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Determination of pharmaceutical residues in sediment using solid phase extraction and high performance liquid chromatographic technique

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ABSTRACT: Pharmaceutical residues (PRs) are emerging contaminants reaching the aquatic environment through treated and untreated wastewater from several sources. Pharmaceutical residues can remain in the dissolved phase or be adsorbed on the sediment. This study focused on the occurrence, characterization, and quantification of PRs in the sediment of Oke-afa canal in Isolo, which joins Amuwo-Odofin through Mile-2 River and Badagry Creek of Lagos, Nigeria. Surface sediments were collected bi-monthly for twenty-four months from five locations using grab method into polyethylene bags. They were air-dried, pulverized, and sieved with a 2 mm sieve. Ten pharmaceutical compounds (Ibuprofen, Diclofenac, Acetaminophen, Amoxicillin, Metronidazole, Sulfadoxine, Ofloxacin, Ciprofloxacin, Pyrimethamine, and Caffeine) were extracted from the sediments with 2% NH_4OH in (MeOH), followed by extraction with 2% formic acid in MeOH and then MeOH only. The resulting extracts were subjected to solid phase extraction on OASIS HLB cartridges, C_{18} with a mobile phase consisting of 10 mM ammonium acetate and MeOH (pH=4.8) and then High-Performance Liquid Chromatographic analysis. The results showed that caffeine and pyrimethamine had maximum concentrations of 3.25±2.0 ng/g and 1.50±0.9 ng/g respectively. Ofloxacin, amoxicillin and ibuprofen had concentrations 0.70±0.3, 0.33±0.1 and 0.04±0.1 ng/g respectively. Diclofenac, acetaminophen and pyrimethamine were detected in 60% of the samples analysed. The order of concentrations of PRs in the sediment was Caff > Pyrim > Oflo > Amox > Aceta > Sulf > Metro > Diclo > Ibu. The correlation was observed between PRs. Continuous monitoring of these contaminants in the environment ensures the safety of man and the environment.

Keywords: Badagry Creek, Cartridges, high performance liquid chromatography, Mile-2 River, Oke-afa canal, pharmaceutical residues, pollution, sediment.

INTRODUCTION

The analysis of environmental pharmaceutical residues (PRs) has drawn significant scientific attention because of the potential risks that they pose to ecosystems and human health in general (Buchberger, 2007; Carvalho *et al.*, 2013; Darwano *et al.,* 2014). Pharmaceuticals can enter the wastewater system and thereafter pass through the wastewater treatment plants (WWTPs) into the natural environment at detectable concentrations (Bossio *et al.*, 2014). Many of these PRs can partition themselves into environmental solid matrixes such as sediment and soil (Minten *et al.*, 2011). Different extraction procedures for organic pollutants such as pharmaceutical residues from environmental matrices which include sediments have been reported. These methods are based on microwave-assisted extraction (MAE) (Azzouz and Ballesteros, 2012; Varga *et al.*, 2010) and pressurized liquid extraction (PLE) commonly known as accelerated solvent extraction (ASE) (Zuloaga *et al.*, 2012). Although these methods are complex and require very little solvents, they are not popular because the instrument are complicated them selves

and are also expensive to purchase (Blackwell *et al.,* 2004; Chen *et al.,* 2015). However ultrasonic-assisted extraction is usually an alternative technique for the extraction of pharmaceutical residues from sediment (Zuloaga *et al.,* 2012). Some of its merits are short extraction time, little solvent requirement, robustness, affordability, and ease of use (Aznar *et al.*, 2017; Zhou *et al*, 2011; Duan *et al.*, 2013). Many pharmaceutical residues find their way into natural waters through wastewater treatment plants (WWTP), hospitals, industrial, households, and agricultural effluents. Excretion from humans and other animals after therapeutic usage is one of the major sources of pharmaceutical pollution in water and soil. Approximately 5 to 90% of ingested doses are excreted through urine or faeces as a metabolite or parent compound depending on the chemical properties of the compound (Dinh *et al.*, 2011; Da Silva and Oliveira 2018; Wise, 2002). Several other analytical techniques which have been employed in analysing pharmaceuticals are liquid chromatography-mass spectrometer, gas chromatographic methods, and many others. Toxic chemicals are known to be the cause of several cancers, scale rot, and fin rot in fish (WHO, 2015). Toxic chemicals can also accumulate in fish, making many fish too dangerous for human consumption (WHO, 2015). Studies have shown that sediment contamination can lead to adverse effects on aquatic organisms (Chaves *et al.,* 2020; Fonseca *et al*., 2019; Madikizela *et al*., 2020).

Nigeria is a developing country with different challenges which include environmental pollution and seasonal outbreak of diseases. Malaria infections from mosquito bites is a reoccurring illnesses among the inhabitants. Ten drugs belonging to different therapeutic classes were analysed. They include (1). Ciprofloxacin, ofloxacin, metronidazole, amoxicillin (antibiotics); (2). Pyrimethamine, sulfadoxine (anti-malaria); (3). Ibuprofen, paracetamol, diclofenac (analgesics); (4) Caffeine (stimulant). The binding of PRs to sediment can effect their bioavailability and bioaccumulation (Dai, 2015; Tamura, 2013). Also, when the sediment is scoured by the river water, pharmaceutical residues are released back into the water environment causing secondary pollution (Yang *et al*., 2021; Wu *et al*., 2020). To understand the contamination of urban sediment, ten pharmaceutical residues (Ibuprofen, diclofenac, acetaminophen, amoxicillin, ciprofloxacin, ofloxacin, metronidazole, sulfadoxine, pyrimethamine and caffeine) commonly encountered in our locality were investigated and quantified in this study. Thus, this study was designed to: (a) determine the levels of the pharmaceutical residues (PRs) in sediment. (b) assess the environmental risk of the drug residues, and (c) generate data for future studies, compare the results obtained with other literature, and also know the extent of correlations between the pharmaceutical residues. Therefore this study will enhance formulation of policy towards safe and better environment.

