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RESEARCH ARTICLE

Occurrence of selected pharmaceuticals in water and sediment of Umgeni River, KwaZulu-Natal, South Africa

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Abstract Selected pharmaceuticals including antibiotics, antipyretics, a stimulant, an antiepileptic and an antipsychotic drug were determined in wastewater, surface water and sediment along the Umgeni River which is the main source of water to Durban City in KwaZulu-Natal, South Africa. Samples were analysed using high-performance liquid chromatography coupled to a mass spectrometer (HPLC-MS/MS) after clean up and pre-concentration by solid phase extraction (SPE). At the wastewater treatment plant outlet, the antipyretic ibuprofen was detected in concentrations up to 12.94 μg/L and 15.96 ng/g in wastewater and bio-solids, respectively. The antipsychotic clozapine was detected in concentrations up to 14.43 μg/L and 18.75 ng/g in wastewater and bio-solids, respectively. Other pharmaceuticals namely sulfamethazine, sulfamethoxazole, erythromycin, metronidazole, trimethoprim, acetaminophen, caffeine and carbamazepine were also detected but in lower concentration compared to clozapine and ibuprofen (<10 μg/L or 10 ng/g). Clozapine and ibuprofen were detected at high concentrations in the surface water and sediment of Umgeni River. The highest concentration of clozapine (78.33 μg/L) was detected at the business park, while that for ibuprofen (62.0 μg/L) was detected at the point where a tributary, Msunduzi, joins Umgeni. Metronidazole was only detected in sediment, and caffeine (2243.52 ng/g) was detected at the highest concentration in the sediment at the blue lagoon sampling site. The antibiotic sulfamethoxazole was also detected in appreciable amounts up to 507.34 ng/g in the sediment at the Msunduzi tributary sampling site. The data collected implies that while insufficiently treated wastewater contributes to surface water contamination, human activities also contribute appreciably to the pharmaceutical loading of River Umgeni.

Keywords Pharmaceuticals · Surface water · Sediment · Wastewater · Umgeni River

Introduction

Pharmaceutical compounds are known emerging contaminants and have been detected in various water bodies worldwide (Löffler and Ternes 2003; Kümmerer 2009; Fatta-Kassinos et al. 2011; Rehman et al. 2013; Camacho-Muñoz et al. 2014). They are regarded as chemicals of environmental concern because of the risk to aquatic life associated with their exposure in water and the risks to humans when they reach drinking water (Kümmerer 2009, 2010; Deblonde et al. 2011). While several papers and reviews have been published about their occurrence in Asia, Europe and the USA, data about their presence in water bodies in Africa is limited (Fatta-Kassinos et al. 2011), yet water needs to be regularly monitored for these compounds especially because the specific types of pharmaceuticals and/or their metabolites found in water sources can differ between countries or regions depending on social, cultural, technological and agricultural factors (Dehghani et al. 2011), for example ibuprofen, paracetamol,

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sulfamethoxazole and zidovudine were found in high concentration (about 10–30 μg/L) in the determination of priority pharmaceuticals which were selected based on consumption data in the Nairobi River basin in Kenya (Oreje et al. 2012).

This study focussed on the determination of selected pharmaceutical compounds in the Durban area. Umgeni River and one wastewater treatment plant (WWTP) in this catchment area i.e. northern water works were selected because it is the primary source of water to the city of Durban in the KwaZulu-Natal (KZN) Province of South Africa. Umgeni River has a catchment about 441 km^2 and length of 225 km from source to mouth. It has four (4) large dams in its catchment basin: Albert Falls, Inanda, Midmar and Nagle Dam (http://www.dwaf.gov.za/iwqs/rhp/state_of_rivers/state_of_umngeni_02/ecoregions.html). This river passes through the most densely populated parts of KwaZulu-Natal and therefore presents an opportunity to study and monitor the level of pharmaceuticals as it passes through rural to urban areas.

Various pharmaceutical compounds have been reported in different water bodies around the world; however, in this study, ten pharmaceuticals (acetaminophen, ibuprofen, erythromycin, sulfamethazine, sulfamethoxazole, trimethoprim, metronidazole, caffeine, carbamazepine and clozapine) were selected representing five therapeutic classes of antipyretics, antibiotics, stimulants, antiepileptic and antipsychotic drugs. Selection of pharmaceuticals investigated was based on drug consumption data for the pharmaceutical industry in South Africa as obtained from ImpactRx data management (Pty) Ltd (http://www.impactrx.co.za). The estimated consumption in South Africa was projected as shown in Table 1 with the percentage use in KwaZulu-Natal projected at 15 %; the statistics for KwaZulu-Natal show that antipyretics are the most commonly used prescriptions as shown in Fig. 1 and, in the selection of our "priority" pharmaceuticals, we ensured that the different therapeutic groups were represented.

