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Pharmaceutical residues in water and sediment of Msunduzi River, KwaZulu-Natal, South Africa

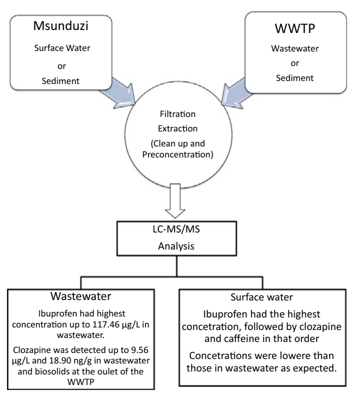
Solomon Matongo [a], Grace Birungi [b,*], Brenda Moodley [a], Patrick Ndungu [a]

[a] University of KwaZulu-Natal, School of Chemistry and Physics, Private Bag X 54001, Durban, South Africa
[b] Mbarara University of Science and Technology, Department of Chemistry, P.O. Box 1410, Mbarara, Uganda

HIGHLIGHTS

- Data on pharmaceutical contamination of African water bodies is limited.
- We determined pharmaceutical residues in Msunduzi River in KwaZulu-Natal.
- Wastewater & bio-solids from a treatment plant in the catchment were also analysed.
- Residues were found in surface water, sediment, wastewater and bio-solids.
- The antipyretic ibuprofen exhibited the highest concentration in the samples.

GRAPHICAL ABSTRACT



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ABSTRACT

The little data about pharmaceutical residue contamination in African water bodies motivated our study on the occurrence of pharmaceutical residues in the water and sediment of Msunduzi River in the KwaZulu-Natal province of South Africa; and in the Darvill wastewater treatment plant found in Msunduzi catchment. Samples collected along the River and wastewater treatment plant were extracted and analysed for pharmaceutical residues selected based on statistics of drug usage in South Africa i.e. antipyretics, antibiotics, caffeine, an antiepileptic and an antipsychotic drug were determined using HPLC–MS/MS.

In all the matrices investigated, the antipyretic ibuprofen had the highest concentration of up to 117 $\mu g\,L^{-1}$, 84.60 $\mu g\,L^{-1}$ and 659 $ng\,g^{-1}$ in wastewater, surface water and sediment respectively. Antibiotics were detected in generally low concentrations of <10 $\mu g\,L^{-1}$ in surface water samples and up to 34.50 $\mu g\,L^{-1}$ in wastewater; moreover they were not completely removed during wastewater treatment. The percentage removal efficiency of the studied group was 6.55–98.00% for antipyretics, 73.33–98.90% for antibiotics, 48.80% for the anti-epileptic drug and 86.40% for Caffeine. Clozapine exhibited a negative removal.

In surface water, Henley dam exhibited a high concentration of the pharmaceutical residues and the highest concentration of metronidazole in sediment (up to 1253.50 $ng\,g^{-1}$) detected. Metronidazole was only detected in sediment and bio-solids.

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* Corresponding author. Tel.: +256 785507881.
E-mail address: gbirungi@must.ac.ug (G. Birungi).

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1. Introduction

Pharmaceuticals are known chemicals of environmental concern due to health risks associated with exposure of aquatic life to these compounds and possible risks to human health when they reach drinking water (Kümmerer, 2009b, 2010; Deblonde et al., 2011); therefore water sources should be monitored regularly. Several authors have reported the occurrence of pharmaceutical residues in waters in Europe, Asia and the USA (Chapman et al., 2002; Heberer, 2002; Löffler and Ternes, 2003; Kümmerer, 2009a; Fatta-Kassinos et al., 2011; Rehman et al., 2013; Manickum and John, 2013; Camacho-Muñoz et al., 2014; Luo et al., 2014) but there is limited information about their occurrence in African water bodies yet literature reports indicate that types of pharmaceuticals and/or their metabolites commonly detected are dependent on social, cultural, technological and agricultural factors (Dehghani et al., 2011; Agunbiade and Moodley, 2014) and therefore may be unique for different geographical areas and water bodies.

A study in Kenya reported occurrence of ibuprofen, paracetamol, sulfamethoxazole and zidovudine at a high concentration (~10–30 μg L^{-1}) in the Nairobi River basin (K'oreje et al., 2012) while studies on Umgeni River in KwaZulu-Natal, South Africa revealed presence of antibiotic, antipyretic, antiepileptic, antipsychotic drug residues and caffeine in surface water and sediment. While most of these pharmaceutical residues were <10 μg L^{-1} in surface water, antipyretics were generally higher (Agunbiade and Moodley, 2014; Matongo et al., 2015). It is therefore important to study the occurrence and fate of pharmaceuticals in various water bodies because drug consumption patterns may differ by region. The consumption of pharmaceuticals in the Republic of South Africa for the period December 2012 to November 2013 as shown in Fig. 1 indicated that antipyretics were the most consumed followed by antibiotics. This consumption data was provided by ImpactRx Data Management (Pty) Ltd (http://www.impactrx.co.za/about-us) a South African company which reports pharmaceutical usage.

