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Antibiotic Residues in Waste Impacted Surface Waters from Lagos, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

In the past few decades, there has been increasing interest and concern about the environmental presence of human and veterinary pharmaceutically active chemicals (PHACs). and the implication of such on ecosystem health at organismal and population levels This study was conceived, to identify and quantify the concentrations of an important sub-group i.e., the pharmaceuticals. Which have been shown to have ecological implications on various aquatic life-forms. In surface water bodies in Lagos Nigeria.

Study Design: water specimens taken from six locations in the city of Lagos in Nigeria were analysed using SPE coupled with tandem LC/MS.

Place and Duration of Study: The project, split site collaboration. Spanned a period of nine months between 30.09.2013 to 30.04.2014. Analysis of water specimens was done at the IWW Water Centre. Mulheim, Germany.

Methodology: Analysis of water samples were carried out by IWW Water Centre, Mulheim, Germany according to published guidelines or validated in-house methods. Waters Acquity ultra performance liquid chromatography (UPLC-TQD/PDA and UPLC-TQS) (Milford) was used to carry out LC-MS/MS analyses. For GC-MS analyses an Agilent GC-MS system (6890 GC and 5973 MSD single quadrupole mass analyzer was used.

Results: In surface water samples, 12 pharmaceutical agents were detected. Of these Six antibiotics, Viz: Chloramphenicol,Erythromycin,Erythromycin-A dehydrate,Sulfadiazine, and Sulphaamethoxazole.

Trimetoprim were detected out of thirteen screened for, at environmentally significant concentrations.

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Conclusion: This study has established the precence and locational prevalence of primary antibiotic and antibiotic degradates in surface waters in Lagos, Nigeria More studies are required to investigate the ecological implications of such presences.

Keywords: Antibiotic; prescriptions; vertebrates; invertebrates.

1. INTRODUCTION

An increasing number of pharmaceutical products are being used on a daily basis as the pharmaceutical industry continues to introduce new and enhanced products for the Prophylaxis and active treatment of traditional infectious/transmissible, and increasingly important non communicable, diseases. These pharmaceuticals have been demonstrated to be incompletely removed from waste waters by current sewage treatment regimes, with some entirely unchanged. Antibiotics are among the most widely prescribed and used pharmaceutical classes in human and veterinary therapeutics, and non-prescription antibiotic use is widespread, especially in developing countries where these medicines are widely available for purchase and use without prescriptions [1,2,3] (Morgan et al., 2011), due to a lack of regulation and monitoring for compliance. In these settings, antibiotics are seen as “cure alls” for virtually every real and imagined illness, and are used indiscriminately by individuals ignorant of the implications of such self-medication, especially the development of antibacterial resistance, and the associated human and environmental sequelae [4]. Antibiotics have been described in wastewaters and sewage treatment influents and effluents consequent on human and veterinary use by several investigators including, Hirsch et al, [5], Chang et al., [6], Kemper, [7], and Gao et al., [8]. In third world urban situations, where waste water treatment is almost completely absent, PhACs, including antibiotics, could potentially enter surface waters without any preliminary treatment, and the effects consequent on this fact, especially on non target species such as fish and other aquatic fauna, could potentially be even more profound than conjectured or realised at present. Several in vitro studies detail the acute and chronic effects of antibiotics on aquatic species. Indeed, the antibiotics are the singular most studied pharmaceutical class for acute toxicity effects on aquatic vertebrates and invertebrates [9,10] with about 40 studied till date [11]. Lagos, the commercial capital of Nigeria, with an estimated population of about twenty one million people, is one of the world’s fastest growing metropolises, already gaining megacity status. Lagos is estimated to be one of the fastest growing megacities in the world. High population density clusters in largely unplanned urban and peri-urban locations, poverty and the overstretched public infrastructure and works, are largely descriptive of living conditions in Lagos. The generally poor sanitary conditions in most of the city and suburbs ,aggravated by the tropical climate characterized by seasonal high precipitation levels, and a lack of primary sewage treatment make wastewater impaction on surface waters a stark and ongoing reality. This study, which is consequent on an earlier investigation into pharmaceutical use and disposal patterns in households in Lagos, seeks to identify and quantify the levels of antibiotic residues in surface waters from six deliberately chosen locations within Lagos municipality and to compare detected concentrations with existing information from other studies for perspective.

2. MATERIALS AND METHODS

2.1 Sampling Locations

Selection criteria for the locations surveyed included five intra- municipal locations Amuwo-Odofin, via Badagry, Isolo, Ojo, and Agbara.

