

# Assessment of the Occurrence and Risks of Emerging Organic Pollutants (EOPs) in Ikpa River Basin Freshwater Ecosystem, Niger Delta-Nigeria

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**Abstract** The levels of some emerging organic pollutants (EOPs) including endocrine disrupting compounds, pharmaceuticals and personal care products were quantified in surface water of a freshwater ecosystem, the Ikpa River Basin, Nigeria using liquid chromatography/high resolution tandem mass spectrometry (LC–MS/MS). In addition, leachates and storm water samples collected from nearby dumpsites were also analysed to assess the effect on water quality. Seventeen compounds were detected at the nanogramme-per-litre levels and the ecological risks of selected compounds assessed based on predicted no-effect concentrations derived from comparison of toxicity data recorded for green algae, fish and invertebrate with the maximum measured environmental concentrations, to obtain risk quotients. Some of the compounds showed some level of widespread occurrence or persistence. Also, bisphenol A, chloramphenicol, erythromycin, triclocarban and triclosan were the most important EOPs detected in the study area that may pose detrimental effects to the aquatic organisms based on the outcome of the risk assessment.

**Keywords** Emerging organic pollutants · Risk assessment · Ikpa River · Nigeria

The Niger Delta of Nigeria covers an estimated area of between 19,100 and 30,000 km<sup>2</sup> based on hydrological, ecological as well as political boundaries (SPDC 2006; UNDP 2006 and Inam et al. 2014). The Niger Delta region which is the petroleum belt of Nigeria is a water-rich region with plenty of water resources but scarce drinking water supplies. The region has been characterized by remarkable resource of renewable supply of freshwater and long marine coastline with complex ecosystems that connect inland brackish (estuarine), euryhaline, humic-freshwater systems to near-shore marine waters. Unfortunately, this water resource has been suffering the deleterious effects of anthropogenic activities since the 1990s.

Many thousands of emerging organic pollutants (EOPs) such as poly-chlorinated biphenyls (PCBs), organo-chlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzofurans (PCDFs), dibenzo-*p*-dioxins (PCDDs), pharmaceutical and personal care products (PPCPs) and endocrine disruptive compounds (EDCs) have been produced and, in parts, released into the environment. Due to direct discharges or to hydrologic and atmospheric processes (Stegeman and Hahn 1994; Oost et al. 2003; Essien et al. 2012) the aquatic environment has become the ultimate sink for many of these contaminants. It is also clear that, the presence of a xenobiotic compound in a segment of an aquatic ecosystem does not, by itself, indicate that adverse effects would have incurred. Connections must be established between external levels of exposure, internal levels of tissue contamination and early adverse effects.

The occurrence of many EOPs and their metabolites in the Niger Delta of Nigeria are yet to be identified. On the

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other hand, two studies have reported the occurrence of trace phenolic and other emerging contaminants in some water bodies in the Western and Southeastern parts of Nigeria (Oketola and Fagbemigun 2013; Arukwe et al. 2012). These studies either focused on trace phenolics that could easily be monitored using optimized methods of gas chromatography/mass spectrometry or on personal care products; pharmaceutically active compounds were not considered. The Ikpa River Basin is suspected to be receiving run-offs from nearby municipal landfill and hospital dumpsite. The river basin serves as one of the major source of water for irrigation, drinking and other domestic uses for about eight hundred thousand inhabitants of its catchment. There are several human activities located within close distances to the water body namely: rubber and asphalt processing industries, sanitary landfill site, hospitals and a commercial beach amongst others. Previous studies on the basin revealed human impacts and contamination (Udosen and Essien 2001; Dennis et al. 2013). However, studies on emerging organic pollutants in the basin have not been reported. Therefore the exposure, fate and effects of contaminants in freshwater ecosystems of the petroleum belt of Nigeria need to be extensively investigated. In this report we assessed the occurrence and risks of emerging organic pollutants (EOPs) in Ikpa River Basin Freshwater Ecosystem, Niger Delta-Nigeria.