In this study we selected pharmaceutical residue targets basing on: annual consumption in South Africa, their persistent detection in water bodies world-wide as seen from the literature, their reported adverse effects and consideration to represent several therapeutic classes. Pharmaceutical residues were selected to represent the therapeutic classes of antipyretic, antibiotic, stimulant, antiepileptic and antipsychotic drugs because they were consumed in large amounts and also due to their reported ecotoxicological effects (Martin et al., 2012; Patrolecco et al., 2014).

Despite the various studies on the occurrence of pharmaceuticals in water bodies of Europe, Asia and USA, little data can be found in the literature concerning findings of pharmaceuticals in sediments, wastewater and surface water of African countries. In this study we investigated pharmaceutical residues in Msunduzi River which is found in South Africa. The quality of water of Msunduzi River (tributary length 115 km), an important tributary of Umgeni River in the KwaZulu-Natal Province of South Africa, is of concern. A recent investigation of its quality revealed microbial contamination with organisms associated with waste disposal such as *Salmonella* spp, *enterococci* and *E. coli* (Gemmell and Schmidt, 2013). This deterioration in quality attributed to increasing urbanization and large informal settlements within the Msunduzi catchment (size of 875 km^2), is associated with environmental problems such as contamination and pollution as a result of industrial waste, refuse dumping, and urban run-off.

The Msunduzi River runs through the Midlands of the KwaZulu-Natal (KZN) province in Eastern South Africa and includes a stretch through the provincial capital city of Pietermaritzburg. It joins the Umgeni River between Nagle and Inanda dams and flows out into the Indian Ocean at Durban (http://www.arocha.org/int-en/work/sites/past/g5/945-DSY.html). It is a source of water for domestic agricultural and industrial use in the Msunduzi Municipality. In a recent study on the Umgeni, pharmaceutical residues were detected at a higher concentration at the sampling point where Msunduzi River joins Umgeni (Matongo et al., 2015).This observation motivated investigation of the Msunduzi River to determine whether it may be contributing to the pharmaceutical loading of the Umgeni.

The discharge of insufficiently treated municipal wastewater into rivers has been identified as a major pathway responsible for surface water contamination with pharmaceuticals and personal care products (PPCPs); some pharmaceutical compounds are not completely removed by conventional treatment processes and eventually end up in drinking water (Okuda et al., 2009). Therefore we investigated Darvill a wastewater treatment plant

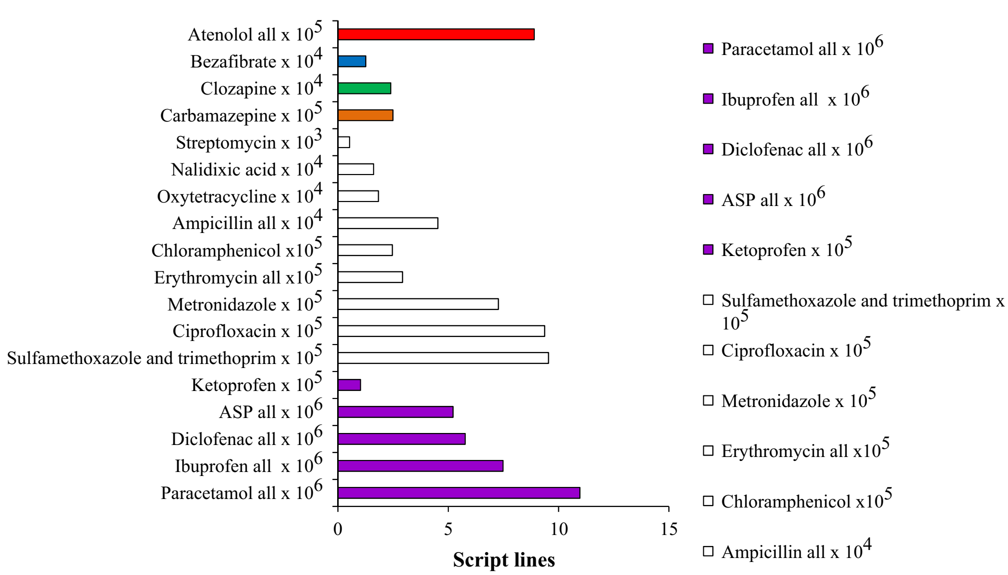

Fig. 1. Script lines in RSA. Paracetamol all includes all paracetamol and paracetamol combinations with or without psycholeptics, ibuprofen all includes all ibuprofen and ibuprofen combinations with or without psycholeptics. Similarly diclofenac includes all diclofenac and diclofenac combinations with or without psycholeptics.

which releases it treated water into the Msunduzi to determine whether it contributes to River Msunduzi contamination.

2. Materials and methods

2.1. Chemicals and reagents

Standards of acetaminophen, ibuprofen, erythromycin, sulfamethazine, sulfamethoxazole, trimethoprim, carbamazepine and caffeine; acetic acid, ammonium solution, methanol, acetonitrile, acetone, ethyl acetate were purchased from Sigma Aldrich (South Africa). All reagents were of HPLC grade. Metronidazole and clozapine tablets were purchased over the counter. Ultra-pure water, purified using Elix Millipore water system, was used in preparation of all standards.