MATERIALS AND METHODS

Study area

The study area covers some three industrial areas; Isolo, Ikeja and Amuwo-Odofin with the river channel passing through Isolo, Amuwo-Odofin, and Ojo with populations of 732,848, 57,800 and 499, 503 (Oshodi, 2023) respectively in Lagos State. Lagos State is located in the South-Western part of Nigeria, on the narrow plain of the Bight of Benin. Lagos stretches over 180 km along the Guinea Coast of the Bight of Benin on the Atlantic Ocean. Isolo is a city located to the northwest of Lagos, Southern Nigeria on latitude (6.514193), and longitude, 3.308678. The area is characterized by heavy industrial activities. Some industries located within the area are pharmaceutical, beverage industries, chemical producing industries, lots of car battery/automobile sales outlets, and mechanic shops. The pharmaceutical industries produce several household drugs such as anti-inflammatories (ibuprofen, diclofenac, and acetaminophen), antibiotics (ciprofloxacin, ofloxacin, amoxicillin, and metronidazole), stimulants (caffeine), anti-malaria (sulfadoxine, pyrimethamine) and so on (Figure 1 and Table 1). Wastewater from industries and various households was discharged into the nearby surface water with partial or no treatment. The area is also characterized by heavy vehicular emissions and other human activities. Urbanisation has led to an increase in the population of the area over the decades.

Sample collection and preparation

A 1 kg of surface sediment was collected from five different locations in the river in polyethylene bags bi-monthly for twenty-four (24) months. Sediments were sampled from the top 5 cm surface layer. They were transported to the laboratory, air-dried, homogenized with pestle and mortar after which they were sieved with a 2 mm sieve and stored at 4±1°C before use. Extraction of the sediment was done in three cycles.

Extraction of pharmaceutical residues from sediment

The pharmaceutical residues were extracted from the sediments using an ultrasonic water bath (65 W, 35 kHz) in three different extraction cycles. A 5 g of sediment (dry weight) was weighed into a 50 mL centrifuge tube. In the first cycle, 10 mL of 2% NH_4OH in MeOH was added and the mixture was then vortexed for 15 seconds. The slurry was ultrasonicated for 15 min and later agitated at 250 rpm for 10 min. The slurry was then centrifuged at 4500 rpm for 10 min. The supernatant was filtered through a 0.45 µm glass filter and decanted into a 500 mL Erlenmeyer flask. The sediment residue was then further extracted with 10

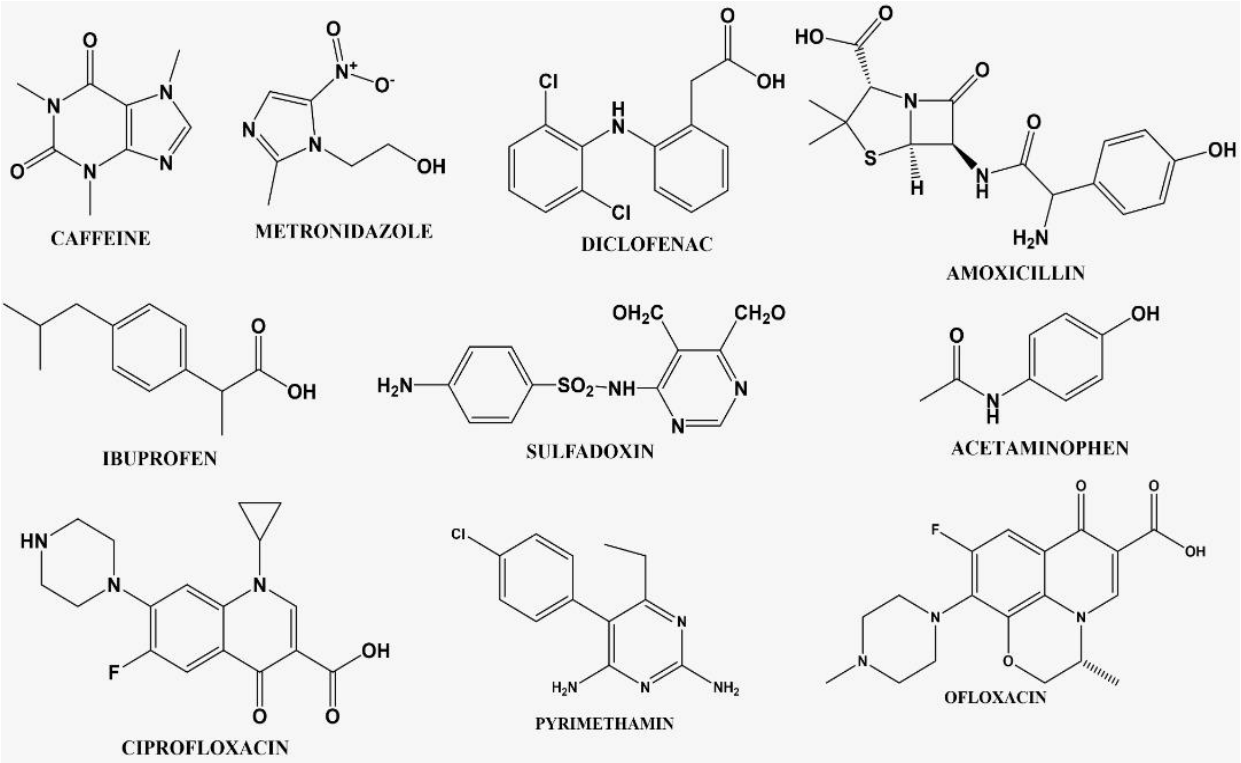

Figure 1. Pharmaceutical compounds and their structures.

Table 1. Classification of drugs

Analyte	Characteristics	OTC/Ethical	pH
Ibuprofen	NSAID (Non-steroidal anti-inflammatory)	OTC	Acidic
Diclofenac	NSAID (Non- steroidal anti- inflammatory)	OTC	Acidic
Amoxicillin	Antibiotic	Ethical	Acidic
Acetaminophen	Analgesic	OTC	Acidic
Metronidazole	Antibiotic	Ethical	Basic
Ofloxacin	Antibiotic	Ethical	Acidic
Ciprofloxacin	Antibiotic	Ethical	Acidic
Caffeine	Stimulant	Ethical	Acidic
Pyrimethamine	Anti parasitic (anti malaria)	Ethical	Acidic
Sulfadoxine	Anti parasitic (anti malaria)	Ethical	Acidic

mL of 2% formic acid in MeOH in the second cycle and then with 5 mL of MeOH in the third cycle. All the supernatants from the three steps were then combined. The MeOH was allowed to evaporate overnight. The extracts were filtered using 0.45 µm glass filters with the aid of a vacuum pump into Erlenmeyer flasks and diluted with distilled water to a total volume of 400 mL (MeOH < 5%) (EPA, 2007).