500 ml. sub- surface water samples were collected in duplicate, on each collection date from each of the five locations. s into amber PET capped bottles. Suggested by the USGS publication National field manual for the collection of water-quality data (USGS, 2006). All locations were lotic water sites. On the spot water parameter estimation were done using a handheld Henna instruments ® model HI-98129 meter (Table 1). Following collection, water bottles were placed in Styrofoam coolers with ice packs and transferred to the laboratory where kept at -20 degrees centigrade until analysed.

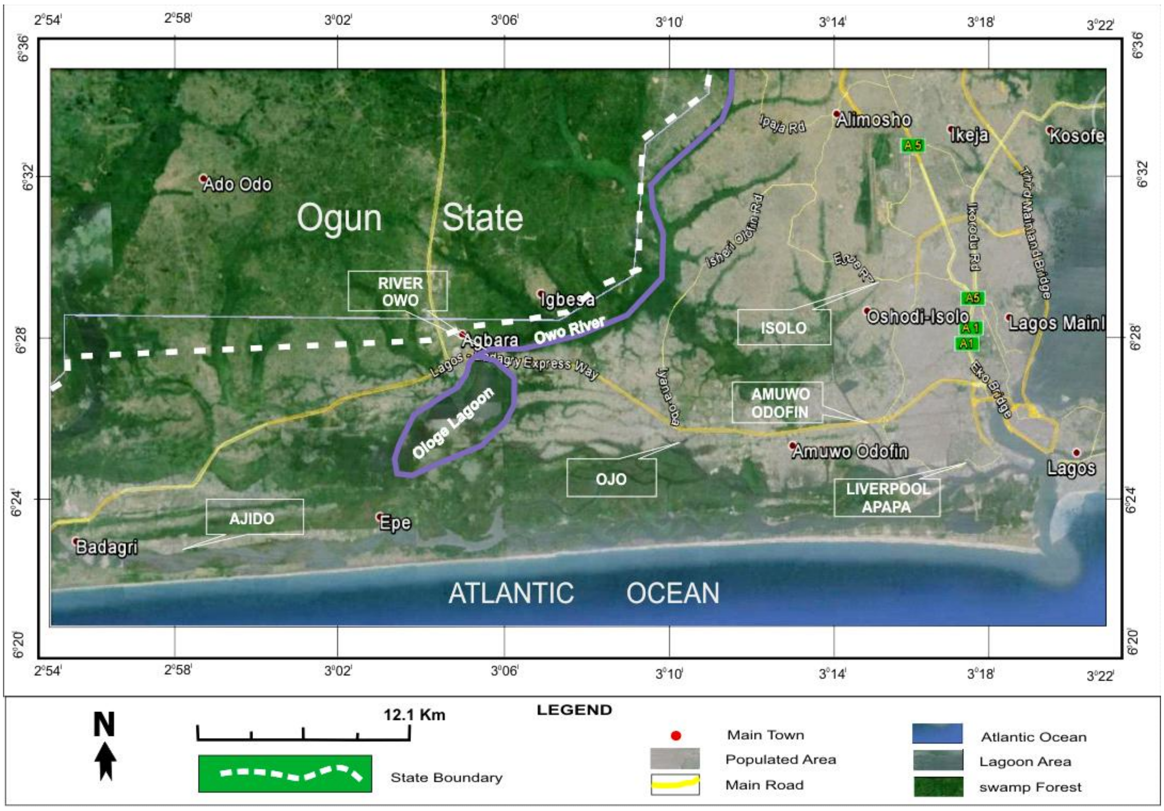

Fig. 1. Sampling locations

Table 1. Showing locational details of water collection points and water quality measurements of samples

Sample ID	Location	GPS	Temp. (C)	DO (PPM)	Conductivity (µs)	pH
243598	River Owo	$6^0$29’54.77”N; $3^0$6’11.98”E	26.4 ^{0}C	68	134	7.06
243600	Ojo	$6^0$22’31.24”N;$3^0$12’28.76”E	31.4 ^{0}C	2000	3999	7.83
243601	Liverpool	$6^0$26’39.34”N;$3^0$21’49.32”E	34.7 ^{0}C	64	3999	6.6
243597	Ajido	6°24'23.87"N;2°56'52.32"E	29^{0}C	123	488	7.65
243602	Isolo	$6^0$31’45.41”N;$3^0$18’57.06”E	27.7^{0}C	245	492	7.45
243599	Amuwo Odofin	$6^0$28’47.5”N;$3^0$17’47.5”E	28.2^{0}C	2000	3999	7.6