Stock solutions (1000 ppm) of reference compounds were prepared by dissolving the standard (0.01 g) in 10 mL of 50:50 (v/v) methanol and milli-pore water. Standards of metronidazole and clozapine were prepared from their tablets of 200 mg and 100 mg active material respectively by grinding each in a porcelain mortar. 0.012 g of the sample was dissolved in 10 mL of 50:50 (v/v) methanol and milli-pore water. The resultant solution was stored in the fridge at 4 °C until analysis. Standard mixtures, at different concentrations were prepared daily by appropriate dilution of the stock solutions using methanol. Standards prepared using tablets were first tested for interference that may result from binders and other components before use in Calibration.

2.2. Sample collection and preparation

2.2.1. Sampling sites

Msunduzi River passes through highly industrialized areas and receives runoff from rural communities and the municipalities therefore it provides an understanding of the sources and fate of anthropogenic pollutants along its course. Five (5) sampling sites along the river and three (3) sites from Darvill wastewater treatment plant (WWTP) were purposively selected to represent domestic, agricultural, industrial and municipal activities taking place along the Msunduzi catchment. A map of sampling sites is shown in Fig. 2. Sampling was done in September 2013 during the spring sampling season. Global positioning system (GPS) was used to verify the location of each sampling point. Site coordinates, activities and physicochemical parameters of the water during the sampling season are presented in Table 1.

The Darvill WWTP is the main wastewater treatment plant for the Msunduzi Municipality, serving a large population of over 300 000 people and treating raw municipal wastewater as well as treated industrial wastewater. It has a design capacity of ±75 ML day^{-1}, together with some storm water and operates through an activated sludge process which removes excess phosphorus. When the plant operating temperature is 12–24 °C, the activated sludge process (hydraulic capacity 110 ML day^{-1}) has a Solids Retention Time (SRT) of ±8 days, and a mean Hydraulic Retention Time (HRT) of 7 h. Typical effluent values for Chemical Oxygen Demand (COD), ammonia (NH_3), nitrate anion (NO_3^-) and Soluble Reactive Phosphate (SRP) are 75 mg L^{-1}, 10 mg L^{-1}, 15 mg L^{-1} and 1000 μg L^{-1} respectively (Barnard, 1976). The three (03) sampling sites at this WWTP were: one at the influent, inside the WWTP and at the effluent discharge as shown in Table 1.

2.2.2. Sampling

A grab sampling technique was used to collect wastewater or surface water samples from a depth of 1–2 cm from the water surface. Samples were collected in 2.5 L amber bottles, which were pre-washed with phosphate free, soap (dDynaChem), rinsed with tap water followed by distilled water and finally rinsed with