Solid phase extraction (SPE)/clean-up

The sediment extracts were diluted to 400 mL with distilled water and adjusted to pH of 10 with NH_4OH solution before solid phase extraction (SPE). The 6 mL (10 g sorbent) OASIS HLB cartridges which were used for the SPE were pre-conditioned with 6 mL of MeOH and 10 mL of distilled water. The diluted sediment extracts were then loaded onto the SPE cartridges at a flow rate of 10 mL/min with the aid of a vacuum pump. Cartridges were later rinsed with 10 mL of 5% MeOH in distilled water and dried at room temperature for 30 min. The dried cartridges were eluted with 2 x 2.5 mL MeOH and 1 mL of 2% NH_4OH in MeOH. The eluates were dried under a gentle stream of nitrogen at 40°C and reconstituted to 1 mL with water: MeOH (20:80). Filtration was done with a 0.45 µm glass filter. The filtered extracts were subjected to high-performance liquid chromatographic analysis (EPA, 2007).

Instrumental analysis

High performance liquid chromatographic equipment coupled with a diode array detector (DAD) was used for the quantification of the analytes present in the cleaned-up extracts. A reverse phase C18 column (150 mm, 4.6 mm, 5.00 mm, Zorbax Eclipse x DB – C18) was used for the separation and quantification of the extracts. Mobile phase comprising 10 mM ammonium acetate/acetic acid buffer (pH 4.8) and ACN were also used at a flow rate of 1.0 mL min^{-1}. The injection volume was 0.7 µL as separation and quantification were achieved under room temperature. Two mobile phases (A and B) comprising 10 mM ammonium acetate/acetic acid buffer (pH 4.8) and ACN respectively were used at a flow rate of 1.0 mL/min.

Method validation

Validation was based on instrumental as follows:

1. Linearity, sensitivity (instrument detection limits (LOD) and quantification limit (LOQ)), and precision using standard solutions of the pharmaceuticals.
2. The calibration curves were done by the analysis of at least five concentration levels in duplicate ranging from 5, 10,15,20,25 µg/L.
3. The LOD and LOQ were calculated using signal-to-noise ratios of 3.3 and 10, respectively.
4. The precision was determined by repeated analysis of the sample of two concentrations which was expressed as the relative standard deviation.

RESULTS AND DISCUSSIONS

Concentrations of pharmaceutical residues in surface sediment

The PRs in sediments were analysed using the HPLC technique. The chromatographic conditions of the HPLC are shown in Table 2. Figures 2 and 3 show the chromatograms of each pharmaceutical standard.

The concentrations of the various pharmaceutical residues in sediments are presented in Table 3. Diclofenac, acetaminophen, and pyrimethamine were detected in over 60% of the samples with average concentrations of 0.05±0.04, 0.14±0.02, and 1.50±0.9 ng/g, respectively. Ciprofloxacin was not detected in the sediments. Caffeine had a maximum concentration of 4.98±0.3 ng/g in sediment E with a mean value of 3.25±2.0 ng/g. Amoxicillin ranged from 0.26±0.3 to 0.39±0.02 ng/g. Pyrimethamine recorded a maximum concentration of 2.51±0.01 ng/g in sediment B with a mean value of 1.50±0.9 ng/g. Ofloxacin and metronidazole had average concentrations of 0.70±0.3 ng/g, and 0.08±0.1 ng/g respectively. Pharmaceutical residues were detected in many of the samples at different concentrations. Ciprofloxacin was not detected in the sediment. Many of the PRs were acidic in nature. Acidic pharmaceuticals are consumed in large quantities and are also found in various concentrations in the aqueous environment. This study is consistent with similar works of Vazquez-Roig *et al*. (2012), which investigated the distribution and fate of seventeen (17) pharmaceuticals in water, sediment, and soil samples in the pego-oliva marsh, Spain. They found that acetaminophen (87%) was frequently detected at sites impacted by discharge from wastewater treatment plants (WWTPs) and caffeine was detected at high concentrations of 16.7 ng/g.

The detection frequencies of pharmaceuticals are often consistent with their persistence in WWTPs or septic systems and associated differences in partitioning behaviour and biotransformation of the individual compound (Caliman *et al*., 2009). In this study, caffeine had the highest concentration of 4.98±0.3 ng/g in sediment D with a mean value of 3.25±2.0 ng/g. Caffeine had been used as a chemical marker for human excretory products discharged from WWTPs (Buerge *et al*., 2003). The high concentration of caffeine in this sediment may be due to the excretion of caffeine from (coffee, beverages) in wastewater which accumulated in stream sediment over a period. It could also be a result of wastewater discharged from the various pharmaceutical industries operating within the area. This suggests that these compounds are not removed during wastewater treatment. It has been reported that natural processes such as photodegradation greatly reduces caffeine in rivers (Ngo *et al*., 2021). Acetaminophen had much higher removal efficiencies of 87 to 99% in WWTPs (Benotti and Brownawell, 2007; Gómez *et al*., 2007). This may be attributed to the short biodegradation rate of acetaminophen ($t_{½}$ = 1 to 11 days) (Benotti and Brownawell, 2009). The concentrations of PRs in the sediments are presented in Figures 4 to 8 while Figure 9 represents the average concentrations of each pharmaceutical residue in all the samples. The values obtained from this study were compared with those from other studies as shown in Table 4. Some pharmaceuticals are hydrophilic compounds such as ciprofloxacin, this means that they are more likely to be found in water than in a solid matrix. A recent study investigated the sorption of seventy-five (75) pharmaceuticals and discovered that only fourteen (14) have a strong affinity with sludge (solid phase), whereas thirty-seven (37) were present in the liquid phase (Hörsing *et al*., 2011). The ability of pharmaceuticals to sorb to sediment is affected by their octanol–water partitioning coefficient (K_{ow}), pKa, and pH of the water (Lorphensri *et al*., 2007). The greater the log K_{ow} for a given compound, the greater the tendency to partition to a solid phase such as sediment. The sorption potential of pharmaceuticals in sediments is affected by several factors such as pH, total organic carbon (TOC) content, redox potential, ionic interactions among others (Al-Khazrajy and Boxall, 2016). Other physicochemical

