



ORIGINAL ARTICLE

Analysis of Oxytetracycline and Doxycycline in Surface water sources and treated drinking water in Harare Metropolitan using Ultrasonic Assisted Dispersive Solid Phase Extraction (UA-DSPE) and RP-HPLC-UV Technique

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ABSTRACT

The occurrence of oxytetracycline (OTC) and doxycycline (DC) in surface water sources and treated drinking water from Harare Metropolitan was investigated. Samples were analyzed using ultrasonic assisted dispersive solid phase extraction and high performance liquid chromatography coupled to ultra violet detection. Average recoveries, $n = 3$ of oxytetracycline and doxycycline from river water samples were greater than 90%. Limit of detection for OTC and DC was 50 and 80ng/L while limit of quantification was 821 and 369ng/L respectively. Doxycycline was detected at the highest concentrations of 0.57617 μ g/L in Mukuvisi River. DC was detected in both the upper and lower reaches. Occurrence of oxytetracycline depended upon the distance from sewage discharge points. Sampling sites that were found in the upper reaches and near sewage discharge points recorded higher levels of oxytetracycline. Marimba River recorded the highest concentration of oxytetracycline, 0.61413 μ g/L. All sampled sites from Lake Chivero and Prince Edward dam revealed presence of oxytetracycline and doxycycline. Lake Chivero and Prince Edward dam are located in the lower reaches of Harare and receives all the runoff and effluents. Detected oxytetracycline likely originated from veterinary applications in swine and poultry farms while doxycycline came from sewage effluents. Antibiotics were most frequently detected in areas that received municipal effluents and in the lower reaches of farming activities. Oxytetracycline and doxycycline antibiotics were not detected in all treated drinking water samples. Persistence of oxytetracycline and doxycycline in Harare surface waters may result in the buildup of toxic levels or may trigger microbial resistance and therefore underscores the need to consider regulating their use in animal husbandry and improving management and treatment of sewage effluents.

Key words: Oxytetracycline, doxycycline, ultrasonic assisted dispersive solid phase extraction, HPLC-UV

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INTRODUCTION

Occurrence of pharmaceuticals in surface and treated drinking water is becoming of great concern world over because of their propensity to induce microbial resistance in aquatic environment [1;2;3]. Pharmaceutical induced resistance in the environment can be transferred to humans through drinking water and food chain. This may result in compromising the effectiveness of current human medication [4]. There is also a general fear that omnipresence of pharmaceuticals in surface waters may disrupt self containing nature of ecosystems and result in unforeseen effects. Pharmaceuticals such as tetracyclines readily adsorb to sediment and loosely held molecules can be desorbed back to the aqueous phase by water currents [5]. It is possible therefore that the sediment can act as a reservoir such that toxic levels can build up in environmental waters.

Oxytetracycline (OTC) and doxycycline (DC) were chosen for analysis because they are the widely prescribed antibiotics in Zimbabwe. Oxytetracycline is administered as medication in chickens, pigs, cattle and sheep. It is also added to feeds in micro-gram per litre level where it acts as prophylactic and

growth promoter. While in other countries doxycycline is now administered as medication to livestock [6], in Zimbabwe it is used only to treat human ailments such as sexual transmitted diseases, pneumonia and complicated malaria. Both humans and animals do not metabolize efficiently drugs administered as medication such that over 70% is passed out unchanged as urine or faeces [7;8;9]. Excreted pharmaceuticals can enter surface waters either directly through runoff and municipal effluents or indirectly through spreading of manure in vegetable gardens and fields [10]. Chronic effects of tetracyclines on humans include nephrotoxicity, hepatotoxicity, skin hyperpigmentation in areas exposed to the sun and hypersensitivity reactions [11]. Tetracyclines antibacterials can also cause development of hypouricemia, hypokalemia, proximal and distal renal tubular acidosis. If children of 0-8 years and pregnant women continue to drink water contaminated with tetracyclines there is a risk of developing secondary tooth discoloration [11]. Previous investigations [12;13;14;15] reports tetracyclines levels in the nano-grams to low micrograms per litre range in USA, Asian and European aquatic environments. Concentrations of antibacterials in the environment depend on antibiotic consumption and use patterns therefore vary among areas and countries [16]. Occurrence of antibacterials in aquatic systems is also affected by their chemical stability, partition and sediment characteristics [17]. Tetracyclines tend to adsorb to soil, sediments and organic matter through cation bridging and cation exchange. Currently there are few studies reporting the state of events in African surface and drinking waters despite huge application of pharmaceuticals in animal husbandry and human medications [18]. Limited data on the occurrence of pharmaceutical drugs in surface water and drinking water is a drawback in assessing potential human health risks from exposure to trace concentrations of pharmaceuticals in drinking-water. Currently majority of countries do not have regulatory laws that restrain disposal of pharmaceuticals in surface waters. People who are involved in treating drinking water are not compelled to look for or design processes that ensure that water is free from pharmaceuticals. Routine monitoring programmes to screen drinking water for pharmaceuticals as is the case for regulated chemical and microorganisms are not always present in most countries. It is important therefore that targeted surveys or research investigations are done to screen for pharmaceuticals in surface and finished drinking water. Thus the present study aimed at determining levels of oxytetracycline and doxycycline in surface waters and finished drinking water in Harare Metropolitan, Zimbabwe.