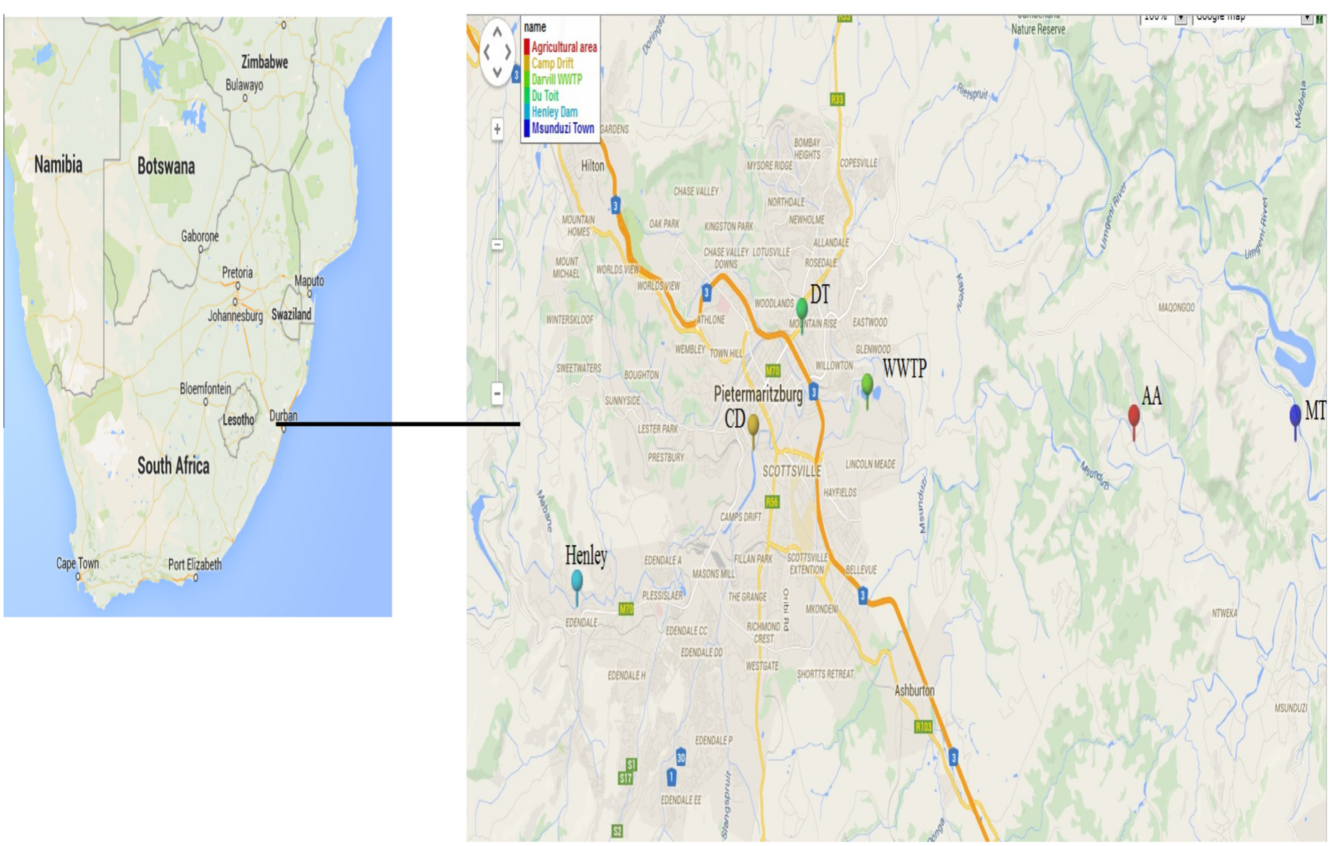

Fig. 2. Sampling points. Henley – Henley dam outlet, CD-Camps Drift, DT-Du Toit, WWTP – Darvill WWTP, AA – Agricultural area, MT – Msunduzi Town.

Table 1
Sampling points along the Msunduzi River.

Site	pH	Temperature		Coordinates		Activities at Sampling Site
		Ambient	Water	South	East	
Msunduzi town	8.92	24	20	29° 39′ 40″	30° 38′ 10″	Domestic and commercial activities.
Agricultural area	8.72	28	24	29° 36′ 40″	30° 33′ 32″	Agricultural and domestic activities.
Darvill WWTP (inlet)	7.24	29	21	29° 36′ 15″	30° 25′ 52″	Influent of treated domestic waste
Darvill WWTP (after treatment)	7.84	28	22	29° 36′ 15″	30° 25′ 52″	Effluent of treated domestic waste
Darvill WWTP (Effluent)	9.20	28	22	29° 36′ 15″	30° 25′ 52″	Effluent of treated domestic waste
Du Toit	7.49	25	18	29° 35′ 15″	30° 24′ 00″	Domestic and commercial activities
Camp drift	8.05	24	21	29° 36′ 47″	30° 22′ 36″	Domestic and commercial activities
Henley dam	7.52	22	19	29° 38′ 51″	30° 17′ 32″	Domestic activities

HPLC grade acetone, and n- hexane to eliminate polar and non-polar contaminants prior to sampling. A 1 mL aliquot of 50% nitric acid was added to each of the samples immediately after collection to prevent microbial degradation of the samples. Samples were kept cool on ice during transportation to the laboratory and thereafter were kept in the fridge at 4 °C until extraction following the method described by Hilscherova et al. (2003). At each site, at least three samples were taken ($n \geqslant 3$) and all samples were extracted within a week of sample collection.

Bio-solids were collected by scrapping 0–10 cm of the reservoir using a stainless steel spade and sediment samples were collected by scooping approximately 0–10 cm of the sediment from the river bed with a stainless steel spade. The samples were packed in glass bottles and covered with lids lined with acetone pre-washed aluminium.

2.3. Sample preparation

Surface water and wastewater samples were filtered using Whatman Econofilt filter paper (125 mm diameter) and stored in the fridge below 4 °C until SPE extraction. Surface water samples were extracted using the method reported by Babić et al. (2006) after pH optimization in order to improve the recovery of target analytes. Oasis Hydrophobic-Lipophilic Balance (HLB) SPE cartridges were used to achieve simultaneous extraction of the targeted analytes due to its versatility and application to extraction of basic, neutral and acidic drugs (Löffler and Ternes, 2003; Babić et al., 2006; Okuda et al., 2009). The optimized extraction method can be briefly described as follows: The HLB (60 mg, 3 cc) was conditioned with 5 mL methanol and equilibrated with 5 mL water adjusted to pH 4.20 with acetic acid. Surface water (300 mL) was loaded to the cartridge after adjustment of the pH to 4.20 with either acetic acid or ammonium solution. The flow rate was maintained at 4 mL min^{-1}. Subsequently, the solid phase was dried completely by vacuum for 30 min and analytes were eluted with (1 × 10 mL) of methanol followed by (1 × 5) mL of acetone in each case at flow rate of 2 mL min^{-1}. Elutes were evaporated to dryness under vacuum and reconstituted with 1 mL of methanol.

Wastewater samples were extracted and prepared as described for surface water except that 100 mL wastewater samples were used.