Pre-processing of water samples for LC/MS

2.2 Sample preparation and Cleanup

An off-line Solid Phase Extraction (SPE): procedure was used for clean-up and pre-concentration of samples. All experiments were performed using automated sample preparation equipment, fitted with an external pump for dispensing samples through the SPE cartridges and with a switching valve for the selection of samples. Recovery studies were performed using surface water samples spiked to final concentrations of 0.1 and 1 lg/L) of each pharmaceutical. The recoveries were achieved working in the neutral pH range using Oasis HLB 500 mg extraction cartridges. The conditions for Oasis HLB extraction were: SPE cartridges were conditioned with 6 mL methanol followed by 6 mL HPLC water at a flow-rate of 1 mL/min. One litre of filtered water sample was loaded at 60 mL/ min. The cartridges were then washed to reduce highly polar interferences by running 1 mL 5% methanol in HPLC water through the cartridge. Elution of the analytes from the cartridge was done by first eluting with two 3 mL aliquots of methanol containing 5 mM Tetrabutylammonium chloride (TBACl). The eluted volume was then dried in a water bath at 30^{0}C under a stream of nitrogen. The sample was reconstituted with 300 µL of a water-methanol solution (30:70, v/v). Finally, 20 µL were injected into the LC-MS-MS system.

2.3 Analysis of Water Samples

LC/MS Analysis: of water samples were carried out by IWW Water Centre, Muelheim, Germany according to published guidelines or validated in-house methods (**Error! Reference source not found.**). Waters Acquity ultra performance liquid chromatography (UPLC-TQD/PDA and UPLC-TQS) coupled with an electrospray ionization tandem mass spectrometric system (Milford) was used to carry out LC-MS/MS analyses. For GC-MS analyses an Agilent GC-MS system (6890 GC and 5973 MSD single quadrupole mass analyzer) equipped with an automatic sampler (MPS 2) and Cooled Injection System (CIS 4, Gerstel) was used. Data acquisition, processing and evaluation were carried out using Agilent ChemStation software combined with Gerstel Maestro software package. The limit of detection (LOD) was defined by a signal to noise ratio of 3:1 for all applied methods. Tables 1 and 2 show the results of water sample analysis by location. Fig. 1 shows the results of some simple statistical analyses on results from Table 1 depicted as box and whisker plots.

3. RESULTS AND DISCUSSION

In the present study 6 antibiotics falling into two bloc areas, the sulfa (3), macrolide (1), macrolide derivative (1) categories, and one unique entity (chloramphenicol), were determined and discovered at environmentally significant concentrations. The concentrations of the four sulfonamides, sulfamethoxazole, sulfadiazine, and trimethoprim, ranged from a minimum of 0.02 µg/L (Amuwo Odofin) to 1.5 µg/L in the sample from Isolo. Occurrence patterns were similar to earlier reports which indicate the sulfa antibiotics as very widespread in occurrence worldwide. Trimethoprim was detected in two samples (Amuwo Odofin and Isolo) at levels ranging from 0.12-0.40 µg/L. These figures are comparatively higher than recorded for sewage treatment facility (STF) influents and surface waters in several previous studies. Li and Zhang, (2011), reported concentrations of Trimethoprim in STF influents as ranging between 0.1-0.154 µg/L, and 0.0844-0.12 µg/Lin effluents. Other studies include Karthikeyan and Meyer, [12], 0.44 µg/L, in influents, and 0.39µg/L in effluents. Gulkowskaa et al*.,* [13] reported maximum concentrations in STF influents from five municipal STFs at 0.32 µg/L and Chang et al*.*, [6] 0.00034 µg/L in river samples, and 0.42 µg/L in STF influents.

Sulfamethoxazole has been widely described in both influents and effluents of STFs all over the world, including the USA by several investigators including the USA [12], and in other countries by investigators, including Batt et al*.*, [14] (2.8 µg/L); Spongberg and Witter [15] (0.2610 µg/L), Göbel et al*.*, [16] (0.57 µg/L), Lindberg et al*.*, [17] (0.674 µg/L), Clara et al*.*, [18] (0.145 µg/L), and Choi et al*.*, 2008 (0.193 µg/L). The sulfamethoxazole concentrations detected in this study ranged from between a minimum of 0.09 µg/L and a maximum of 1.5 µg/L, exceeding the levels reported in the references above. Sulfamethoxazole is the sulfa antibacterial detected at the highest concentrations in environmental waters (Garcia-Garlan et al*.*, 2011).