MATERIALS AND METHODS

Chemicals and materials

Standard oxytetracycline hydrochloride, HPLC solvents (methanol and acetonitrile) primary secondary amine sorbent material (57738-U-SUPELCO supelclean PSA), and disposable filter units (MILLPORE 0.45 μm) were obtained from Sigma Aldrich (Germany). Doxycycline hyclate 99% was bought from Sigma Aldrich, St Louis-Missouri USA. Orthophosphoric acid, Nitric acid, Sodium hydrogen phosphate, citric acid and disodium ethylenediamine tetraacetate (Na_2EDTA) were of analytical grade obtained from SKYLABS, South Africa. Standard stock solutions were prepared by weighing exactly 0.1 g of the substance into a 100 ml volumetric flask and methanol was added to the mark making a concentration of 1×10^{-3} g/ml. Working standard solutions were then made from the stock solutions by serial dilution using methanol. Dilutions were made by taking 1 ml, 2 ml, 3 ml, 4 ml and 5 ml from stock solutions into volumetric flasks and topping to the mark. The concentration range of these working standards varied from 0.01-10 $\mu\text{g/ml}$.

Sample collection and storage

Several sampling sites (Fig 1) were established to investigate levels of oxytetracycline and doxycycline in surface and treated drinking water in Harare. Oxytetracycline and doxycycline were chosen because they are the widely used antibiotics. Oxytetracycline is sold under trade names teramycin and terranox. Water samples were collected from locations of different characteristics Table 1. Ten samples were selected from Mukuvisi River, another ten from Marimba River, eight from Zimphos stream and six from Glenlorne stream (Enterprise road). Ten samples each were also collected from Lake Chivero, Prince Edward Dam and Cleveland Dam. Treated drinking water was collected from a total of ten tapes, three were from high density suburbs, and two were from low density suburbs and five from tapes in the CBD. A total of five 2L bottled water (from different companies) sold in supermarkets and streets were also bought. One hundred millilitres of water samples were collected in brown polythene bottles, placed in a cooler box and transported straight to the laboratory where they were stored (not more than a week) in a deep freeze waiting analysis.

Sample preparation

Samples were filtered to remove suspensions. Five millilitres of McIlvaine buffer (pH 4) and 5ml of 0.01 EDTA were added to chelate any metals present prior to extraction. Pre-concentration and clean up was done using dispersive solid phase extraction (DSPE). Filtered water samples were vigorously shaken with 10ml of acetonitrile in a separating funnel. Magnesium sulphate and sodium chloride 0.5g each was then

added to displace the extraction equilibrium towards the organic phase. The contents were centrifugation at 3000 rpm for 10 minutes and the organic supernatants were transferred to a conical flask followed by addition of 40mg of primary secondary amine sorbent material (57738-U-SUPELCO supelclean PSA) to remove interferences such as humic acid. The mixture was ultrasonicated for 15 minutes and centrifuged at 3000 rpm for 10 minutes. The organic supernatants were collected and evaporated to almost dryness under vacuum and then redissolved in 500 μ L of methanol. The contents were filtered through a 0.45 μ m glass Millipore filter to remove any particulate matter and then placed into amber vials and stored in a fridge until HPLC-UV analysis.

Table 1 Characteristics of sampling sites.