Sediment samples were extracted using a method reported by Löffler and Ternes (2003); after optimization. Briefly, the sediments (50 g) were extracted successively in an ultrasonic bath using methanol (2 × 50 mL) followed by acetone-acetic acid (20:1 (v/v)) (50 mL) and ethyl acetate (1 × 50 mL) in 250 mL glass beakers. The slurries of the solvent-sediment mixtures were thoroughly hand shaken and then ultrasonicated for 15 min at 35 °C. Afterwards the slurries were centrifuged (DuPont instrumentsSS-automatic centrifuge) for 7 min and the supernatant solvent phases were filtrated through Whatman Econofilt filter paper (125 mm diameter). Supernatants were combined and evaporated by rotary evaporation at 60 °C (Heidolph Instruments GmbH & Co.kG) until only one aqueous phase remained. The sediment extracts were diluted with 200 mL of double distilled water. Furthermore, the flasks used for rotary evaporation were rinsed using 3 mL of methanol which was then combined with double distilled water. The crude extract was cleaned up using the SPE method described for the wastewater section above.

2.4. LC–MS detection of selected pharmaceuticals

Determination of the selected analytes was performed using HPLC Agilent 1200 series equipped with an automatic injector coupled with an 1100 series MSD Trap mass spectrometer (Agilent Technologies). Zorbax C_{18} (100 × 2.1 mm i.d, 3.5 μm particle size) column was used for separation and quantification of the target analytes. Analytes were separated by a gradient method using a mobile phase composition of 0.1% acetic acid in milli-pore water (Mobile Phase A), 100% Acetonitrile (Mobile Phase B) as shown in Table 2. Ions were acquired in the multiple reaction monitoring (MRM) modes with dwell time of 7.0 ms. The MS analyses were performed in the positive electrospray ionization ESI (+) and negative electrospray ionization ESI (−). Ibuprofen were detected in the negative ionization mode, all other analytes were determined in the positive mode. Method validation parameters are shown in Table 3.

External calibration over a range of 0.1–100 μg L^{-1} was used. Limits of Detection were calculated using a signal to noise ratio of 3 whereas Limits of Quantification were calculated using signal to noise ratio of 10.

3. Results and discussion

Selected pharmaceuticals residues were determined in samples collected along Msunduzi River and Darvill wastewater treatment plant in Pietermaritzburg, KwaZulu-Natal. The results obtained from these places are presented in Fig. 3 and Table 4 and described below.

3.1. Pharmaceutical residues in Darvill wastewater treatment plant

Antipyretics acetaminophen and Ibuprofen were detected in the wastewater and bio-solids. Acetaminophen was detected in both

Table 2
LC/MS/MS gradient program.

Time (Min)	% B	Flow rate (mL min^{-1})
0	5.0	0.250
25	90.0	0.250
27	90.0	0.250
32	5.0	0.250
37	5.0	0.250

Column Thermostat @ 35 °C.

Table 3
Calibration data and method validation parameters.

					Wastewater		Surface Water		Sediments		
				$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$ng\ g^{-1}$	$ng\ g^{-1}$	
Analytes	*m/z*	Therapeutic class	R_t/min	Linear range	LOD	LOQ	LOD	LOQ	LOD	LOQ	R^2
Acetaminophen	151	Antipyretic	3.5	0.100–100	0.008	0.273	0.003	0.091	0.016	0.547	0.993
Caffeine	195	Stimulant	7.2	0.347–100	0.312	1.042	0.104	0.347	0.624	2.084	0.997
Carbamazepine	237	Anti-epileptic	14.3	0.297–100	0.268	0.891	0.089	0.297	0.535	1.782	0.996
Clozapine	327	Anti-psychotic	12.6	0.445–100	0.400	1.331	0.133	0.444	0.799	2.662	0.993
Erythromycin	734	Antibiotic	12.2	0.001–100	0.001	0.001	0.001	0.001	0.001	0.003	0.991
Metronidazole	172	Antibiotic	4.4	0.962–100	0.866	2.886	0.289	0.962	1.732	5.771	0.993
Ibuprofen	205	Antipyretic	8.8	0.271–100	0.244	0.813	0.081	0.271	0.488	1.626	0.992
Sulfamethoxazole	254	Antibiotic	11.7	0.414–100	0.372	1.241	0.124	0.414	0.744	2.481	0.994
Sulfamethazine	279	Antibiotic	9.1	0.227–100	0.204	0.681	0.068	0.227	0.409	1.363	0.991
Trimethoprim	291	Antibiotic	7.8	0.500–100	0.123	0.411	0.041	0.137	0.246	0.822	0.995

LOD – limit of detection.
LOQ – limit of quantitation.