## Materials and Methods

Sampling was done between April and June, 2013. This period was characterised by medium to heavy rainfall during the year. The sampling stations were divided into three (Ntak Inyang, Ibaoku and Anua) based on suspected sources of contamination. As indicated in Fig. 1, the Ntak Inyang station is located near an abandoned asphalt plant (A), the Ibaoku station is located near a major municipal landfill (B), while the Anua station is located close to hospital dumpsites (C). Samples including nearby dumpsite leachates, surface run-offs and surface waters were collected into 1 litre amber bottles. Storm water sample was collected between 20 and 45 min after rain, in the early hours (7 a.m.), by carefully scooping them from natural drainages leading to the River. Leachates from dumpsites were collected by installing amber glass containers at the bottom of landfills (about 50 cm from top soil). A total of seven samples were collected. Field grab samples were preserved by adding 250 mg/L sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). All samples were filtrated using Pall water filtration apparatus with 47 mm, 5 micron glass micro-filter membrane into a clean amber bottle using a vacuum pump.

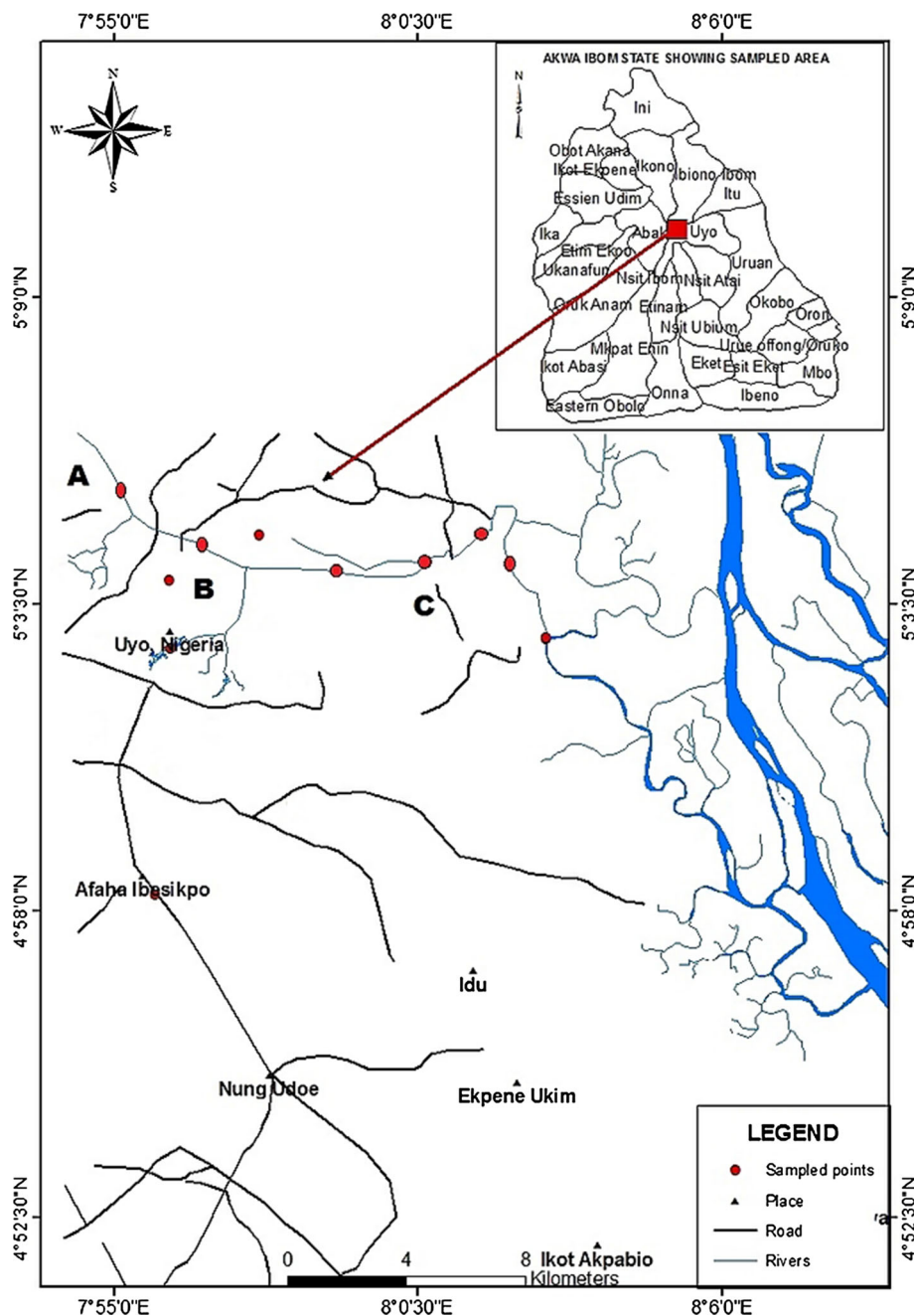
Before the extraction, 2 g of ethylenediamine tetracetic acid (EDTA) and 10 mL of 0.25 M ammonium acetate