Table 2. Chromatographic conditions of the HPLC equipment

Compound	MP	FR (mL/min)	Wave length (nm)	IV (µml)	RT (min)	LOD
Ibuprofen	Methanol, 10 mM KH_2PO_4 at pH3.0(40:60)	0.70	248	20.0	2.0	0.09
Sulfadoxine	Methanol, 10 mM KH_2PO_4 at pH3.0 (40:60)%	0.70	278	20.0	2.20	0.05
Acetaminophen	Methanol, 10 mM KH_2PO_4 at pH3.0 (40:60)%	0.70	260	20.0	4.30	0.03
Diclofenac	Methanol, 10 mM KH_2PO_4 at pH3.0 (40:60)%	0.70	283	20.0	4.80	0.02
Pyrimethamine	Methanol, 10 mM KH_2PO_4 at pH3.0 (40:60)%	0.70	230	20.0	12.70	0.038
Amoxicillin	Methanol, 10 mM KH_2PO_4 at pH3.0 (40:60)%	0.70	229	20.0	4.14	0.116
Caffeine	Methanol, 10 mM KH_2PO_4 at pH3.0 (40:60)%	0.70	254	20.0	3.29	0.27
Metronidazole	Methanol, 10 mM KH_2PO_4 at pH3.0 (40:60)%	0.70	298	20.0	2.71	0.0016
Ofloxacin	Methanol, 10 mM KH_2PO_4 at pH3.0 (40:60)%	0.70	294	20.0	1.94	0.055

LOD: Limit of detection. IV: Injection volume. RT: Retention time.

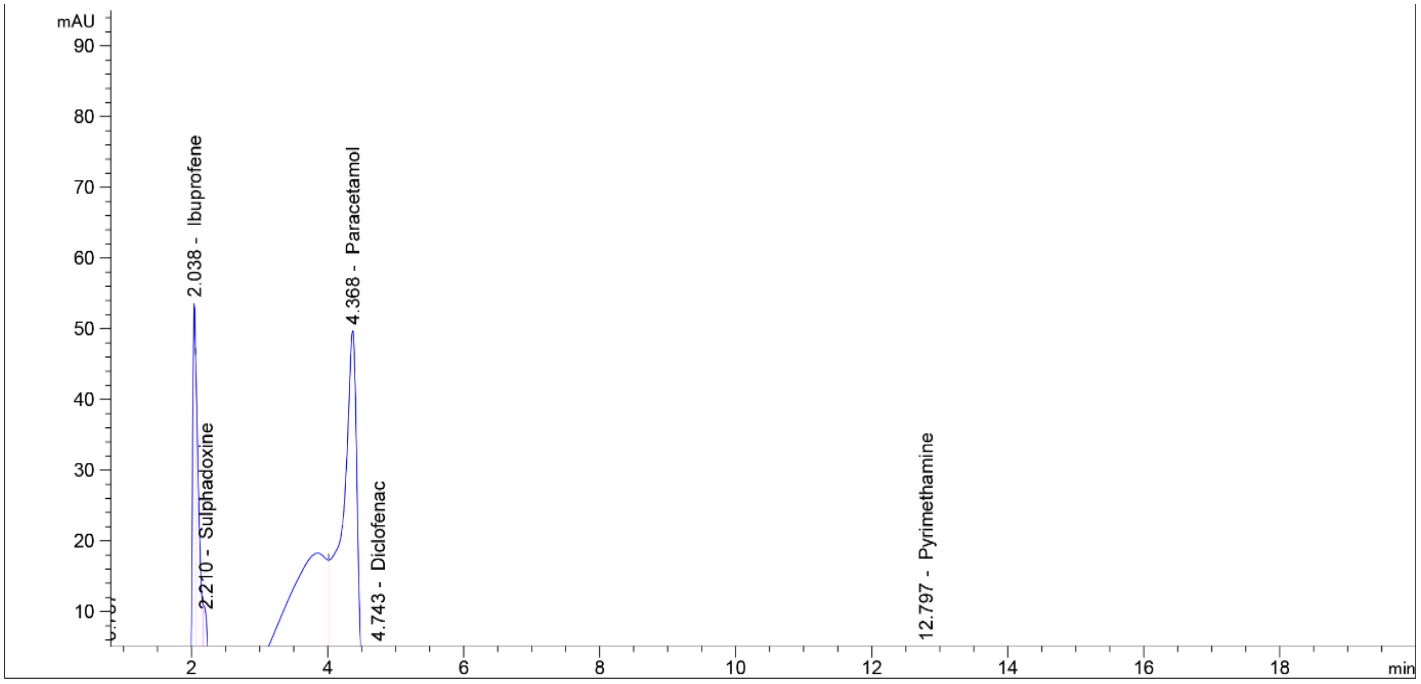

Figure 2. Concentrations of mixed standards of Ibuprofen, Sulfadoxine, Acetaminophen, Diclofenac and Pyrimethamine.

properties that influence the variation of partitioning of PRs in sediments include adsorption coefficient [Kd], and dissociation constant [pKa] (Álvarez-Esmorís *et al.,* 2020; Felis *et al.,* 2020). Many studies have reported that the sorption of sulfonamide antibiotics tends to reduce as the pH increases (Figueroa-Diva *et al*., 2010, Park *et al*., 2016; Chen *et al.,* 2017), but in some cases, surface complexation may affect the general behaviour of sorption for organic compounds (Klement *et al* ., 2018). During the sorption process, different types of interaction mechanisms can occur between the compounds and the sediments. These interactions include, surface complexation, and chemical bonding. These may however influence the sorption behaviour of the compound under investigation. Higher concentrations of PRs in the sediment may be a result of hydrophobicity of the compounds. pH and hydrophobicity are very important factors for the sorption of organic compounds to sediments (Klement *et al*., 2018). The process pf PRs transport into soils, sediments and ground water includes adsorption, migration and degradation. For example, chemicals in the soil surface may be transported downward to the lower layers and further into the saturated and unsaturated zones. Laws *et al.* (2011) revealed that although they are reduced by natural attenuation, PRs can still reach the ground water. The fate of PRs during this movement and the changes in the surface environment is mainly influenced by the environmental factors and the