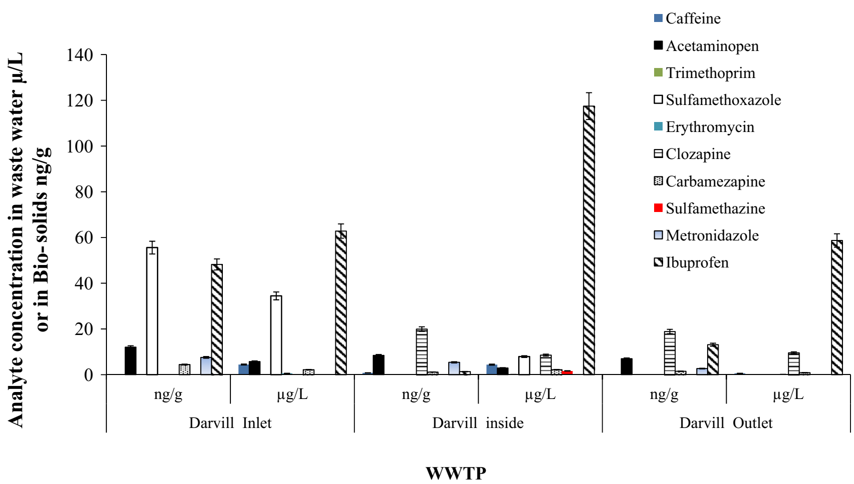

Fig. 3. Analytes detected in wastewater and bio-solids of Darvill WWTP.

Table 4
Pharmaceutical residues in Darvill WWP ± RSD%.

m/z	Analytes	Darvill WWTP inlet		Darvill WWTP inside		Darvill WWTP outlet	
		Waste water ($\mu g\ L^{-1}$)	Bio- ($ng\ g^{-1}$)	Waste water ($\mu g\ L^{-1}$)	Bio-solid ($ng\ g^{-1}$)	Waste water ($\mu g\ L^{-1}$)	Bio-solid ($ng\ g^{-1}$)
195.1	Caffeine	4.48 ± 0.17	<MDL	4.42 ± 0.23	<MDL	0.61 ± 0.45	<MDL
152	Acetaminophen	5.76 ± 7.89	12.08 ± 0.32	2.97 ± 4.53	8.44 ± 0.23	<MDL	7.02 ± 3.45
291.2	Trimethoprim	<MDL	<MDL	0.14 ± 3.12	<MDL	<MDL	<MDL
254	Sulfamethoxazole	34.50 ± 1.34	55.60 ± 3.56	7.93 ± 0.96	<MDL	<MDL	<MDL
735	Erythromycin	0.61 ± 0.87	<MDL	<MDL	<MDL	0.16 ± 0.73	<MDL
327.2	Clozapine	<MDL	N.D	8.59 ± 0.24	19.97 ± 2.87	9.56 ± 0.56	18.90 ± 1.24
237.1	Carbamazepine	2.21 ± 0.41	4.45 ± 0.64	2.21 ± 1.07	1.18 ± 0.81	0.91 ± 1.22	1.52 ± 0.84
279	Sulfamethazine	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
172	Metronidazole	N.D	7.59 ± 0.14	N.D	5.44 ± 0.46	N.D	2.71 ± 3.39
205	Ibuprofen	62.82 ± 4.23	48.24 ± 0.73	117.46 ± 1.34	1.38 ± 18.25	58.71 ± 1.82	13.15 ± 6.76

N.D – Not detected.
MDL – Method limit of detection.

wastewater and bio-solids. In general a slightly higher concentration was observed in bio-solids (up to 12 $ng\ g^{-1}$) compared to wastewater (<10 $\mu g\ L^{-1}$). Acetaminophen was efficiently removed from the wastewater however the bio-solid still contained >50% during our study period although the concentration in the bio-solid at the outlet was low (<10 $ng\ g^{-1}$). The concentration detected at the Darvill WWTP was comparable to that at the Northern wastewater treatment plant in the Umgeni Catchment (Matongo et al., 2015) but was lower reported in literature (Miege et al., 2009).

Ibuprofen was detected in both wastewater and bio-solids in much higher concentrations up to117 $\mu g\ L^{-1}$ and 48.24 $ng\ g^{-1}$ respectively. This concentration was higher than that detected at the Northern wastewater treatment plant (NWWTP) along the