Site name	Sampling sites	Site characteristics
Mukuvisi River	Mk ₁ , Mk ₂ , Mk ₃ , Mk ₄ , Mk ₅ , Mk ₆ , Mk ₇ , Mk ₈ , Mk ₉ , Mk ₁₀	The river passes through the city of Harare and industrial areas into Lake Chivero. It has many storm drains coming from different parts of the city.
Marimba River	Ma ₁ , Ma ₂ , Ma ₃ , Ma ₄ , Ma ₅ , Ma ₆ , Ma ₇ , Ma ₈ , Ma ₉ , Ma ₁₀ ,	The river drains the City of Harare and discharge into Lake Chivero. Receives discharges from the Workington Industrial Area and sewage effluents from Crowborough Sewage Treatment Works
Zimphos Stream	Z ₁ , Z ₂ , Z ₃ , Z ₄ , Z ₅ , Z ₆ , Z ₇ , Z ₈	Located around Msasa industrial area.
Glenlorne Stream	G ₁ , G ₂ , G ₃ , G ₄ , G ₅ , G ₆ , G ₇ , G ₈ ,	Receives run off from low density suburbs, Chisipite, Glenlorne and Alexander park.
Lake Chivero	L ₁ , L ₂ , L ₃ , L ₄ , L ₅ , L ₆ , L ₇ , L ₈ , L ₉ , L ₁₀ ,	The lake is situated 35 km downstream of the city of Harare and supplies approximately most of the domestic water needs in Harare, Chitungwiza and Ruwa. The lake feed Morton Jaffray water works with a capacity of 614ML/day
Prince Edward Dam	P ₁ , P ₂ , P ₃ , P ₄ , P ₅ , P ₆ , P ₇ , P ₈ , P ₉ , P ₁₀ ,	Source of drinking water. The dam feed Prince Edward Water Works which has a capacity of 90ML/day
Cleveland Dam	C ₁ , C ₂ , C ₃ , C ₄ , C ₅ , C ₆ , C ₇ , C ₈ , C ₉ , C ₁₀ ,	Receives runoff from Msasa and Glendale suburbs.
Budiriro	B ₁	High density suburb tape water. Place characterised by, sewer and water pipe burst and back yard chicken raring. Almost every house hold has a vegetable garden. Chicken droppings are used as manure in the gardens.
Glenview	G ₁	High density suburb tape water. Place characterised by, sewer and water pipe burst and back yard chicken raring. Almost every house hold has a vegetable garden. Chicken droppings are used as manure in the gardens.
Dzivarasekwa 2	D ₁	High density suburb tape water. Place characterised by, sewer and water pipe burst and back yard chicken raring. Almost every house hold has a vegetable garden. Chicken droppings are used as manure in the gardens.
Mount Pleasant	Mp ₁	Low density suburb tape water. Some households practice back yard chicken farming and have vegetable gardens.
Masasa	Ms ₁	Low density suburb tape water. Some households practice back yard chicken farming and have vegetable gardens.
Harare (CBD)	Cb ₁ , Cb ₂ , Cb ₃ , Cb ₄ , Cb ₅ ,	Tape Water
Bottled water	B ₁ , B ₂ , B ₃ , B ₄ , B ₅ ,	Bottled water from registered and unregistered companies.