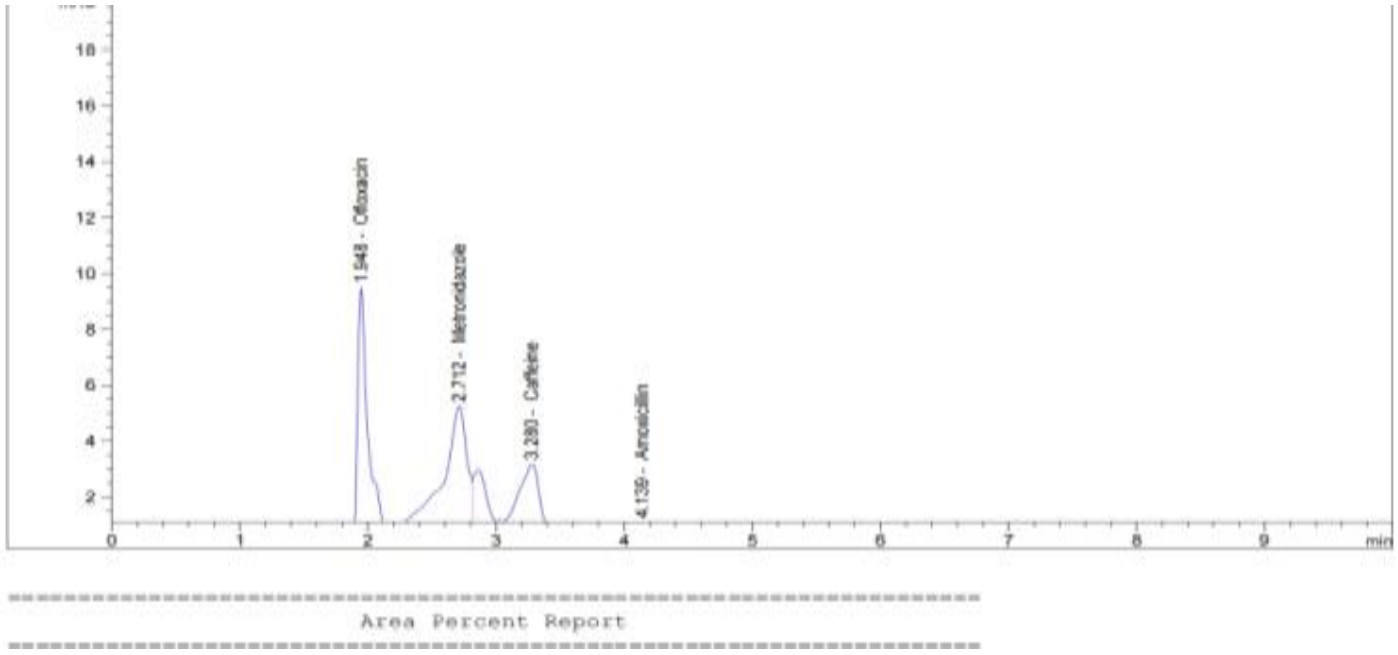

Figure 3. The chromatogram for the mixed standard of Ofloxacin, Metronidazole, Amoxicillin and Caffeine.

Table 3. Concentrations (ng/g) of pharmaceutical residues in sediment

Sample ID	Sed A	Sed B	Sed C	Sed D	Sed E	Range	Mean±SD
Ibuprofen	<LOD	<LOD	0.13±0.1	-	-	<LOD-0.13	0.04±0.1
Diclofenac	0.09±0.1	0.02±0.03	0.03±0.01	-	-	0.02-0.09	0.05±0.04
Amoxicillin	-	-	-	0.39±0.2	0.26±0.3	0.02-0.09	0.33±0.1
Sulfadoxine	0.38±0.5	<LOD	<LOD	-	-	<LOD-0.38	0,13±0.2
Ofloxacin	-	-	-	0.46±0.1	0.94±0.2	0.46-0.94	0.70±0.3
Ciprofloxacin	<LOD	<LOD	<LOD	-	-	<LOD	<LOD
Caffeine	-	-	-	1.52±0.1	4.98±0.3	1,52-4.98	3.25±2.0
Acetaminophen	0.16±0.1	0.13±0.3	0.14±0.4	-	-	0.13-0.16	0.14±0.02
Metronidazole	-	-	-	0.02±0.01	0.14±0.01	0.02-0.14	0.08±0.1
Pyrimethamine	1.45±1.7	2.51±0.01	0.71±0.2	-	-	0.71-2.51	1.50±0.9

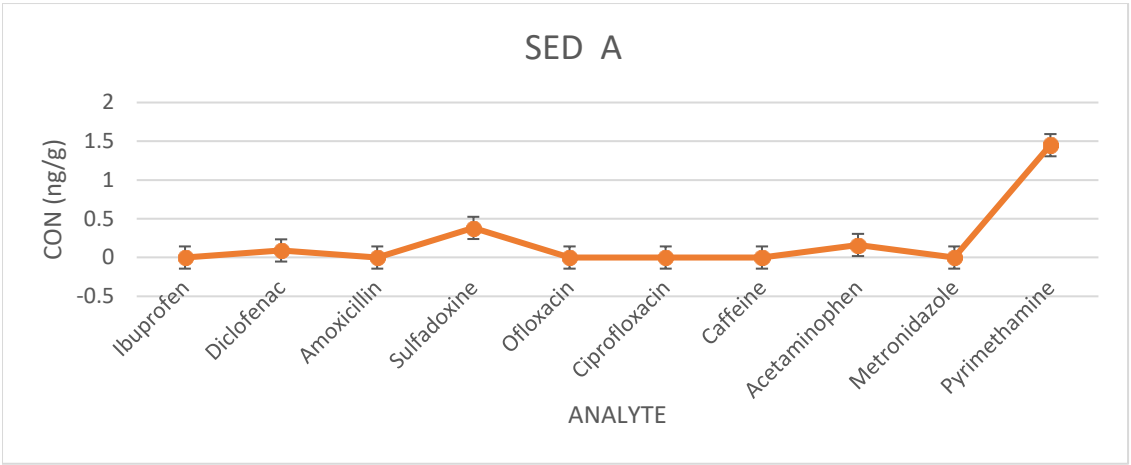

Figure 4. Concentrations of PRs in Sediment A.

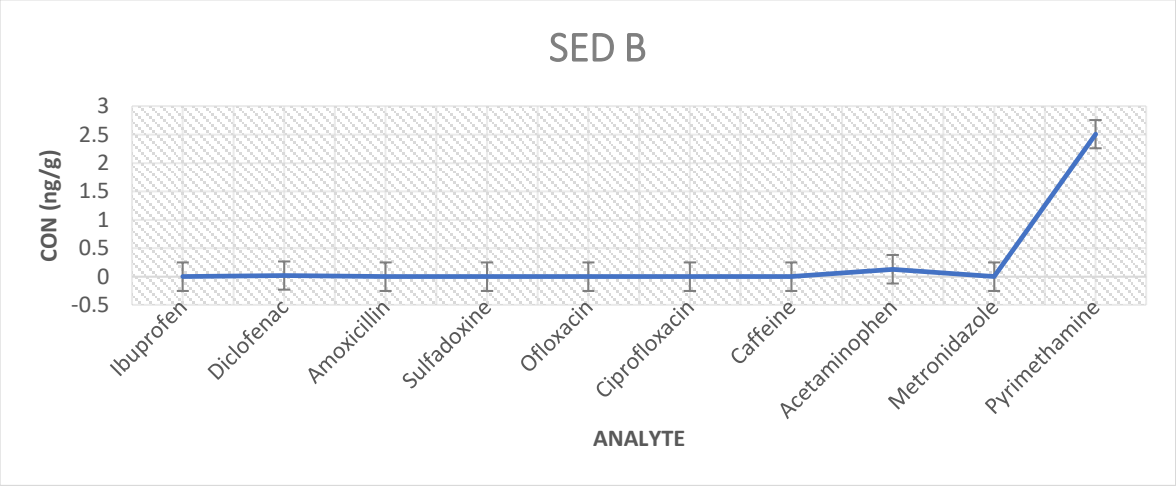

Figure 5. Concentrations of PRs in Sediment B.