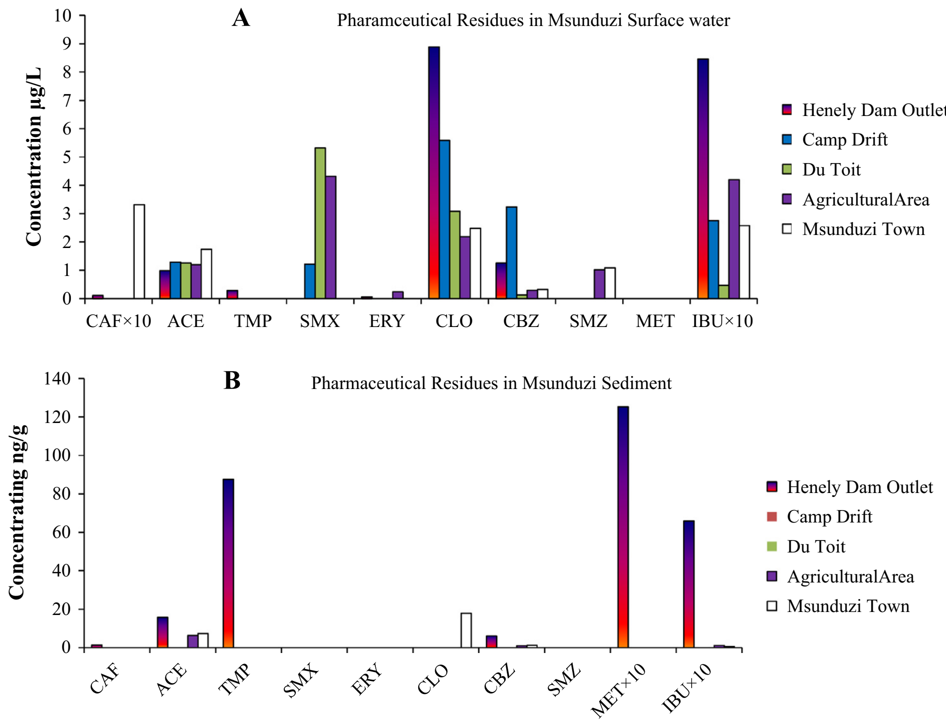

Fig. 4. Pharmaceutical residues in the Msunduzi River. The sites are as described in Table 1.

Umgeni River in KwaZulu-Natal (Matongo et al., 2015) moreover it was poorly removed as shown in Fig. 3. This implies a possible source of contamination of Msunduzi River from treated wastewater and eventual contamination of the Umgeni River by Msunduzi tributary. The concentration of ibuprofen was lower that detected in urban sewage treatment plants in Italy (Patrolecco et al., 2014) but was generally higher than studies conducted elsewhere, even though it among the common antipyretics detected in wastewater (Weigel et al., 2004; Lee et al., 2005; Vieno et al., 2005; Miege et al., 2009). The high concentration of ibuprofen urban water treatment is likely to be associated with higher population in urban areas.

The antibiotic sulfamethoxazole was detected at the inlets of the WWTPs in both the wastewater and bio-solids (34.50 µg L^{-1} and 55.60 ng g^{-1} respectively). These concentrations are comparable to those determined in Spain (Gros et al., 2010) but higher than in studies elsewhere, (Bhandari et al., 2008; Miege et al., 2009) although a good percentage (>90%) was removed by the treatment. This implies a limited possibility of contamination of Msunduzi water by antibiotics from treated wastewater. The concentrations detected were comparable to those at the northern wastewater treatment plant (NWWTP) along the Umgeni River which is in the same geographical region and the removal efficiency (98.9%) was only slightly better that of the NWWTP (93.7%) (Matongo et al., 2015).

Trimethoprim was detected at a low concentration inside the WWTP (0.14 µg L^{-1}) in the wastewater but was not detected in the bio-solids. Sulfamethazine was not detected while metronidazole was only detected in bio-solids at low concentrations (<10 ng g^{-1}) at all the WWTP sites as shown in Fig. 3. Erythromycin was detected at a low concentration of 0.61 µg L^{-1} in the wastewater which is higher that detected at the Northern wastewater treatment plant on the Umgeni (up to 0.24 µg L^{-1}) (Matongo et al., 2015) and up to 74% was removed by treatment.

3.1.1. Other pharmaceutical residues

Caffeine was detected in wastewater at the Darvill WWTP in low concentration (up to 4.48 µg L^{-1}) but was not detected in the bio-solids. Carbamazepine up to 2.21 µg L^{-1} and 4.45 ng g^{-1} was detected in the wastewater and bio-solids respectively as shown in Fig. 3 and Table 4. These concentrations observed were less than those observed for urban wastewater treatment plants elsewhere (Ternes, 1998; Weigel et al., 2004; Subedi et al., 2013; Patrolecco et al., 2014).

Clozapine was not detected at the inlet of the wastewater treatment plant but was however detected inside and at the outlet of the WWTP up to 9.56 µg L^{-1} and 19.97 ng g^{-1} in wastewater and bio-solids respectively. This concentration was higher than that detected in Beijing municipal wastewater treatment plants (Sheng et al., 2014). Clozapine is a positively charged pharmaceutically active compound. The phenomena where an analyte not detected in the influent but found in the effluent or sludge also termed "negative removal" has been reported in literature and has been attributed to formation of unmeasured products of human metabolism and/or transformation products that pass through the plant and convert back to the parent compounds (Jelić et al., 2010).

3.2. Selected pharmaceuticals in surface water

All the pharmaceutical residues of interest were detected in surface water along Msunduzi River with the exception of metronidazole which was only detected in sediment as shown in Fig. 4 and Table 5. Ibuprofen had a significant concentration in the surface water of Msunduzi.

Among antipyretics Ibuprofen had the highest concentration in all sites reaching a concentration of 85 µg L^{-1} in surface water at the Henley Dam outlet sampling site. On average the concentration of Ibuprofen observed for River Msunduzi was higher than that observed for River Umgeni located in the same geographical region (Matongo et al., 2015) and it was also higher than that detected in surface waters elsewhere (Vieno et al., 2005; K'oreje et al., 2012). This may be attributed to their ease of access and hence use since they can be purchased over the counter and these high quantities are in agreement with the data from ImpactRx (ImpactRx, 2013).

Table 5
Pharmaceutical residues in the Msunduzi River.