This study was guided by the following research questions: Were these selected pharmaceuticals present in the wastewater, surface water and sediments of Umgeni River? If they are there, in what concentrations are they found?

Table 1 Predicted percentage pharmaceutical consumption by South African Provinces

Province	Rank	Script lines
		100 %
Gauteng	1	37 %
Western Cape	2	18 %
Kwazulu Natal	3	15 %
Eastern Cape	4	8 %
Mpumalanga	5	6 %
Free State	6	5 %
North West	7	5 %
Limpopo	8	3 %
Northern Cape	9	2 %

From http://www.impactrx.co.za

Materials and methods

Chemicals and reagents

Standards of acetaminophen, ibuprofen, erythromycin, sulfamethazine sulfamethoxazole, trimethoprim, carbamazepine and caffeine were purchased from Sigma-Aldrich (South Africa). Metronidazole and clozapine tablets were purchased over the counter. Ultra-pure water, purified using Elix Millipore Water system, was used in preparation of standards. Acetic acid, ammonium solution, methanol, acetonitrile, acetone and ethyl acetate were purchased from Sigma-Aldrich. All reagents were of HPLC-grade. Stock solutions (1000 ppm) of reference compounds (excluding metronidazole and clozapine tablets) were prepared dissolving the standard (0.01 g) in 10 mL of 50:50 (*v*/*v*) methanol and Millipore water. The resultant solution was stored in the fridge at 4 °C until analysis (within 1 week of preparation). Standard mixtures, at different concentrations, were prepared daily by appropriate dilution of the stock solutions using methanol.

Metronidazole tablets of 200 mg metronidazole and clozapine tablets of 100 mg clozapine (as shown on labels) were used. In each case, one tablet was ground in a porcelain mortar, and then 0.012 g of the sample was weighed and dissolved in 10 mL of 50:50 (*v*/*v*) methanol and Millipore water. The mixture was hand shaken and stored in the fridge at 4 °C until analysis. This was used in calibration.

External calibration over a range of 0.1–100 μg/L 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.

Sample collection and storage

River Umgeni passes through highly industrialized areas and receives runoff from rural communities and the municipalities along its course as well as from agricultural areas. These contribute to the levels of pollutants in the water.

Fifteen (15) sampling sites were purposively selected to represent various anthropogenic activities taking place along these rivers (Fig. 2 and Table 2). They include 12 sites along the river from the source in Midmar Dam to the mouth where the river empties into the Indian Ocean at Blue lagoon and three sites at the northern wastewater treatment plant (NWWTP) which discharges its treated water into the Umgeni River.

Wastewater influent and effluent, surface water and sediment were collected along the course of the river northern water works treatment plant in September 2013 during the spring sampling season. Global Positioning System (GPS) was used to verify the location of each sampling point for future reference. The sampling sites coordinates, site activities and physicochemical parameters of the water during the sampling season are presented in Table 2.

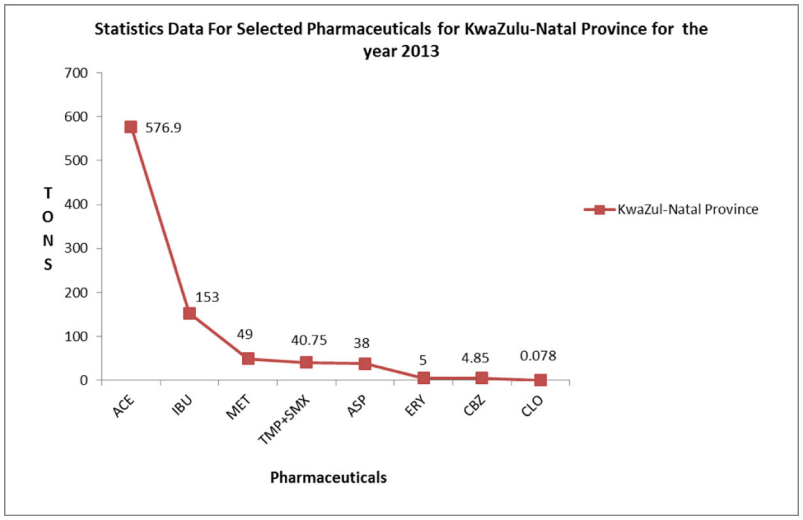

Fig. 1 Statistics of target analytes for the period of December 2012 to November 2013 (http://www.impactrx.co.za). *ACE* acetaminophen, *IBU* ibuprofen, *MET* metronidazole, *TMP* trimethoprim, *SMX* sulfamethoxazole, *ASP* aspirin, *ERY* erythromycin, *CBZ* carbamazepine, *CLO* clozapine

Wastewater or surface water samples were collected in 2.5-L amber bottles, which were washed with phosphate-free soap (dDynaChem), rinsed with tap water and distilled water, and finally rinsed with HPLC-grade acetone and *n*-hexane to eliminate polar and non-polar contaminants prior to sampling. Bottles were rinsed twice with the river water to be sampled before the water sample from the river was collected.