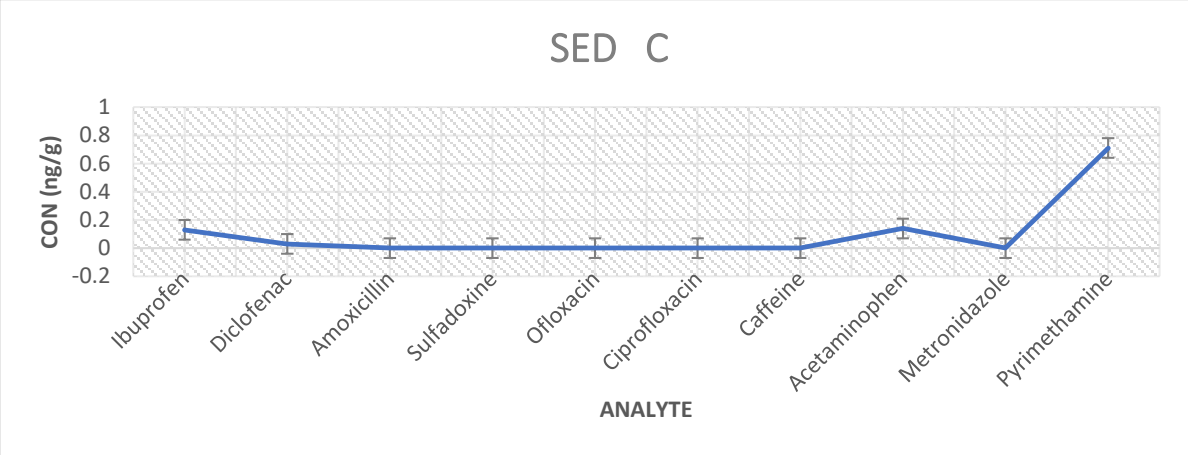

Figure 6. Concentrations of PRs in Sediment C.

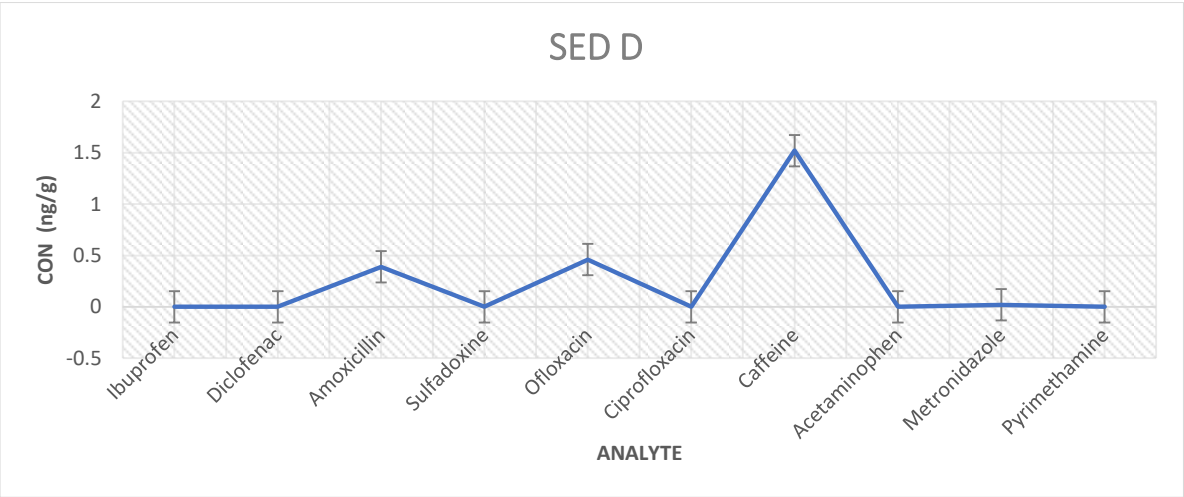

Figure 7. Concentrations of PRs in Sediment D.

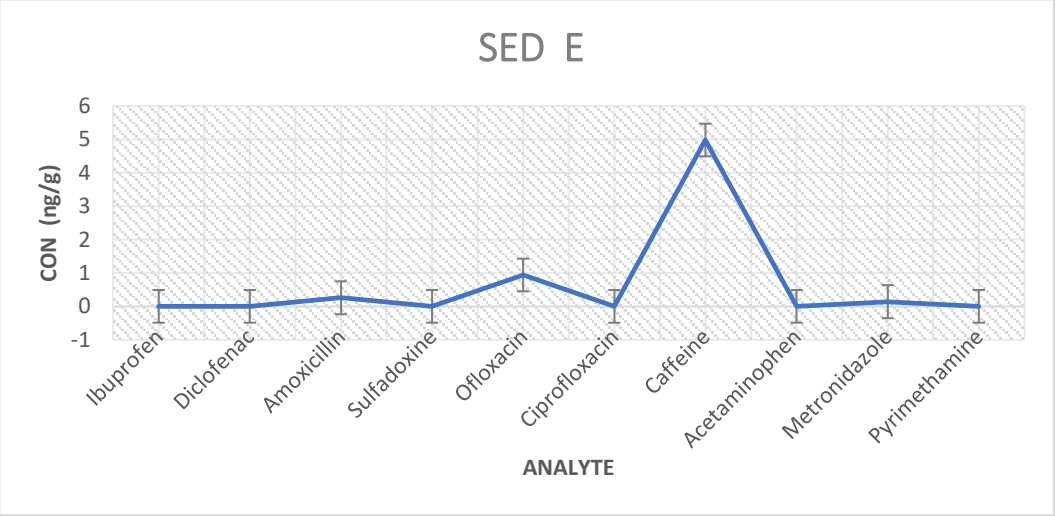

Figure 8. Concentrations of PRs in Sediment E.