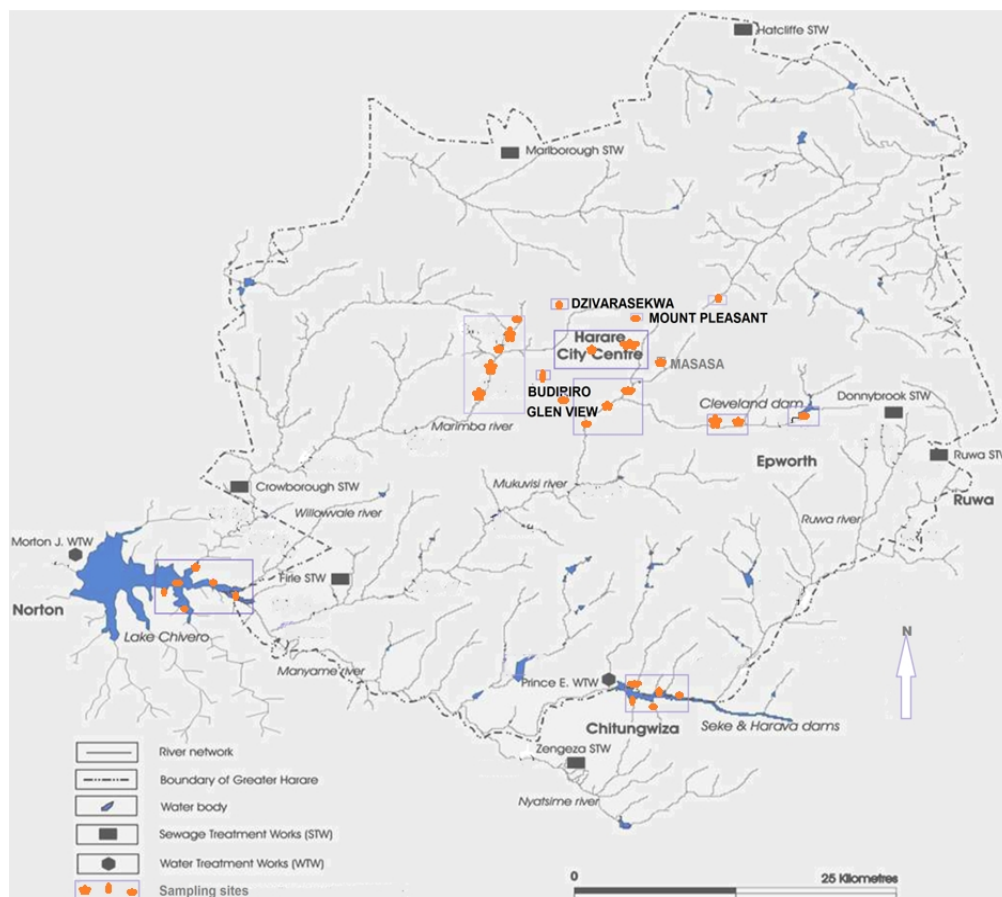


Fig 1. Location map of sampling sites, river networks, water bodies, sewage and water treatment works in the city of Harare.

Quality assurance and control

Strict quality control protocols were followed. All water sampling containers were sterilized by soaking in 5% HNO_3 for 48 hours. Containers were washed with a detergent and rinsed using distilled water followed by acetone and burned in an oven. The containers were then rinsed three times with the sample water at the site prior to collection. Field blank, preservation and field replicate blank samples were used to ascertain accuracy of analysis. At weighing stage analytical balance (Sanotorious) was calibrated before readings were taken. This was achieved through the use of a 200 g standard weight and a reading of 200.00003 g was obtained which fell within the accepted range of 200 ± 0.00005 g. Verification was also done using a 0.1g weight which gave a reading of 0.10002 g which also fell within the range of 0.1 ± 0.00005 g. The pH meter (Mettler Toledo MP 200) was also calibrated using pH 4 and 7 buffer solutions prior to taking readings. Percentage recovery was determined by analysing spiked river and ultrapure water samples. River water was collected from a less polluted area. Two spiking concentrations were used 0.01 and $10 \mu\text{g}/\text{ml}$ and results were analysed three times. Linearity was determined by analysing standard samples in the range 0.01 to $10 \mu\text{g}/\text{ml}$. Method detection limit (LOD) and quantification limit (LOQ) (Table 2) were assayed as the minimum detectable amount of analyte of interest with signal to noise ratio of 3 and 10 respectively [4]. Selectivity of the method was performed by analysing samples from the upper reaches of Mukuvisi River (Control) where there was a lower probability of pollution and no antibiotics were found.

HPLC analysis

Analysis for antibiotics was performed on a HPLC-UV Vis, Shimadzu LC Solution 10 AVP-20 AHT, Mobile phase was prepared by mixing methanol, acetonitrile and 0.01 M aqueous oxalic acid at pH 3.0 (adjusted using concentrated NH_3) in the ratio of 1:1.5:5. It was filtered through a $0.22 \mu\text{m}$ Millipore filter unit. A sonicator (Perkin Elmar) was used to mix and remove air bubbles. Wavelength of 255 nm established by scanning on a ThermoFisher UV-Vis instrument (GENESYS 10S UV-Vis v4.003 2L9Q129001) was used to analyze samples. Sample injection volume was 20 μL . Flow rate of mobile phase was kept at 1.0 ml/min. Column used was PLRP-S 100 \AA , 5 μm , 250x4.6 mm (P/N:15/2-5500). Ambient room temperature was used on the column. Typical chromatograms for standard analytes obtained are shown in Fig 2 and 3

below. Quantitation was based on peak area. Calibration curve method (Table 2) was used for quantitation.