solution were added to all filtered samples after which the pH of each sample was adjusted to  $6.95 \pm 0.05$  using 10 % (w/v) NaOH and 10 % (v/v)  $\text{H}_2\text{SO}_4$ . In addition to the water samples, 400 mL deionized water each was used to prepare blank and 2 spiked samples (300  $\mu\text{L}$  of isotope dilution quantitation standards) (Hao 2008). A total of fifty-one compounds were targeted and their limits of detection and recoveries determined. The average recoveries for the compounds recorded were 32 %–644 % while the limits of detection calculated ranged from 0.004 to 5.1 ng/L. Target analytes were extracted using hydrophilic lipophilic balance (HLB) cartridges (Oasis HLB 6 cc, 200 mg) from Waters Corporation (Milford MA, USA). The HLB cartridges were preconditioned with 5 mL of 10 % (v/v) methanol/water at 2 mL/min and then 400 mL of samples were loaded onto the solid phase extraction system (SPE) at 10 mL/min to extract target compounds, after which cartridges were rinsed with 10 mL water and 5 mL 5 % methanol at 2 mL/min. This was followed by cartridge drying by gentle nitrogen streaming for 30 min. The target compounds were then eluted from the SPE cartridge with 5 mL methanol at 1 mL/min. Samples were concentrated to 1 mL using TurboVap<sup>®</sup> Concentration Evaporator Workstation (Life Sciences, USA) and transferred to vials before analysis.

Analysis of PPCPs/EDCs was done using a Thermo Scientific<sup>™</sup> Dionex<sup>™</sup> UltiMate<sup>™</sup> 3000 HPLC consisting of an HRG-3400RS binary pump, WPS-3000 autosampler, and a TCC-3400 column compartment. Separation was performed by injecting 5 mL extracts onto a  $2.1 \times 100$  mm (3  $\mu\text{m}$  particle size) Thermo Scientific<sup>™</sup> Betasil<sup>™</sup> C18 column for positive mode MS analysis and a Thermo Scientific<sup>™</sup> Hypersil GOLD<sup>™</sup>,  $2.1 \times 100$  mm (3  $\mu\text{m}$  particle size) column for negative mode MS analysis (part numbers 71503–102130 and 25003–102130, respectively). The HPLC was interfaced to a Thermo Scientific<sup>™</sup> Exactive<sup>™</sup> Plus hybrid quadrupole-Orbitrap mass spectrometer using a heated electrospray ionization (HESI-II) interface. High-purity nitrogen (>99 %) was used in the HESI-II source (35 arbitrary units). Spray voltages used were 2500 and –3200 V for positive and negative modes, respectively. Mobile phase and gradient elution information are listed in Table 1. The Thermo Scientific<sup>™</sup> TraceFinder<sup>™</sup> software was used to perform quantitative analysis for 51 EOPs.

The risk posed by certain contaminants in aquatic environment can be evaluated through the calculation of risk quotients (RQ) as described elsewhere (EMEA 2006; Santos et al. 2007). An RQ value of a single contaminant for aquatic organisms was calculated from the maximum measured environmental concentrations (MEC) of the EOPs in water samples and predicted no effect concentration (PNEC) using the equation shown below:

**Fig. 1** The Ikpa River Basin showing sample locations and stations



$$RQ = MEC/PNEC$$

PNEC values were calculated from the measured effective concentration ( $EC_{50}$ ) or lethal dose ( $LD_{50}$ ), or the no-observed-effect concentration (NOEC) for fish, green algae and invertebrate for each compound obtained from literature and the assessment factor (AsF) of 1000 following the equation below:

$$PNEC = EC_{50} \text{ or } NOEC \text{ or } LD_{50}/1000$$

The concept of AsF has been introduced to account for extrapolation from intra- as well as inter-species/media

variability in sensitivity (Hernando et al. 2006). Furthermore, errors are still inherent in the PNEC derivation since toxicity data are significantly affected by many factors, including the lifecycle stage of the organism, properties of the surrounding environment, and the experimental conditions (Zhu and Chen 2014). A commonly used risk ranking criteria was applied:  $RQ < 0.1$  means minimal risk,  $0.1 \leq RQ < 1$  means medium risk, and  $RQ \geq 1$  means high risk (Hernando et al. 2006). In the case of compounds for which  $EC_{50}$  values were not readily obtainable, the NOEC or  $LD_{50}$  values were used to derive