A grab sampling technique was used to collect water samples from a depth of 1–2 cm from the water surface. A 1-mL aliquot of 50 % sulphuric 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. (Hilscherova et al. 2003). At each site, at least three samples ($n \geq 3$) were taken, and all samples were extracted within a week of sample collection.

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 fully in glass bottles (no space). The lids of the glass bottles were lined with acetone pre-washed aluminium. Bio-solids were collected in a similar manner by scooping about 0–10 cm from the base of the reservoir.

Sample preparation

Surface water samples were extracted using the method reported by Babić et al. (2006). In their method, hydrophobic-lipophilic balance (HLB) sorbents were used in extraction of

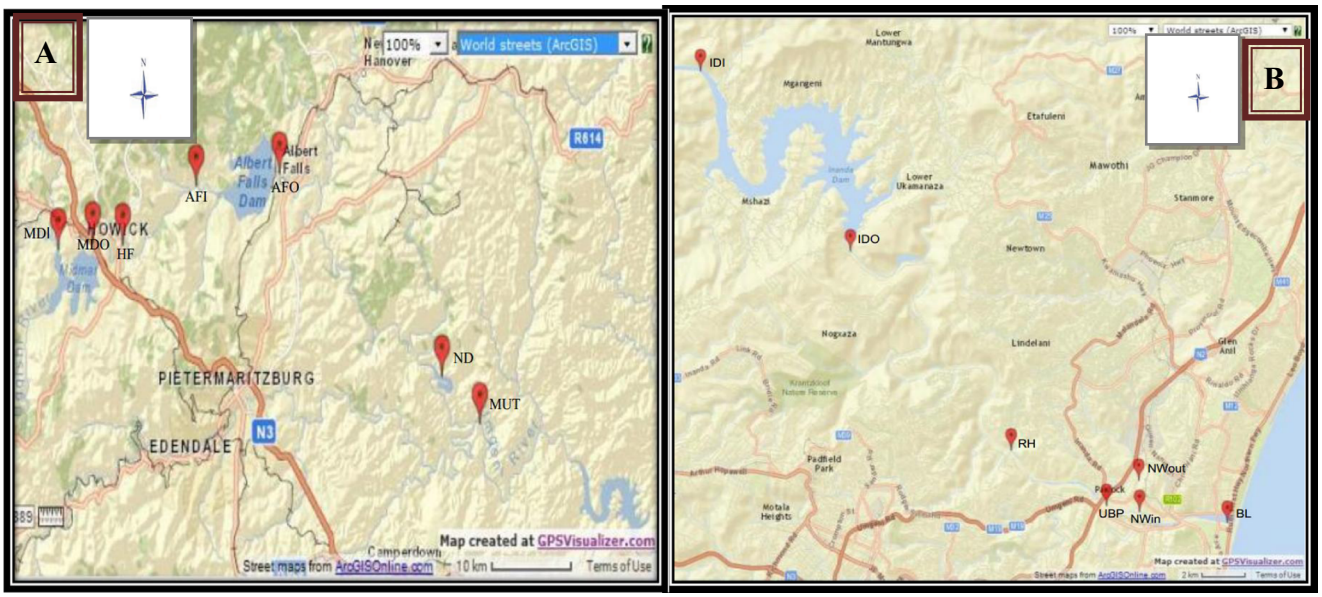

Fig. 2 Map of Umgeni sampling site with the sample collection locations identified in *red pin shapes* (maps were generated from GP coordinates using an online tool—GPS visualize; Google 2013: http://www.gpsvisualizer.com)