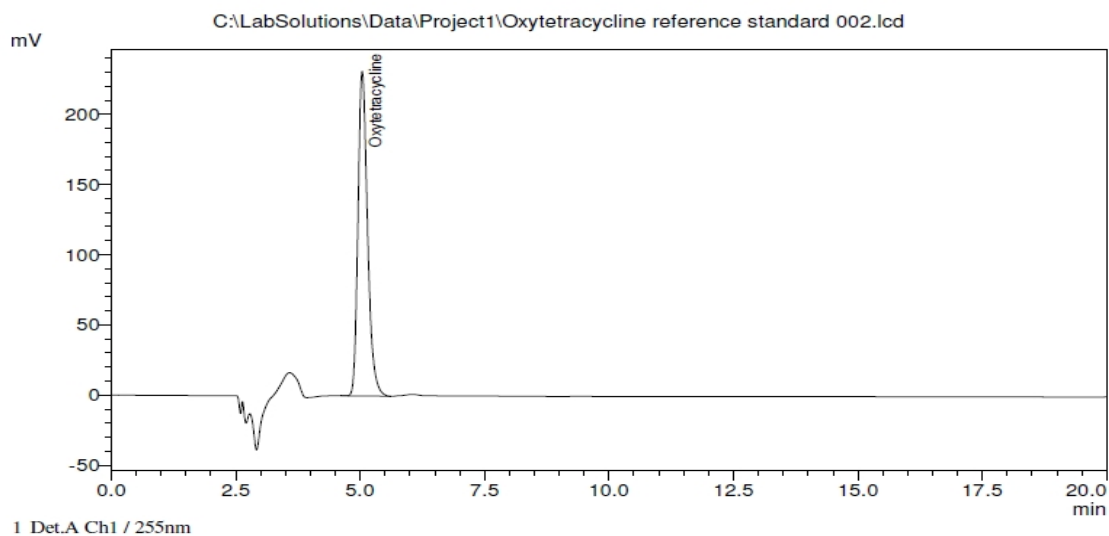


Fig 2. A typical oxytetracycline HPLC chromatogram, retention time around 5.05 minutes

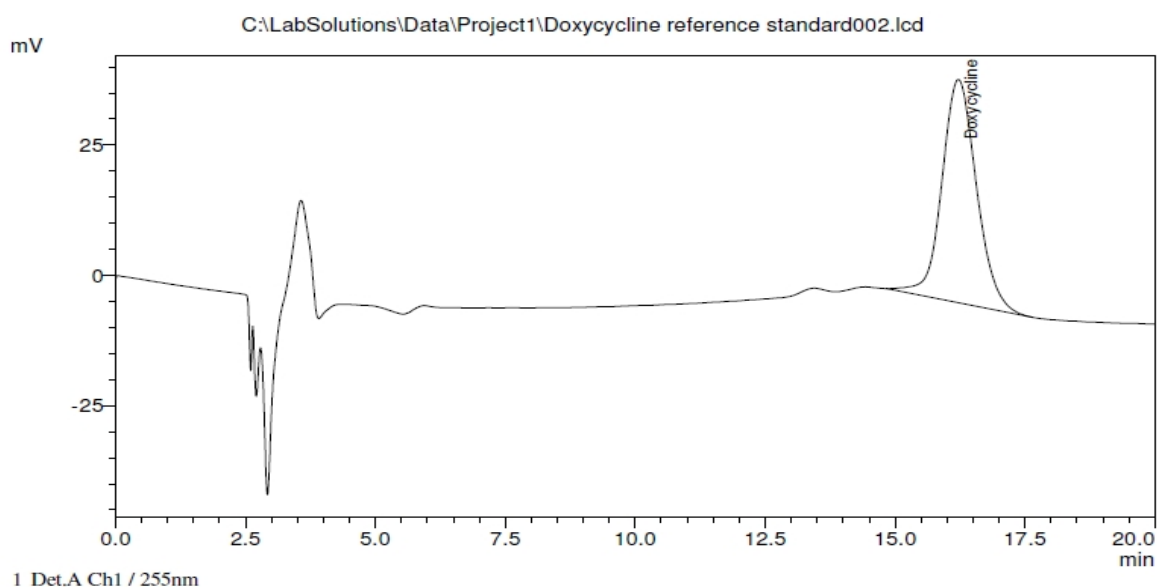


Fig 3. A typical doxycycline HPLC chromatogram, retention time around 15.50 minutes