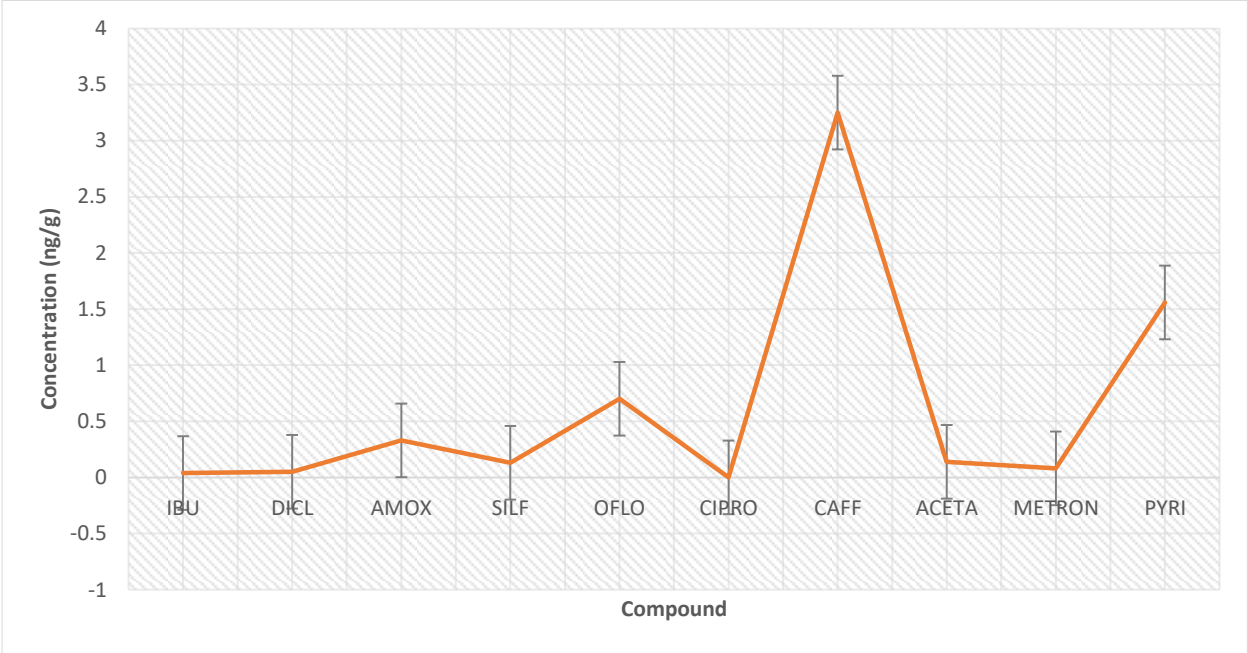

Figure 9. Average concentrations of PRs in all the samples.

physicochemical properties of the chemicals. Adsorption can influence the fate of PRs in the underground environment by affecting their movement, plant uptake, and also bioavailability (Lin *et al.,* 2011). The compound with strong sorption to sediment are usually less mobile in soil and also have very limited leaching abilities while those with weak sorption capacity are more likely to move down gradient and penetrate into the ground water. The hydraulic connection between ground water and surface is that surface water supplies ground water (Chen *et al.,* 2021).

The results obtained from this study were also compared with other similar previous studies on pharmaceutical residues. It was observed that the sediment contained more residues than the surface water perhaps as a result of accumulations over the years and the ability of the sediment to act as a sink for many pollutants that include organic and inorganic contaminants, trace heavy metals, pollutants among others (Chiaia-Hernández *et al.,* 2023). Sediments also play an important role in mediating pollutants across environmental compartments in aquatic ecosystems (An *et al.,* 2020).

Table 4. Comparison of results with other literature

Compound	Sample type	This study	Other literature	References
Acetaminophen	Sed	0.10 ng/g	222 ng/g	Savci, 2013
	SW	0.40 ng/L		
Ibuprofen	Sed	0.40 ng/g	19.20 ng/g	Savci, 2013
	SW	0.40 ng/L		
Caffeine	Sed	0.20 ng/g	0.2-24.38 ng/g	Yang *et al.,* 2015
	SW	0.30 ng/L		
Diclofenac	Sed	0.04 ng/g	3.63 ng/g	Yang *et al.,* 2015
	SW	1.10 ng/L		
Ofloxacin	Sed	0.70 ng/g	1290 ng/g	Martín et al., 2010
	SW	0.50 ng/L		
Ciprofloxacin	Sed	<LOD	653 ng/g	Martín et al., 2010
	SW	0.20 ng/L		

The results obtained in this study were compared with the one obtained from a similar study of pharmaceutical residues in the surface water of the study area (Nnodum and Yusuf, 2022). It was observed that the sediment contained more residues than the surface water perhaps as a result of accumulations over the years and the ability of the sediment to act as a sink for many organic pollutants among other factors. Pharmaceutical residues have the ability to adsorb to the sediment matrix. The ability of PRs to adsorb onto sediment is related to their physicochemical parameters such as the molecular structure, water solubility, and hydrophobicity. However other environmental conditions such as the ionic strength (IS) and pH may also have some effects on the adsorption rate of PRs to sediment. Chen *et al.* (2011) examined the effects of solution chemistry like the ionic strength a(IS) and pH on the retention and transport of two antibiotics sulfamethoxazole and ciprofloxacin, in saturated porous media. The results showed that pH and ionic strength (IS) played vital roles in controlling the transport of ciprofloxacin but showed little effect on sulfamethoxazole under experimental conditions. There are many pharmaceutical production industries within the study area which discharge their wastewater into the river channel. Few of them might not properly treat their wastewater such that organic pollutants such as pharmaceuticals residues are not completely removed before discharge into nearby rivers resulting in their presence in the aquatic environment and subsequent adsorption to the sediment. Other methods of such as the construction of wet land could further help in the natural filtration of contaminants. Zhang *et al.* (2020) reported that constructed wet lands (CWs) could achieve a high removal efficiency of sulfamethoxazole (SMX) (> 98%) and the concentrations of sulfamethoxazole were higher in the sediment than in the surface water.