**Table 1** HPLC mobile phase and gradient used in the analysis

Parameter	Setting			
Column oven temperature	35°C			
Flow rate	450 µL/min			
Mobile phase (positive)	A: 5 mM ammonium formate/0.1 % formic acid in methanol/water (10:90, v/v) B: Methanol/water (90:10, v/v)			
Mobile phase (negative I)	A: Acetonitrile/water (10:90, v/v), pH 6.95 ± 0.3 B: Acetonitrile			
Mobile phase (negative II)	A: 5 mM ammonium acetate in acetonitrile/water (10:90, v/v), pH 6.95 ± 0.3 B: Acetonitrile			
HPLC gradient	Time (min)	% A	% B	Curve
	0.0	95	5	5: linear
	2.0	25	75	5: linear
	10.0	5	95	7: concave upward (mid slope)
	15	5	95	5: linear
	15.2	95	5	5: linear

PNECs. In whichever case, appropriate assessment factors were used based on information in literatures.

## Results and Discussion

Analysis of EOPs has revealed the presence of seven antibiotic drugs (acetamidophenol, chloramphenicol, ciprofloxacin, erythromycin, lincomycin HCl, roxythromycin, and sulfamethoxazole), three bactericides/antimicrobial agents (sulfathiazole, triclosan and triclocarban), an antiepileptic drug (carbamazepine), an analgesic drug (diclofenac sodium), a resin precursor (bisphenol A), a sunscreen product (oxybenzone), a hormone (equilin), an insect repellent (DEET), and a stimulant (caffeine) in surface water samples from Ikpa River Basin as well as in the storm water from hospital dumpsite and municipal landfill leachate discharged into the freshwater body through run-offs. The average concentrations of the seventeen compounds detected are presented in Table 2. Their distribution shows that acetamidophenol, lincomycin HCl and sulfathiazole were detected in the municipal landfill leachate only. Caffeine was detected in both the municipal landfill leachate and storm water run-off of the hospital dumpsite.

The results show that EOPs occurred in the Ikpa River basin but at very low concentrations (within the nanogramme per litre range). This observation is generally attributed to dilution and degradation factors, particularly in the surface waters of the river. In rivers, natural attenuation of these contaminants may be caused by biotransformation, photolysis, and dispersion or a combination of some of these processes (Pal et al. 2010). This might be

responsible for the detection of some EOPs in the landfill leachate and storm water from run-offs of hospital but not in surface waters where they are discharged into. Their presence may also be influenced by distribution by means of partitioning into different compartments, such as sorption to soil particles and volatilization (Al-Odaini et al. 2013). The monitored EOPs are generally different in terms of chemical structure and functional groups present and as such it would be expected that their behaviour in the environment would differ even under similar conditions. The most frequently detected compounds were bisphenol A, oxybenzone, triclocarban and triclosan with 100 % occurrence rate in all the samples analysed. This was followed by DEET and chloramphenicol with over 60 % occurrence rate. As expected, the levels of EOPs in the municipal landfill leachate and storm water run-offs from hospital dumpsite were comparatively higher than concentrations recorded for the surface water samples from Ibaoku, Anua and Ntak Inyang stations (Table 2), although the values were generally within the lower ranges reported elsewhere (Li 2014).