Statistical analysis

Results are presented as mean \pm relative standard deviation of three replicate analyses. One way ANOVA $p = 0.05$ was applied to determine differences among replicate determinations and results from different sampling sites. Student *t*- test $p = 0.05$ was used to determine differences between recoveries from ultrapure water and river water so as to ascertain matrix effects. All statistical analyses were performed using SPSS 16 software (SPSS Inc., Chicago, IL, USA).

RESULTS AND DISCUSSION

Validation parameters

Levels of tetracyclines in surface and treated water was analysed by an HPLC coupled to ultraviolet detection. Ultrasonic dispersive solid phase extraction was used as a preconcentration and cleanup technique. Method validation parameters are shown in Table 2. Average recoveries, $n = 3$ of oxytetracycline and doxycycline from river water samples were more than 90%. Spiking rate was 0.01 and 10 μ g/ml. Results of precision were in the acceptable range > 20 [19]. Good linearity for OTC and DC was observed within the range 0.01 – 7.5 μ g/ml and 0.01 - 10 μ g/ml respectively. The regression equation of OTC was $y = 30625x + 60528$ with an R^2 of 0.998 while that for DC was $y = 20366x - 6306$ with an R^2

value of 0.999. Limit of detection for OTC and DC was 50 and 80ng/L while limit of quantification was 821 and 369ng/L respectively. Matrix effects were determined by extracting and analysing blank samples from four different river sources. Chromatograms recorded at 255nm were free of interfering peaks and background absorption. Peak purity was greater or equal to 99%. Results were compared with extraction recoveries from ultra pure water and no significant difference was observed (ANOVA, $p = 0.05$).

Table 2 Results of validation parameters.

Validation parameter	Results			
	OTC		DC	
Linear regression equation	$y = 30625x + 60528$		$y = 20366x - 6306$	
R ²	0.998		0.999	
Linear dynamic range	0.01 – 7.5µg/ml		0.01 - 10 µg/ml	
Limit of detection (ng/L)	50		80	
Limit of quantification (ng/L)	821		369	
Level of spiked samples (µg/mL)	0.01	10	0.01	10.00
Recoveries (%)	96.77	98.31	98.64	97.95
Relative standard deviation (%)	6.78	3.29	10.05	5.57

Occurrence of OTC and DC in Harare surface waters and drinking water

Both OTC and DC were detected in surface waters Table 3 – 9. The maximum level that was detected was 0.61413 ± 14.90 for OTC and 0.57617 ± 7.03 µg/L for DC. Antibiotics were not detected in tap and bottled water for all sampled areas Table 10 and 11. All samples obtained from Mukuvisi River consisted of oxytetracycline and doxycycline antibiotics. OTC levels ranged from 0.00163 ± 17.70 to 0.21013 ± 11.00 µg/L while DC levels ranged from 0.01210 ± 2.57 to 0.57617 ± 7.03 µg/L. Mukuvisi river recorded the highest level of DC. Occurrence of OTC depended upon the distance from sewage discharge points. Sampling sites Mk₁ to Mk₄ were near sewage discharge points and levels of OTC were highest in these points. Sampling sites Mk₅ to Mk₁₀ were found in the lower reaches. Occurrence of DC was independent of position of sampling sites. DC was detected in both the upper and lower reaches. Higher levels of oxytetracycline were detected in sites Ma₁ to Ma₅. These are mainly located in the upper reaches and near municipal effluent discharges and storm drains. DC antibiotic residues were found in all sites irrespective of site position. Marimba River recorded the highest oxytetracycline levels. Marimba River receives run off from farms, low and high density suburbs where there is wide spread chicken rearing. Chicken droppings are applied in vegetable gardens as manure. Oxytetracycline residues may have been washed from vegetable gardens and farms through run off. Doxycycline detected in the rivers and lakes likely came from municipal effluents since doxycycline is only used as an antibiotic in humans in Zimbabwe. Differences in the distribution of oxytetracycline and doxycycline in the rivers and dams is due to differences in properties of the two drugs. OTC readily adsorb to soil and sediment particles [4] such that its mobility from source of contamination is low. Sediment adsorbed antibiotics can be desorbed back to the aqueous phase [5] therefore acting as reservoir. Jodeh and Awartani, [20] investigated the fate and mobility of oxytetracycline and doxycycline in soil columns and found out that doxycycline had a higher mobility than oxytetracycline. Higher levels of doxycycline were observed in the leachate water than oxytetracycline. OTC was not detected in Zimphos and Glenlorne stream. This may be as result of the location of these sites. The streams receive run off from low density suburbs were application of OTC is low. Presence of doxycycline in site G₃ might be as a result of contamination from sewage effluents.

