low risk (Megahed et al., 2015; Kawaguchi et al., 2012). The results could be used to measure the potential ecological risk. The HQ values for phenolic derivatives in the Buffalo river water were generally below unity, implying a relatively low level of ecological risk (Kawaguchi et al., 2012; Megahed et al., 2015). Also, if amount of the pollutants take in regularly is greater than 10⁻⁴ (i.e. ADD > 10⁻⁴) it indicates probably life cancer risk. LADD and cancer risk values greater than 10⁻⁶ (i.e. LADD and cancer risk value > 10⁻⁶) suggest the possibility of having cancer and levels above 10⁻³ will require a protective measure (US EPA, 2005, 2012; US EPA-IRIS, 2007). The ADD and cancer risk values for phenolic derivatives in this study were below the permissible limits, indicating there will be no likelihood of the dwellers along this river having cancer. However, the value of LADD greater than the recommended 10⁻³ implies potential hazard (US EPA, 2005; US EPA-IRIS, 2007; Yahaya et al., 2017).

4. Conclusion

Based on the investigation, the concentrations of the analytes were higher than the USEPA guidelines. This could be attributed to increase in the influx of biodegradation of pesticides, agricultural wastes and pharmaceutical drugs which could possibly be as a result of the water runoff. The major pollutant detected was 2-NP and a management of 2-NP pollution source will significantly reduce the pollution load of the phenolics in the Buffalo River. The results of this study showed that the human and wildlife exposure to the organic pollutants needs to be further controlled by regular checking of the river water quality.

Acknowledgement

The authors are grateful to (NRF), and (SAMRC) for financial assistance for this study.

Conflicts of interest

The authors declare that they have no competing interests about the publication of these research findings.

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