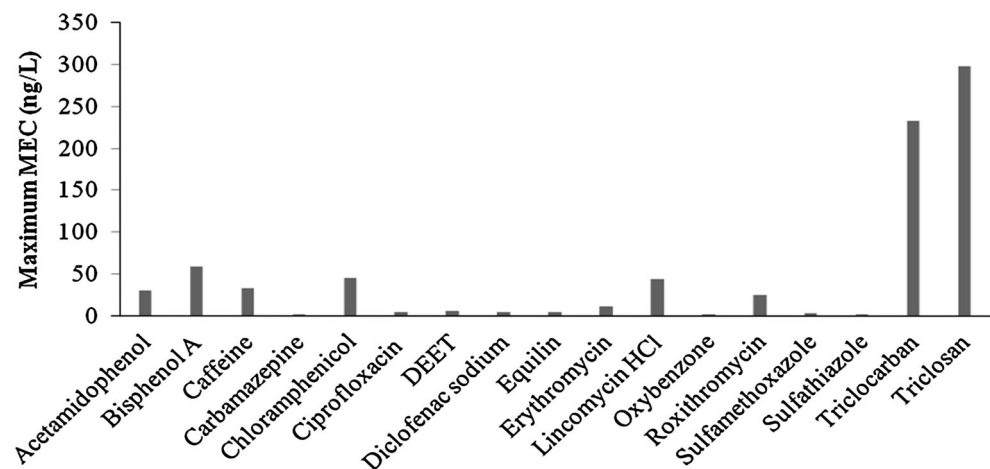
Comparative analysis of the occurrence and distribution of target EOPs using their maximum measured environmental concentrations (upper range values presented in Table 2) are presented in Fig. 2. The occurrence and distribution of EOPs in the media studied varied widely as indicated in Fig. 2. The variability may be due to their individual characteristics regarding environmental fate and transport. For instance, diclofenac, which is one of the compounds detected at very low concentrations, has been reported to be non-persistent in aquatic environment, possessing a short half-life of <1 day and vulnerable to photodegradation (Ashton et al. 2004). On the other hand,

**Table 2** Average concentrations of EOPs in surface water of Ikpa River Basin and Leachates/Storm Water run-offs of nearby Dumpsites (ng/L)

EOPs	Sampling stations					Frequency of detection (%)	Range	Literature concentration range for surface water
	Udo landfill leachate (n = 1)	Ibaoku (n = 2)	Anua hospital dumpsite storm water (n = 1)	Anua (n = 2)	Ntak Inyang (n = 1)			
ACT	30.1	BDL	BDL	BDL	BDL	14.29	BDL–30.1	4.1–74 (1)
BPA	59.2	2.3	1.7	46.1	1.7	100	1.6–59.2	Up to 1992 (2)
CAF	32.4	BDL	4.0	BDL	BDL	28.57	3.0–32.4	BDL–215 (3)
CBZ	BDL	0.02	BDL	BDL	BDL	14.29	BDL–0.04	Up to 735 (4)
CLP	BDL	0.3	0.5	22.6	0.6	57.14	BDL–45.2	Up to 53.8 (5)
CPF	BDL	2.3	BDL	BDL	BDL	14.29	BDL–4.6	Up to 77 (4)
DEET	5.9	0.3	0.3	BDL	BDL	57.14	BDL–5.9	55–660 (6)
DIC	3.6	0.7	BDL	BDL	BDL	28.57	BDL–3.6	1.1–82 (7)
EQU	BDL	BDL	BDL	2.0	BDL	28.57	BDL–3.9	NA
ERT	BDL	BDL	BDL	5.7	BDL	14.29	BDL–11.4	1.8–4.8 (1)
LNM	43.8	BDL	BDL	BDL	BDL	14.29	BDL–43.8	NA
OXB	1.1	1.0	1.0	1.1	0.8	100	1.0–1.2	1.2–2.7 (1)
RXM	BDL	BDL	2.5	12.6	BDL	28.29	BDL–25.2	Up to 35.5 (5)
SMX	BDL	1.4	BDL	0.5	BDL	28.29	BDL–2.8	NA
SMZ	0.7	BDL	BDL	BDL	BDL	14.29	BDL–0.7	Up to 170 (4)
TCC	45.7	39.3	47.2	191.4	47.3	100	35.6–232.4	1.9–1425 (6)
TCS	55.1	59.8	63.6	218.7	56.4	100	55.1–297.7	<0.1–2300 (6)

(1) Kim et al. (2007), (2) Arukwe et al. (2012), (3) Santhi et al. (2012), (4) Li (2014), (5) Choi et al. (2008), (6) Brausch and Rand (2011), (7) Pal et al. (2010)

ACT acetamidophenol; BPA bisphenol A; CAF caffeine; CBZ carbamazepine; CLP chloramphenicol; CPF ciprofloxacin; DEET N, N – dimethyl-3-methylbenzamide; DIC diclofenac sodium; EQU equilin; ERT erythromycin; LNM lincomycin HCl; OXB oxybenzone; RXM roxythromycin; SMX sulfamethoxazole; SMZ sulfathiazole; TCC triclocarban; TCS triclosan; BDL concentration below detection limit; NA not available