Higher levels were detected in all sites from Lake Chivero and Prince Edward dam. This is probably because both dams collect all the water from rivers and streams passing through Harare Metropolitan Fig 1. Lake Chivero and Prince Edward dam are located in the lower reaches of Harare. OTC may have been washed through run off from poultry farms and vegetable gardens around the city [21] while DC was directly discharged from hospital, pharmaceutical, and municipal effluents. Harare sewage system is very old and frequently characterized by pipeline burst Fig 4. Sewage from Crowborough and Firle treatment works may be the major source of pollution for Lake Chivero since current sewage treating systems do not look for or are not designed to remove pharmaceuticals [22]. Ruwa and Donnybrook treatment works Fig 1 discharge effluents into Prince Edward dam. OTC was not detected from Cleveland Dam while DC was only detected from sites, C₂, C₃ and C₄. DC detected on these sites might have originated from municipal sewage systems. Cleveland Dam is situated in the upper reaches of Mukuvisi River Fig 1 therefore explaining the low levels of antibiotics detected in this dam.

Table 3. Mukuvisi River

Sampling Site	x 10 ⁻³ OTC (µg/L) ± RSD (%)	x 10 ⁻³ DC (µg/L) ± RSD (%)
Mk ₁	210.13 ± 11.00	12.10 ± 2.57
Mk ₂	169.22 ± 2.10	576.17 ± 7.03
Mk ₃	103.49 ± 8.00	299.04 ± 8.37
Mk ₄	97.65 ± 5.00	18.71 ± 12.22
Mk ₅	5.26 ± 11.05	177.98 ± 3.64
Mk ₆	1.63 ± 17.70	52.33 ± 3.79
Mk ₇	7.22 ± 3.98	105.82 ± 1.33
Mk ₈	9.44 ± 8.15	128.30 ± 12.88
Mk ₉	10.55 ± 7.04	319.80 ± 5.56
Mk ₁₀	32.89 ± 13.12	26.40 ± 9.76

Table 4. Marimba River

Sampling Site	x 10 ⁻³ OTC (µg/L) ± RSD (%)	x 10 ⁻³ DC (µg/L) ± RSD (%)
Ma ₁	614.13 ± 14.90	332.30 ± 9.92
Ma ₂	109.75 ± 2.10	315.18 ± 11.23
Ma ₃	103.49 ± 8.00	98.94 ± 12.01
Ma ₄	63.89 ± 1.70	18.71 ± 6.72
Ma ₅	67.23 ± 1.49	84.48 ± 7.04
Ma ₆	22.63 ± 8.20	21.33 ± 3.79
Ma ₇	1.58 ± 3.98	1.09 ± 8.12
Ma ₈	9.10 ± 2.13	3.30 ± 12.88
Ma ₉	7.50 ± 8.34	110.31 ± 3.33
Ma ₁₀	12.06 ± 10.17	6.90 ± 10.44

Table 5. Zimphos Stream

Sampling Site	x 10 ⁻³ OTC (µg/L) ± RSD (%)	x 10 ⁻³ DC (µg/L) ± RSD (%)
Z ₁	ND	ND
Z ₂	ND	ND
Z ₃	ND	ND
Z ₄	ND	ND
Z ₅	ND	ND
Z ₆	ND	ND
Z ₇	ND	ND
Z ₈	ND	ND

Table 6. Glenlorne Stream

Sampling Site	x 10 ⁻³ OTC (µg/L) ± RSD (%)	x 10 ⁻³ DC (µg/L) ± RSD (%)
G ₁	ND	ND
G ₂	ND	ND
G ₃	ND	1.22 ± 0.16
G ₄	ND	ND
G ₅	ND	ND
G ₆	ND	ND
G ₇	ND	ND
G ₈	ND	ND