Table 2 Sampling points along Umgeni River, KwaZulu-Natal, South Africa

		Temperature (°C)		Coordinates		Activities at sampling site
Site	pH	Ambient	Water	South	East	
Midmar Dam inlet (MDI)	7.80	24	19	29° 29′ 24″	30° 09′ 30″	Dam for water supply (inlet)
Midmar Dam outlet (MDO)	7.33	23	16	29° 29′ 07″	30°12′ 07″	Dam for water supply (outlet)
Howick Falls (HF)	7.66	24	20	29° 29′ 12″	30°14′ 19″	Water Fall
Albert Falls inlet (AFI)	7.65	28	22	29° 26′ 31″	30° 19′ 47″	Dam for water supply
Albert Falls outlet (AFO)	7.58	29	28	29° 26′ 01″	30° 19′ 55″	Dam for water supply
Nagle Dam (ND)	8.87	22	21	29° 35′ 08″	30° 37′ 55″	Dam for water supply
Tributary Umgeni/Msunduzi (MUT)	7.60	26	25	29° 37′ 16″	30° 40′ 46″	Surface Water/River
Inanda Dam inlet (IDI)	9.55	23	24	29° 39′ 05″	30° 52′ 06″	Dam for water supply
Inanda Dam outlet (IDO)	8.37	23	21	29° 42′ 55″	30° 52′ 07″	Dam for water supply
Reservoir Hills axis (RH)	9.61	32	26	29° 47′ 08″	30° 56′ 25″	Domestic and farming area
Umgeni Business Park (UBP)	9.63	28	23	29° 48′ 19″	30°58′ 58″	Industrial and commercial activities
NWWTP influent (NW_{in})	7.47	26	23	29°47′ 47″	30° 59′ 50″	Influent of treated domestic wastewater
NWWTP effluent	9.30	26	26	29° 48′ 27″	30° 59′ 51″	Effluent of treated domestic wastewater
NWWTP after treatment (NW_{out})	10.21	26	23	29° 48′ 27″	30° 59′ 51″	Effluent of treated domestic wastewater
Blue Lagoon (BL)	9.61	26	23	29° 48′ 41″	31° 02′ 12″	Discharge point into the Indian Ocean

veterinary pharmaceuticals from wastewater. HLB sorbent is preferred in multi-residue extraction due to mixed chemistry and has shown good performance in extracting a mixture of acidic and basic analytes (Löffler and Ternes 2003; Babić et al. 2006; Okuda et al. 2009; Amdany 2012). The method of Babić et al. (2006) was optimized for pH in order to improve on the recovery of target analytes in our study. Tap water samples were spiked with standards, and recoveries were investigated at pH 2, pH 4.2 and pH 8. In all these measurements, an 827 pH lab metrohm meter (Herisau, Switzerland) was used.

The optimized extraction method can be briefly described as follows: The solid phase material HLB from Oasis (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 onto 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. 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. Elutes were evaporated to dryness under vacuum and re-dissolved 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*) (1×50 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 instruments SS-automatic centrifuge) for 7 min, and the supernatant solvent phases were filtered through Whatman Econofilt filter paper (125-mm diameter). Supernatants were combined and evaporated by a rotary evaporator at 60 °C (Heidolph Instruments GmbH & Co.kG) until only one aqueous phase remained. The obtained sediment extracts were diluted with 200 mL of double distilled water. Additionally, the flasks used for rotary evaporation were rinsed using 3 mL of methanol which was then combined with double distilled water. Afterward, a solid phase extraction (SPE) was performed using the SPE method described for the wastewater section above.

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, 3.5 μm) column was used for separation and quantification of the target analytes. Ions were acquired in the multiple reaction monitoring (MRM) mode with dwell time of 7.0 ms. Acquisition parameters are shown in Table 2.

The target analytes were separated by a gradient method using a mobile phase composition of 0.1 % acetic acid in Millipore water (mobile phase A), 100 % acetonitrile (mobile

phase B). The gradient program started with 5 % B ramped to 90 % B in 25 min and then back to 5 % B in 2 min and stabilized for 5 min. The flow rate was 0.25 mL/min. The column temperature was kept at 35 °C. An injection volume of 10 μL was used for all analyses. The MS analyses were performed in the positive electrospray ionization ESI (+) and negative electrospray ionization ESI (−). Ibuprofen was detected in the negative ionization mode, all other analytes were determined in the positive mode.

HPLC-DAD-ESI-MS method performance

Analytes were monitored at 254 nm on the diode array detector (DAD). A 10-μL sample was injected and run on a Zorbax C_{18} (100×2.1 mm i.d, 3.5-μm particle size) column at 35 °C. The flow rate was 0.25 mL/min using a gradient flow of ACN: H_2O (0.1 % acetic acid) as the mobile phase. The MS parameters employed and the m/z of the pharmaceuticals detected by the mass spectrometer are shown in Tables 2 and 3. Multiple reaction monitoring (MRM) mode was used for the detection of the selected compounds to reduce on signal suppression that was observed when a full scan mode was used especially for the waste water samples. Calibration parameters are shown in Table 3.

Real sample analysis

The optimized method was used to determine the presence of ten (10) pharmaceuticals along the Umgeni River and at Northern wastewater treatment plant in KwaZulu-Natal as described earlier in the sampling site section.