Precursor	Analyte	HDO	CD	DU	AA	MT
A. Msunduzi surface water ($\mu g\ L^{-1}$) ± RSD (%)						
195.1	CAF × 10	0.11 ± 3.45	ND	ND	ND	3.32 ± 0.98
152	ACE	0.99 ± 5.35	1.29 ± 0.57	1.26 ± 3.47	1.20 ± 0.43	1.74 ± 4.35
291.2	TMP	0.29 ± 048	ND	ND	ND	ND
254	SMX	ND	1.22 ± 3.75	5.32 ± 0.63	4.32 ± 0.56	ND
735	ERY	0.06 ± 13.56	ND	ND	0.24 ± 9.93	ND
327.2	CLO	8.89 ± 4.56	5.59 ± 0.33	3.08 ± 1.84	2.18 ± 0.57	2.48 ± 7.65
237.1	CBZ	1.26 ± 7.65	3.24 ± 0.67	0.13 ± 0.79	0.29 ± 3.95	0.32 ± 2.54
279	SMZ	ND	ND	0	1.02 ± 4.05	1.09 ± 3.45
172	MET	ND	ND	ND	ND	ND
205	IBU × 10	8.46 ± 6.65	2.76 ± 0.63	0.47 ± 1.43	4.20 ± 0.42	±0.76
Precursor ion	Analyte	HDO	CD	DU	AA	MT
B. Msunduzi sediment ($ng\ g^{-1}$) ± RSD (%)						
195.1	CAF	1.32 ± 0.27	<MDL	<MDL	<MDL	<MDL
152	ACE	15.8 ± 0.82	<MDL	<MDL	6.33 ± 0.76	7.30 ± 1.04
291.2	TMP	87.55 ± 4.88	<MDL	<MDL	<MDL	<MDL
254	SMX	<MDL	<MDL	<MDL	<MDL	<MDL
735	ERY	<MDL	<MDL	<MDL	<MDL	<MDL
327.2	CLO	<MDL	<MDL	<MDL	<MDL	17.89 ± 3.55
237.1	CBZ	6.07 ± 1.44	<MDL	<MDL	1.03 ± 6.92	1.16 ± 1.32
279	SMZ	ND	ND	ND	ND	ND
172	MET × 10	125.35 ± 4.33	<MDL	<MDL	<MDL	<MDL
205	IBU × 10	65.90 ± 1.23	<MDL	<MDL	1.13 ± 4.76	0.53 ± 1.04

The highest concentration of acetaminophen (1.74 $\mu g\ L^{-1}$) was found at Msunduzi town associating its presence with human settlement. This concentration is comparable to that found in Umgeni surface water in the spring season (September) (Matongo et al., 2015) but slightly lower that observed in the Autumn season (February to May) (Agunbiade and Moodley, 2014).

In surface water the concentration of antibiotics was generally low (<10 $\mu g\ L^{-1}$) and were generally comparable to those in unpolluted surface waters in the USA (Vaicunas et al., 2013). Sulfamethoxazole was detected at Camp drift, DuToit and the agricultural area associating its presence with human settlement in the rural areas. The concentration of antibiotics observed on the Msunduzi River was lower than in a study in the Nairobi river basin (K'oreje et al., 2012) and in Pakistan where trimethoprim and sulfamethoxazole was detected at 1700 and 2700 $ng\ L^{-1}$ respectively in a river in the vicinity of Lahore city (Khan et al., 2013). The concentrations of trimethoprim (87.55 $ng\ g^{-1}$) and metronidazole (125.35 $ng\ g^{-1}$) were very high in the sediment samples collected at Henley dam (Fig. 4, Table 5) perhaps due to the residence time that water spends in the dam which allows for sorption of the pharmaceuticals on the sediment.

Clozapine, caffeine and carbamazepine were detected in the surface waters along Msunduzi River. The highest clozapine concentration of 8.89 $\mu\ L^{-1}$ and 17.89 $ng\ g^{-1}$ was detected in the surface water at Henely dam and the sediment collected at the Msunduzi town respectively. Caffeine and carbamazepine were detected in sediment at the Henely dam sampling site and clozapine was only detected in the sediment collected at the Msunduzi town sampling site (Fig. 4). Clozapine is a prescription drug therefore its presence is associated with human settlement.

4. Conclusion

Selected pharmaceutical residues occur in wastewater, surface water, bio-solids and sediments along the Msunduzi River in KwaZulu-Natal. Results of this study indicate that while WWTPs contribute pharmaceutical compounds to surface water, anthropogenic activities along the river also contribute greatly.

Msunduzi River generally contained a high concentration of pharmaceutical residues but the concentration of ibuprofen was very high. The generally higher concentration of antipyretic residues detected along the Msunduzi River is in agreement with consumption data of the Republic of South Africa and it indicates that Msunduzi contributes to the pharmaceutical loading of Umgeni River which it joins and therefore may result in deleterious effects to the aquatic life in these water bodies.

Henely dam exhibited the highest concentration of the pharmaceutical residues among all the sites perhaps due to the longer duration of the water in the reservoir.

Wastewater treatment reduced the concentrations of pharmaceuticals in the water before discharge by more than 70% except for carbamazepine which had a removal of 48.8%.

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