Table 7. Lake Chivero

Sampling Site	x 10 ⁻³ OTC (µg/L) ± RSD (%)	x 10 ⁻³ DC (µg/L) ± RSD (%)
L ₁	144.33 ± 8.40	222.90 ± 1.92
L ₂	293.35 ± 2.10	215.14 ± 8.77
L ₃	133.11 ± 10.56	218.00 ± 2.91
L ₄	196.10 ± 11.30	118.94 ± 3.33
L ₅	156.03 ± 7.89	239.40 ± 7.88
L ₆	127.41 ± 8.00	127.13 ± 1.99
L ₇	218.87 ± 12.08	119.83 ± 10.32
L ₈	98.90 ± 3.05	136.90 ± 10.17
L ₉	211.12 ± 8.31	311.65 ± 1.94
L ₁₀	219.05 ± 7.10	313.90 ± 11.45

Table 8. Prince Edward Dam

Sampling Site	$\times 10^{-3}$ OTC ($\mu\text{g/L}$) \pm RSD (%)	$\times 10^{-3}$ DC ($\mu\text{g/L}$) \pm RSD (%)
P ₁	114.32 \pm 4.00	122.10 \pm 1.82
P ₂	229.75 \pm 7.80	221.51 \pm 9.00
P ₃	233.00 \pm 8.60	111.04 \pm 10.31
P ₄	133.09 \pm 11.30	123.01 \pm 13.32
P ₅	117.23 \pm 5.40	114.17 \pm 6.42
P ₆	122.77 \pm 2.30	231.73 \pm 3.72
P ₇	219.79 \pm 3.27	221.08 \pm 3.72
P ₈	129.30 \pm 2.63	151.13 \pm 4.47
P ₉	211.00 \pm 8.11	133.80 \pm 6.22
P ₁₀	210.56 \pm 5.11	203.05 \pm 9.11

Table 9. Cleveland Dam

Sampling Site	$\times 10^{-3}$ OTC ($\mu\text{g/L}$) \pm RSD (%)	$\times 10^{-3}$ DC ($\mu\text{g/L}$) \pm RSD (%)
C ₁	ND	ND
C ₂	ND	1.01 \pm 1.05
C ₃	ND	1.33 \pm 3.03
C ₄	ND	1.67 \pm 1.22
C ₅	ND	ND
C ₆	ND	ND
C ₇	ND	ND
C ₈	ND	ND
C ₉	ND	ND
C ₁₀	ND	ND

Table 10. Tape water

Sampling Site	$\times 10^{-3}$ OTC ($\mu\text{g/L}$) \pm RSD (%)	$\times 10^{-3}$ DC ($\mu\text{g/L}$) \pm RSD (%)
B	ND	ND
G	ND	ND
D	ND	ND
Mp	ND	ND
Ms	ND	ND
Cb ₁	ND	ND
Cb ₂	ND	ND
Cb ₃	ND	ND
Cb ₄	ND	ND
Cb ₅	ND	ND

Table 11. Bottled Water

Sampling Site	$\times 10^{-3}$ OTC ($\mu\text{g/L}$) \pm RSD (%)	$\times 10^{-3}$ DC ($\mu\text{g/L}$) \pm RSD (%)
B ₁	ND	ND
B ₂	ND	ND
B ₃	ND	ND
B ₄	ND	ND
B ₅	ND	ND



Fig 4. Sewage effluent from a burst pipe observed during sampling time.

CONCLUSION

Overall, this study reveals an omnipresence of OTC and DC in surface waters in Harare. This underscores the need to consider robust sewage management practices to look for and remove pharmaceuticals before effluents are discharged into aquatic environment. Presence of OTC and DC in Harare surface waters is of great concern because of their unknown health effects even if they are detected at low levels. Even though OTC and DC antibiotics were detected in Harare surface waters they were not detected in finished water. They may also have been present at much lower levels to be detected. This might indicate their partial removal during water treatment processes. It is important to note that values reported in this study are result of once of scoping survey. There is still a need to perform analysis over a period of time since levels can potentially fluctuate over time. Presence of OTC and DC in surface waters points to the need to carry out further studies to assess levels of these compounds in sediment since it has been observed that sediment can act as reservoir of antibiotics.

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