Results and discussion

Optimization extraction method

Oasis HLB SPE cartridges were used to achieve simultaneous extraction of the targeted analytes at the optimum pH 4.2 as shown in Fig. 3a. HLB was used due to its versatility and application to simultaneous extraction of basic, neutral and acidic drugs (Löffler and Ternes 2003; Babić et al. 2006; Okuda et al. 2009). At pH 4.20, good reproducibility (R.S.D 0.46–14.12) and high analyte recoveries (71.20–118 %) were achieved for most analytes. An improvement in recovery was observed when extraction was performed on sediments (Fig. 3b). This may be attributed to the presence of humic acid and natural salt as reported by Hirsch Roman et al. (1998) and Löffler and Ternes (2003).

Selected pharmaceuticals at northern wastewater treatment plant

Among the antipyretics investigated, acetaminophen was detected in both wastewater and bio-solids. In general, a slightly higher concentration was observed in bio-solids (up to 7.76 ng/g) compared to wastewater. The percentage removal from wastewater as calculated form Eq. (1) was at ~50 % during our study period. While this removal efficiency is lower than that reported elsewhere (Radjenovic et al. 2007; Gros et al. 2010), the effluent had a concentration less than that detected in other countries (Gros et al. 2010; Li et al. 2010).

$$\frac{\text{concentration at in let} - \text{concentration at out let}}{\text{concentration at in let}} \times 100 \qquad (1)$$

Ibuprofen was detected in both wastewater and bio-solids in much higher concentrations compared to acetaminophen

Table 3 Calibration data and method validation parameters

Analytes	m/z	Therapeutic class	R_t/min	Linear range (μg/L)	Wastewater (μg/L)		Surface water (μg/L)		Sediments (ng/g)		
					LOD	LOQ	LOD	LOQ	LOD	LOQ	R^2
Acetaminophen	151	Antipyretic	3.5	0.1000–100	0.0081	0.2733	0.0027	0.0911	0.0162	0.5466	0.9930
Caffeine	195	Stimulant	7.2	0.3473–100	0.3120	1.0419	0.1040	0.3473	0.624	2.0838	0.9973
Carbamazepine	237	Anti-epileptic	14.3	0.2970–100	0.2676	0.891	0.0892	0.2970	0.5352	1.782	0.9960
Clozapine	327	Anti-psychotic	12.6	0.4436–100	0.3993	1.3308	0.1331	0.4436	0.7986	2.6616	0.9931
Erythromycin	734	Antibiotic	12.2	0.0004–100	0.0003	0.0012	0.0001	0.0004	0.0006	0.0024	0.9913
Metronidazole	172	Antibiotic	4.4	0.9619–100	0.8658	2.8857	0.2886	0.9619	1.7316	5.7714	0.9931
Ibuprofen	205	Antipyretic	8.8	0.2710–100	0.2442	0.813	0.0814	0.2710	0.4884	1.6260	0.9928
Sulfamethoxazole	254	Antibiotic	11.7	0.4135–100	0.3720	1.2405	0.1240	0.4135	0.7440	2.4810	0.9944
Sulfamethazine	279	Antibiotic	9.1	0.2271–100	0.2043	0.6813	0.0681	0.2271	0.4086	1.3626	0.9907
Trimethoprim	291	Antibiotic	7.8	0.5000–100	0.1230	0.4110	0.0410	0.1370	0.2460	0.822	0.9952