**Fig. 2** Comparison of maximum MECs of EOPs in the study area

relatively higher maximum MEC for triclosan, triclocarban, bisphenol A, acetamidophenol and caffeine may be attributable to the pattern of their frequent use within the study area. This is so, since occurrence of PPCPs in the environment is to a large extent dependent on the prevalent local diseases, treatment methods and market profiles

which in turn lead to significant variations in pollution profiles (Salgado et al. 2010). However, exceptionally low levels of maximum MEC were recorded for the commonly prescribed antibiotics: ciprofloxacin (2.3 ng/L), erythromycin (11.4 ng/L) and sulfamethoxazole (2.8 ng/L). Nevertheless, for antibiotics such as ciprofloxacin, the low



**Table 3** Potential ecological risk (in terms of RQ) of selected emerging contaminants for green algae (a), fish (f), and invertebrate (i) in the study area using maximum MEC detected

EOPs	MEC ( $\mu\text{g/L}$ )	EC <sub>50</sub> ( $\mu\text{g/L}$ )	Derived PNEC ( $\mu\text{g/L}$ )	Risk quotient, RQ (MEC/PNEC)	Potential risk level
ACT	$3.01 \times 10^{-2}$	134,000 (a) (1)	134	$2.24 \times 10^{-4}$	Low
		378,000 (f)(1)	378	$7.96 \times 10^{-5}$	Low
		41,000 (i) (2)	41	$7.34 \times 10^{-4}$	Low
BPA	$5.92 \times 10^{-2}$	1360 (a) (3) <sup>a</sup>	1.36	$4.35 \times 10^{-2}$	Low-medium
CAF	$3.24 \times 10^{-2}$	46,000 (a) (2)	46	$7.04 \times 10^{-4}$	Low
		151,000 (f) (4)	151	$2.15 \times 10^{-4}$	Low
		410,000 (i) (4)	410	$7.90 \times 10^{-5}$	Low
CBZ	$4.00 \times 10^{-5}$	33,600 (a) (5)	33.6	$1.19 \times 10^{-6}$	Low
		35,400 (f) (6)	35.4	$1.23 \times 10^{-6}$	Low
		13,800 (i) (5)	13.8	$2.90 \times 10^{-6}$	Low
CLP	$4.52 \times 10^{-2}$	64 (*) (7)	0.64 <sup>b</sup>	$7.06 \times 10^{-2}$	Low-medium
CPF	$4.57 \times 10^{-3}$	938,000 (a) (2)	938	$4.87 \times 10^{-6}$	Low
		991,000 (i) (2)	991	$4.61 \times 10^{-6}$	Low
DEET	$5.88 \times 10^{-3}$	388, 000 (a) (8) <sup>d</sup>	388	$1.52 \times 10^{-5}$	Low
		71, 300 (f) (8) <sup>d</sup>	71.3	$8.25 \times 10^{-5}$	Low
		108,000 (i) (8) <sup>d</sup>	108	$5.44 \times 10^{-5}$	Low
DIC	$3.58 \times 10^{-3}$	–	9.70 (9) <sup>c</sup>	$3.69 \times 10^{-4}$	Low
ERT	$1.14 \times 10^{-2}$	4300 (a) (2)	4.3	$2.65 \times 10^{-3}$	Low
		61,500 (f) (6)	61.5	$1.85 \times 10^{-4}$	Low
		–	0.02 (i) (10) <sup>c</sup>	$5.70 \times 10^{-1}$	Medium
LNM	$4.38 \times 10^{-2}$	86,000 (a) (2)	86	$5.09 \times 10^{-4}$	Low
		1391,000 (f) (2)	1391	$3.15 \times 10^{-5}$	Low
		82,000 (i) (2)	82	$5.34 \times 10^{-4}$	Low
RXM	$2.52 \times 10^{-3}$	4000 (a) (2)	4	$6.30 \times 10^{-4}$	Low
		50,000 (f) (2)	50	$5.04 \times 10^{-5}$	Low
		7100 (i) (7)	7.1	$3.55 \times 10^{-4}$	Low
SMX	$2.82 \times 10^{-3}$	51,000 (a) (2)	51	$5.53 \times 10^{-5}$	Low
		562,500 (f) (10)	562.5	$5.01 \times 10^{-6}$	Low
		177,300 (i) (10)	177.3	$1.59 \times 10^{-5}$	Low
SMZ	$6.9 \times 10^{-4}$	85,400 (i) (10)	85.4	$8.08 \times 10^{-6}$	Low
TCC	$2.23 \times 10^{-1}$	20 (a) (8) <sup>d</sup>	0.02	$1.12 \times 10^{+1}$	High
		97 (f) (8) <sup>d</sup>	0.097	$2.30 \times 10^{+0}$	High
		10 (i) (8) <sup>d</sup>	0.01	$2.23 \times 10^{+1}$	High
TCS	$3.00 \times 10^{-1}$	399 (f) (8) <sup>d</sup>	0.399	$7.52 \times 10^{-1}$	Medium
		390 (i) (8) <sup>d</sup>	0.390	$7.57 \times 10^{-1}$	Medium