Sulfadiazine (SDZ) is a sulfonamide widely used as a human and veterinary antibiotic to prevent and treat diarrhoea and other infectious diseases. Sulfadiazine has been reported in wastewaters at levels ranging between 5.10–5.15 µg/L [19]. Garcia-Galan et al*.*, (2011) reported recovery levels of sulfadiazine in surface waters at concentrations ranging from 0.00006-0.00022µg/L. Our studies detected sulfadiazine at levels ranging between 0.02-0.04 µg/L.

Discrete erythromycin was detected at a low of 0.06 µg/L in the water sample from Amuwo Odofin , and at a high in the Isolo sample (1.0 µg/L). Erythromycin-A-dihydrate was detected in water samples from Amuwo Odofin and Isolo at reportable levels of 0.12 and 0.48 µg/L respectively. This compound has been reported as commonly present in waste waters, STF influents and effluents in several other countries. Measured concentrations in other studies include 1.7 µg/L [20], 0.59-1.978 µg/L, and 0.43–2.054 µg/L respectively from two STFs in mainland China [21], 0.226-1.537 µg/L, and 0.361–0.811 µg/L in STFs from Taiwan (Lin et al*.*, 2009). From the USA, Karthikeyan and Meyer, [12] reported E-A-D concentrations at 0.06–0.19 µg/L. In the UK, Kasprzyk-Hordern, et al*.*, [22], and Kasprzyk-Hordern et al*.*, [23] reported 0.144–10.025 µg/L, and 0.23-2.841 µg/L. from two consecutive studies. The concentrations recorded in the present study fall within the lower value ranges recorded for earlier studies, with the concentrations recorded for Asian locations

Table 2. Detected antibiotics

Pharmaceutical Agent	Therapy Group	Analytical Methods		Water Samples from Nigeria					
		Method	LOD	AJIDO	RIVER OWO	AMUWO-Odofin	OJO	LIVERPOOL	ISOLO
			[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]
Chloramphenicol	**Antibiotics**	**LC-MS/MS**	**0,01**	**< 0,01**	**< 0,01**	**0,03**	**0,03**	**0,03**	**0,36**
Chlortetracycline	Antibiotics	LC-MS/MS	0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Clarithromycin	Antibiotics	LC-MS/MS	0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Erythromycin-A dihydrate	Antibiotics	LC-MS/MS	0,06	< 0,06	< 0,06	0,12	< 0,06	< 0,06	0,48
Erythromycin	Antibiotics	LC-MS/MS	0,06	< 0,06	< 0,06	0,06	< 0,06	< 0,06	1,00
Oxytetracycline	Antibiotics	LC-MS/MS	0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Roxithromycin	Antibiotics	LC-MS/MS	0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02
Sulfadiazine	Antibiotics	LC-MS/MS	0,01	< 0,01	< 0,01	0,02	< 0,01	< 0,01	0,04
Sulfadimidine	Antibiotics	LC-MS/MS	0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Sulfamethoxazole	Antibiotics	LC-MS/MS	0,01	< 0,01	< 0,01	0,65	0,14	0,09	1,50
Tetracycline	Antibiotics	LC-MS/MS	0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Trimethoprim	Antibiotics	LC-MS/MS	0,01	< 0,01	< 0,01	0,12	< 0,01	< 0,01	0,40

Table 3. Showing high, low and mean concentrations of detected pharmaceuticals

Pharmaceutical agent	Type	LOD	Low	High	Mean
Chloramphenicol	AB	0.01	0.03	0.06	0.045
Erythromycin	AB	0.06	0.06	1	0.53
Erythromycin-A dihydrate	AB	0.06	0.12	0.48	0.3
Sulfadiazine	AB	0.01	0.02	0.04	0.03
Sulfamethoxazole	AB	0.01	0.09	1.5	0.795
Trimetoprim	AB	0.01	0.12	0.4	0.26

ABBRIVIATION: AB: antibiotic.