LOD limit of detection, *LOQ* limit of quantitation

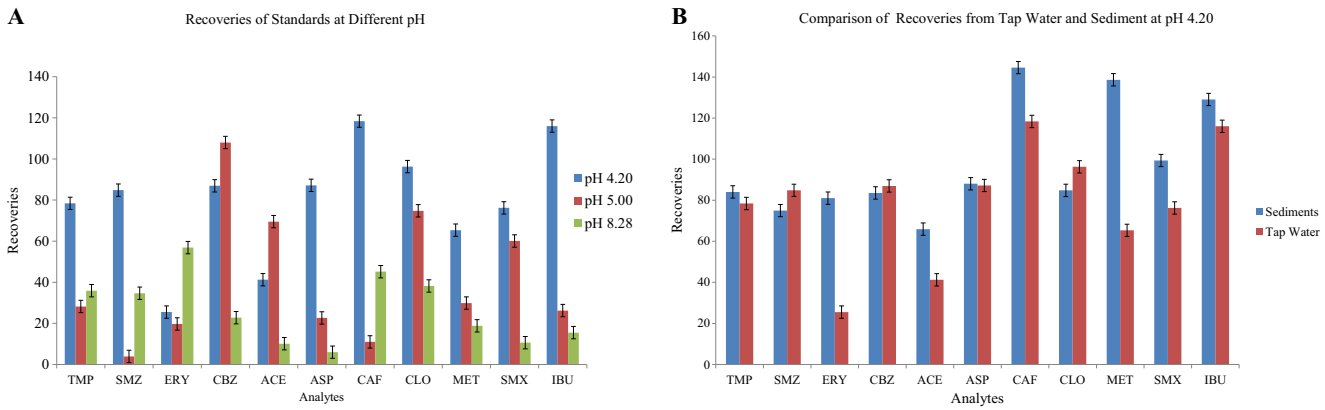

Fig. 3 Recoveries of standards in tap water (**a**). Comparison of extraction of tap water and sediment (**b**)

(up to 12.94±1.03 μg/L and 15.96±6.76 ng/g respectively). The concentration of ibuprofen at the outlet was higher than at the inlet as shown in Fig. 4 and Table 4 signifying poor removal by the treatment at the WWTP; therefore, the water released from this WWTP could potentially pollute the Umgeni River. While the concentrations of ibuprofen in the wastewater and bio-solids were comparable, their concentration was generally higher than that determined elsewhere even though it follows the typical trend of being generally higher than other antipyretics (Weigel et al. 2004; Lee et al. 2005; Gros et al. 2010).

Antibiotics were detected in appreciable amounts at the inlet of the wastewater treatment plant, for example a high concentration of sulfamethoxazole (59.28 μg/L) was detected at the influent of the WWTP. A good percentage (>90 %) of the antibiotics was removed after treatment. These amounts are comparable to those determined in Spain (Gros et al. 2010). Other antibiotics were in low concentrations with the

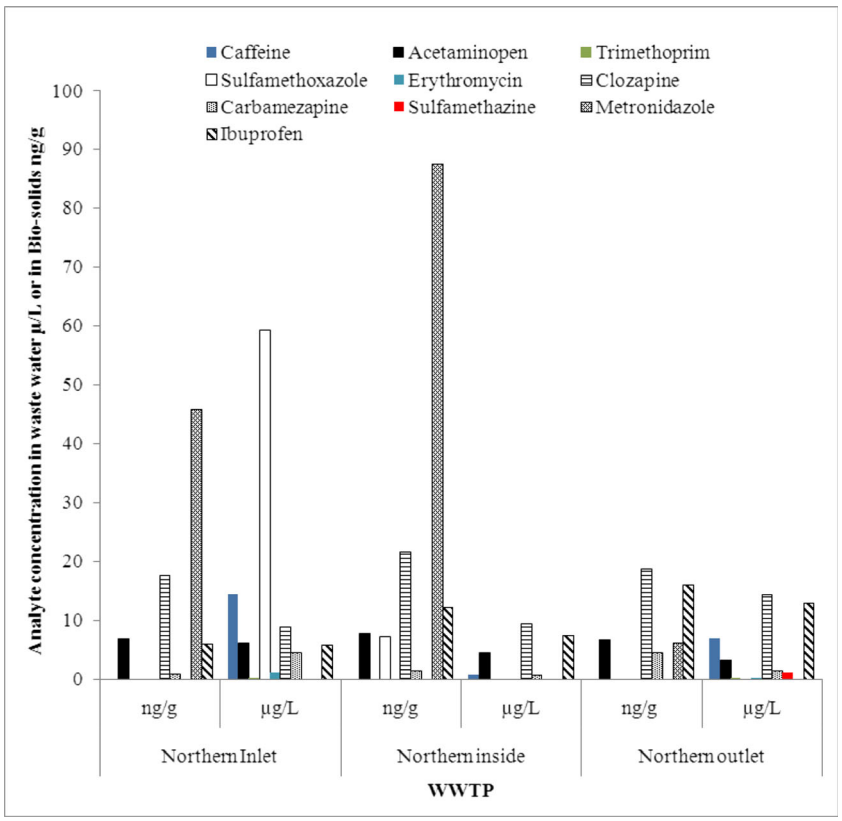

Fig. 4 Analytes in wastewater and bio-solids at northern WWTP

Table 4 Target pharmaceuticals at northern water works WWTP±RSD (%)