(1) Henschel et al. (1997), (2) Sanderson et al. (2003), (3) Oehlman et al. (2008), (4) Russom et al. (1997), (5) Ferrari et al. (2004), (6) Ginebreda et al. (2010), (7) Choi et al. (2008), (8) Brausch and Rand (2011), (9) Zhu and Chen (2014), (10) Lee et al. (2008), (10) Kim et al. (2007)

<sup>a</sup> NOEC data; <sup>b</sup> EC<sub>50</sub> was obtained for freshwater bacterium *Vibrio fischeri* and PNEC value was derived using an assessment factor of 100 according to the cited literature; <sup>c</sup> The derived PNEC was obtained directly from the cited literature; <sup>d</sup> LD<sub>50</sub> data

levels may be ascribed to their ability to precipitate and degrade into new compounds in aquatic environment (Milic et al. 2013). Although in Nigeria information on the prescription profiles of drugs are not handy, it is suspected that the pattern of usage of the persistent antiepileptic drug carbamazepine may have influenced its level of detection in the study area.

In order to assess the ecological risks of some of the EOPs, their predicted no-effect concentrations (PNECs) derived from acute toxicity data reported for green algae, fish and invertebrate in the literature were compared with the their maximum measured environmental concentrations (MECs); MECs/PNECs ratio to obtain risk quotients (RQs). The choice for the maximum MEC was to assess the

worst case scenarios in the environmental compartments analysed. Compounds for which complete toxicity data were not available were not selected for the risk assessment. The estimated potential risk levels (RQs) are presented in Table 3.

Most of the compounds detected had low potential risks levels to the organisms considered. However, potential risks due to bisphenol A and chloramphenicol were approaching the medium risk level for algae and fresh water bacterium *Vibrio fischeri*, respectively. Erythromycin concentration reached potential medium risk level for invertebrate. Also, triclosan concentration reached potential medium risk levels for fish and invertebrate. Potential high risk levels were obtained for the all organisms considered (algae, fish and invertebrate) for the maximum MEC of triclocarban. These findings have shown that the most important compounds in the study area that may pose detrimental effects to aquatic organisms are bisphenol A, chloramphenicol, erythromycin, triclocarban and triclosan. All these fall under the group of pharmaceuticals and personal care products (PPCPs). Bisphenol A has been previously reported in Nigerian surface waters (Arukwe et al. 2012). This indicates that the compound may be one of the most ubiquitous of relevant emerging contaminants in Nigeria. Major concerns are due to triclosan and triclocarban since they were not only detected in all samples analysed, they also occurred at concentrations high enough to pose potential significant risks to aquatic organisms. Similar behaviour of these two bactericides has recently been observed in other studies conducted in Brazil and the United States where urgent regulatory actions were recommended (Montagner et al. 2014; Halden 2014).

It is apparent from this study that Ikpa River Basin is contaminated with trace but detectable levels of emerging organic pollutants. Their occurrence may be linked to their usage and indiscriminate disposal. However ecological risk assessment has revealed the presence of endocrine disruptors, pharmaceutically active compounds and personal care products such as bisphenol A, triclosan, erythromycin and triclocarban at concentrations high enough to pose detrimental effects to some aquatic organisms. Although in trace amounts during the study, it is believed that long-term exposure to these contaminants may lead to detrimental effects on some aquatic organisms and possibly transferred to humans through the food chain. Therefore, steps must be taken to check the entry of wastes and products of wastes into the freshwater ecosystem.

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