Environmental risk assessment of pharmaceutical residues in sediment

To estimate the ecological risk levels of the pharmaceutical compounds in the aquatic environment, the risk quotient (RQ) was evaluated. The RQ of each pharmaceutical residue (PR) in the sediment was determined as the ratio of the measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC), as follows [Eq1]:

$$\mathrm{RQ} = \frac{\mathrm{MEC}}{\mathrm{PNEC}} \qquad \text{Eq.1}$$

If the RQ < 0.01, it represents a negligible risk, 0.01 < RQ < 0.10 indicates a low risk, 0.10 < RQ < 1.00 denotes a medium risk, and RQ > 1.00 means a high risk to aquatic organisms. Environmental risk assessment allows for predicting the concentration of compounds below which adverse effects are not likely to be felt in the ecological communities during acute or chronic exposure (Finizio and Vighi, 2014). PNEC is defined as the ratio of selected ecotoxicological data (median effective concentration (EC50), median lethal concentration (LC50), no observed effect concentration (NOEC), and hazardous concentration for 5% of the species (HC5) to an assessment factor (AF). Therefore, PNEC depends on the available results of ecotoxicological tests on different organisms (Molnar *et al*., 2020). The PNEC values were obtained from Ecological Structural Activity Relationship (ECOSAR) database. Because ecotoxicological data are absent in the case of the sediment matrix, $PNEC_{water}$ values were applied to estimate $PNEC_{sediment}$. The RQ of each pharmaceutical residue in the sediment are presented in Table 5. Isolo community has many pharmaceutical industries and other production industries located within it. All of the discharge their waste water into the Isolo canal which flows into mile two river and finally empties into the Badagry Greek. The detection of some pharmaceutical residues within the water channel is an indication that the residues may have originated from incomplete treatment of wastewater discharged by the industries, house-holds, farm lands and so on. The risk quotient for many of the PRs were below one except for ibuprofen on daphnia and ofloxacin on fish with values of 2.0×10^2 and 6.1×10. The values were greater than one

Table 5. Toxicity assessment of pharmaceutical residues.

Compound	Ectoxicological end point	PNEC (ng/L)	Ref	MEC (ng/g)	RQ
Ibuprofen	Fish	180[e,g]	Hoeger *et al*.,2005	0.04	2.2×10^{-1}
	Algae	40,000[e,f]	Pomati *et al*.,2004		1.0×10^{-3}
	Daphnia	0.2[d]	De Lange *et al*., 2005		2.0×10^{2}
Diclofenac	Fish	50[e,g]	Hoeger *et al*.,2005	0.05	1.0×10^{0}
	Algae	200[d]	Lawrence *et al*., 2007		2.5×10^{-1}
	Daphnia	20,000[e,g]	Haap *et al*., 2008		2.5×10^{-3}
Acetaminophen	Fish	378,000[b]	Henschel *et al*.,1997	0.1	2.6×10^{-4}
	Algae	134,000[b]	Kim *et al*., 2007		7.4×10^{-4}
	Daphnia	2040[b]	Dave and Herger, 2012		4.9×10^{-2}
Ciprofloxacin	Fish	1,000,000[b]	Li *et al*., 2019	-	-
	Algae	5[b]	Jiang *et al*., 2014		-
	Daphnia	10,000[b]	Li *et al*., 2019		-
Ofloxacin	Fish	11.30	Jiang *et al*., 2014	0.7	6.1 × 10
	Algae	-	-		-
	Daphnia	-	-		-

[a.]EC50 was estimated with ECOSAR. [b.]UF = 1000. [c.]LC50 was estimated with ECOSAR. [d.]UF = 50 (uncertainty factor used for lowest observed effect concentrations (LOEC) and no observed effect concentrations (NOEC) in acute toxicity). [e.] long-term data. [f.] UF = 100. [g.] UF = 10 (uncertainty factor used for LOEC and NOEC in chronic toxicity).

Table 6. Correlation of pharmaceutical residues in sediment.

	IBU	DICLO	AMOX	OFLO	CAFF	ACETA	METRO	PYRI	SULFA
IBU	1								
DICLO	0.030	1							
AMOX	-0.407	-0.688	1						
OFLO	-0.373	-0.631	**0.873**	1					
CAFF	-0.336	-0.569	**0.769**	**0.983**	1				
ACETA	0.381	**0.781**	-0.986	-0.906	-0.816	1			
METRO	-0.293	-0.496	**0.652**	**0.938**	**0.986**	-0.712	1		
PYRI	-0.117	0.451	-0.796	-0.731	-0.659	**0.758**	-0.575	1	
SULFA	-0.250	**0.936**	-0.407	-0.373	-0.336	0.522	-0.293	0.271	1

signifying that their levels might be high. The concentrations of other PRs under investigation were within limit (RQ < 1). Monitoring of the area may be necessary to reduce more contamination.

Correlation of pharmaceutical residues in the sediment matrix

Pearson's correlation coefficient was used to calculate the correlation matrix of data between the pharmaceutical residues as shown in Table 6. A positive correlation was observed between sulfa/diclo (r = 0.936), aceta/diclo (r = 0.781), oflo/amox (r = 0.873), caff/amox (r = 0.769), caff/oflo (r = 0.983), metro/oflo (r = 0.938), metro/caff (r = 0.986), and pyri/aceta (r = 0.758). The strong positive correlations among the pharmaceutical residue indicate probable common sources in the aquatic environment under investigation as a well as been of anthropogenic source, mutual dependence and similarity in behaviour (Zeng *et al.,* 2015; Lu *et al*., 2010). Hence increase in concentration of one pharmaceutical residue will naturally call for increase of the PR. The correlation table is presented in Table 6.

Conclusions

This study focused on determination of pharmaceutical residues in sediment of a river channel passing through Isolo, Amuwo-Odofin, and Ojo into Atlantic Ocean using solid phase extraction and high performance liquid chromatographic technique. Ten pharmaceutical compounds (Ibuprofen, Diclofenac, Acetaminophen, Amoxicillin, Metronidazole, Sulfadoxine, Ofloxacin, Ciprofloxacin, Pyrimethamine, and Caffeine) were extracted from the sediments. Nine pharmaceutical residues were detected in the five sediment sampling locations (ofloxacin, pyrimethamine, and caffeine were detected at the highest average concentrations of 0.70±0.3 ng/g, 1.50±0.9 ng/g, and 3.25±2.0 ng/g respectively. The toxicity assessment suggests that the calculated value for ibuprofen in daphnia (2.0×10^2) might not be favourable for their existence in the area. Also, ofloxacin showed RQ >1 for fish (RQ= 6.1×10), signifying that its concentration might have exceeded thresh-hold levels. There is need for more research to be done in this area to know the effects of pharmaceutical residues and their metabolites on aquatic organisms during chronic and acute exposure.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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