Analytes	m/z	Northern inlet		Northern inside		Northern outlet	
		Wastewater (μg/L)	Bio-solid (ng/g)	Wastewater (μg/L)	Bio-solid (ng/g)	Wastewater (μg/L)	Bio-solid (ng/g)
Caffeine	195.1	14.30±0.76	<LOD	0.73±0.34	<LOD	6.87±1.23	<LOD
Acetaminophen	152	6.26±7.34	6.99±0.52	4.58±3.45	7.76±0.98	3.27±3.24	6.70±3.45
Trimethoprim	291.2	0.13±2.78	<LOD	<LOD	<LOD	0.16±2.13	<LOD
Sulfamethoxazole	254	59.28±0.68	<LOD	<LOD	7.35±5.87	<LOD	<LOD
Erythromycin	735	1.13±0.49	<LOD	<LOD	<LOD	0.24±3.12	<LOD
Clozapine	327.2	8.95±0.28	17.73±2.13	9.39±0.82	21.66±0.26	14.43±1.56	18.75±1.24
Carbamazepine	237.1	4.56±0.81	0.88±0.81	0.77±0.62	1.37±0.36	1.46±0.52	4.56±0.84
Sulfamethazine	279	<LOD	<LOD	<LOD	<LOD	1.10±0.36	<LOD
Metronidazole	172	N.D	45.89±0.46	N.D	87.48±0.74	N.D	6.15±3.39
Ibuprofen	205	5.76±2.04	5.98±18.25	7.39±3.92	12.27±6.34	12.94±1.03	15.96±6.76

N.D not detected, *LOD* limit of detection

exception of metronidazole which was detected in bio-solids only as shown in Fig. 2 and Table 4; moreover, it was efficiently removed.

A higher amount of caffeine (14.30 μg/L) at the WWTP was observed in influent wastewater compared to the effluent where ~6.87 μg/L was detected implying that about 50 % could be removed by treatment as shown in Fig. 4. Caffeine was not detected in the bio-solids perhaps due to its high polarity (log K_{OW}=−0.07); moreover, the WWTP is a dynamic system and may not allow for settlement of large amounts of caffeine at the reservoir bed. The concentration of caffeine observed at the northern water works is much lower than what was detected in effluent from sewerage treatment plants in Germany (Weigel et al. 2004).

Carbamazepine, an anthropogenic marker for pharmaceutical contamination which it is mostly associated with medical prescriptions, was detected at the northern WWTP in low concentration (up to 4.56 μg/L) and was efficiently removed during wastewater treatment. Other studies reported detection of carbamazepine in much lower concentrations (Weigel et al. 2004; Clara et al. 2004; Mohapatra et al. 2012). Clozapine was also detected at the northern WWTP, and the concentration in the effluent was slightly higher than at the influent as shown in Fig. 4. Bio-solids contained a higher concentration of clozapine as compared to wastewater implying incomplete removal by the wastewater treatment process and potential for the treated and released water to pollute Umgeni.

Selected pharmaceuticals in surface water and sediment

Table 5 shows concentrations of the ten selected pharmaceuticals detected in Umgeni River surface water and sediment. Acetaminophen was detected in both surface water and sediment in low concentrations <2 μg/L and <10 ng/g, respectively. The highest concentrations were observed at the Umgeni business park (Fig. 5). This site is a centre for several businesses ranging from warehouses, guesthouses, shops and other lifestyle businesses. There are various residential properties as well, implying that the higher concentration of acetaminophen may be associated with the higher population in the area.

Ibuprofen was detected in both surface water and sediment in very high concentrations along the sampling sites of Umgeni River (Fig. 5). These high values of antipyretics are in agreement with the figures obtained from ImpactRx data which shows that these antipyretics are among the highest consumed drugs in South Africa, ImpactRx Data (2013) as shown in Fig. 1 and the highest concentrations were observed at areas associated with human activity such as Reservoir Hill and business park. The highest concentration of ibuprofen in surface water (62.00 μg/L) was observed at the point where Msunduzi River, a tributary of Umgeni River, joins the main Umgeni River. This implied that the tributary could be contributing an appreciable amount. Ibuprofen concentrations were high in all sites, and this may be attributed to the easy access as an over the counter drug; these high quantities are in agreement with the import data from ImpactRx 2013.

Trimethoprim (TMP), sulfamethoxazole (SMX), sulfamethazine (SMZ) and erythromycin (ERY) were detected in a few sites in low concentrations in surface water (<10 μg/L), but higher concentrations were detected in sediment, for example sulfamethoxazole was ~500 ng/g was found at point where the Msunduzi tributary joins Umgeni River. Metronidazole (MET) was only detected in sediment, and the highest concentration of up to 61.93 ng/g was detected at Albert falls (Fig. 5). Organic contaminants are known to transfer from water to sediment, and bed sediments are the main sink for many contaminants in the aquatic environment (Xu et al. 2009). The slightly higher concentration of these pharmaceutical compounds in the sediment could be due to the sediment being the sink.