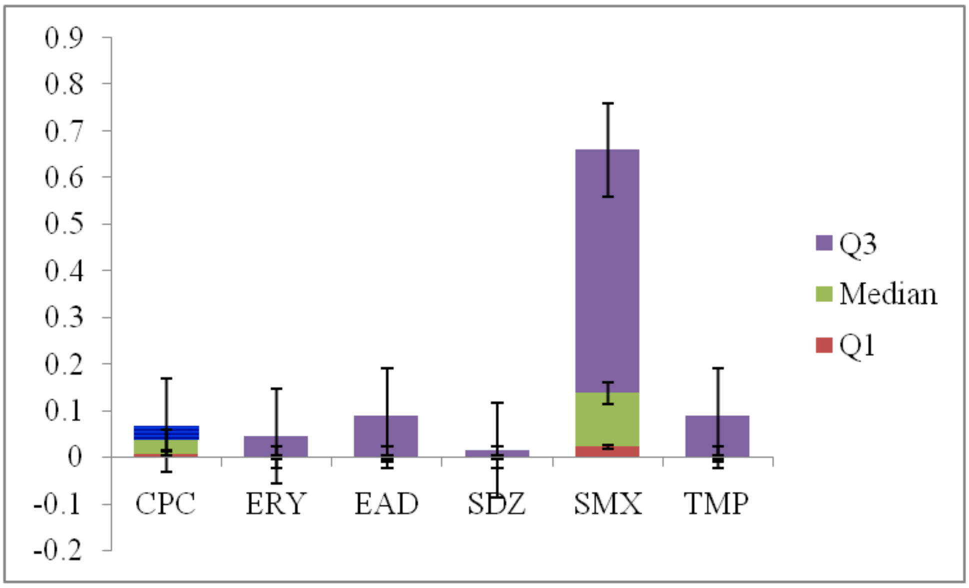

Fig. 2. Box plot showing the median (green), upper (purple) and lower (red) quartiles, and 95 % confidence intervals (error bars), of detected antibiotics across sampling locations

ABBRIVIATION : CPC: Chloramphenicol; ERY: Erythromycin; EAD: Erythromycin-A-dihydrate; SDZ: Sulfadiazine, SMX: Sulfamethoxazole: TMP: Trimethoprim

closest in comparison with present study results. Isolo and Amuwo Odofin were “hotspots” accounting for the highest number of detected antibiotic compounds, and highest total, and individual antibiotic residue concentrations. The latter findings are expressible as functions of very high populations in these locations. and proportionately higher levels of sewage generation compared to other less densely populated locations such as Badagry. In the case of the Isolo sampling location, other possible exacerbating factors apart from population, include the presence of a large municipal “general” hospital, and an active landfill used for the disposal of hospital and hazardous household wastes (among other more innocuous waste types), upstream of the sampling site. It has been documented that leachate plumes could extend considerable distances from landfill sites, and that even closed/inactive landfills could be sources of pharmaceutical water contamination for considerable periods [24,25] (Slack et al., 2005), and this fact could be responsible for the higher levels of pharmaceutical contamination of water, and conceivably other environmental matrices in Isolo. In the absence of more detailed hydrological data it can be reasonably accepted that leachates from the aforementioned landfill could modify the environmental prevalence and concentrations in impacted waters. Another probable exacerbating factor is the lack of municipal liquid sewage stream treatment and poor sanitation, especially in the more crowded and unplanned locations in the city. In locations such as Isolo where waste water impaction is quite high, and water flow rates slow, a possible scenario could be that PHAC concentrations in the water samples could be close to that in undiluted waste water and liquid sewage. Of course dilution in the definitely larger volume of the receiving waters is a factor which could reduce concentrations therein, but probably not by much. In conclusion, antibiotic profiles and presences in the studied locations are higher than in locations where there is effective wastewater and sewage treatment, a fact established through a perusal of extant literature and reviews. In addition, in the absence of reliable prescription, purchase, and usage statistics, these significant antibiotic presences cannot be precisely tied to usage (though as mentioned earlier, they are widely available and abused), but are probably more a consequence of poor sanitation and ineffective sewage treatment in the city of Lagos. Where waterworks do exist.

4. CONCLUSION

In summary, this study has confirmed the presence of antibiotics in waste water impacted surface water bodies in Lagos, Nigeria. The surface waters are used as water sources for recycling and domestic reuse especially for drinking. A possible scenario is that antibiotics are probably detectable in drinking water where available, and the associated sequelae on the consuming public can only be conjectured at this point. More work is required to determine STF clearance, and concentrations of important PHACs in surface, ground and drinking waters, to move information and studies from the "snapshot" establishment of presence status to the level of sustained observation and monitoring.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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