Table 5 Selected pharmaceutical residues in Umgeni River

A. Umgeni Surface Water (μg/L)±RSD (%)												
Analyte	MDI	MDO	HF	AFI	AFO	NAD	MUT	IDI	IDO	RH	UBP	BL
CAF	ND	0.49±2.89	2.15±0.98	2.09±0.67	1.14±1.23	5.53±0.38	2.87±2.00	1.40±9.43	9.25±0.46	1.91±0.37	0.41±4.99	3.01±0.70
ACE	1.13±4.83	1.34±1.05	1.28±1.10	1.33±0.53	1.26±0.56	1.50±4.88	1.36±3.55	1.27±1.12	1.26±2.75	1.55±3.56	1.78±1.57	1.26±1.11
TMP	ND	ND	ND	ND	ND	ND	0.87±1.64	ND	0.85±0.83	ND	0.10±3.56	0.20±1.57
SMX	ND	0.22±3.29	2.25±0.63	0.56±2.57	ND	ND	ND	ND	6.01±1.28	ND	ND	ND
ERY	ND	ND	ND	ND	ND	ND	0.03±20.20	0.26±14.63	0.24±6.15	ND	0.09±7.44	0.03±14.78
CLO×10	0.40±9.43	3.10±4.42	2.80±1.25	1.06±9.92	0.22±6.15	2.43±0.87	1.31±3.31	1.01±13.89	4.10±1.37	0.58±2.48	7.83±0.18	0.39±3.54
CBZ	0.25±5.44	0.24±3.01	0.22±6.05	0.36±1.94	0.21±6.43	0.19±7.07	0.38±5.81	0.62±6.53	0.29±6.96	1.65±0.85	0.49±5.55	0.24±20.20
SMZ	ND	1.02±1.37	0.15±8.84	0.05±32.64	0.51±2.72	0.62±2.24	0.29±4.71	ND	1.24±0.57	0.28±7.19	0.22±4.77	0.32±6.33
ASP×10	1.73±0.41	0.56±1.25	1.10±6.15	0.75±1.86	1.21±1.16	1.10±6.15	15.99±0.18	1.83±0.77	1.26±1.11	6.78±0.21	0.27±5.05	9.59±0.22
MET	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
IBU×10	1.81±0.78	2.62±0.81	4.15±0.51	3.00±1.19	1.37±1.04	1.35±0.52	6.20±1.73	0.85±5.17	2.24±0.32	2.14±1.67	0.23±6.43	5.29±1.08
B. Umgeni Sediment (ng/g)±RSD (%)												
CAF×100	ND	ND	ND	35.67±0.24	131.19±0.63	ND	ND	5.72±0.49	136.01±0.17	1.87±0.76	77.55±0.60	224.35±0.31
ACE	7.75±0.18	8.92±0.32	8.87±0.32	6.57±0.22	8.96±0.32	6.77±0.95	7.36±0.19	7.54±0.56	6.98±0.41	6.03±2.31	8.31±1.10	6.43±1.31
TMP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	N.D	ND
SMX×100	15.95±0.44	ND	ND	2.64±0.54	ND	ND	50.73±0.03	ND	17.26±0.08	ND	N.D	ND
ERY	1.57±0.45	ND	ND	0.14±10.88	ND	ND	ND	ND	ND	0.15±15.71	0.12±5.66	ND
CLO	20.1±2.51	17.52±4.67	18.46±7.93	26.65±4.80	21.34±1.47	17.96±4.51	22.78±0.69	17.38±0.61	20.67±0.38	19.26±0.48	19.94±0.28	17.69±0.60
CBZ	1.09±5.39	1.02±3.38	1.43±7.49	2.32±3.28	1.16±4.14	1.75±0.89	1.26±2.28	1.03±2.69	1.09±0.49	1.44±11.12	1.11±3.93	1.32±2.18
SMZ	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MET	3.48±0.82	13.40±2.69	9.16±0.31	41.19±1.59	61.93±0.47	16.88±0.04	29.01±0.15	17.22±0.12	19.31±0.22	44.13±2.74	23.47±1.80	ND
IBU	13.80±6.65	7.89±1.17	41.41±0.74	7.25±0.20	16.99±1.34	30.66±0.28	9.09±1.16	12.51±0.90	6.53±0.75	18.18±1.04	13.00±2.41	11.70±2.90

Sample sites are as shown in Fig. 2 and Table 2

ND not detected, *MDI* Midmair Dam inlet, *MDO* Midmair Dam outlet, *HF* Howick Falls, *AFI* Albert Falls inlet, *AFO* Albert Falls outlet, *NAD* Nagle Dam, *MUT* Msundizi Tributary, *IDI* Inanda Dam inlet, *IDO* Inanda Dam outlet, *RH* Reservoir Hills, *UBP* Umgeni Business Park, *BL* Blue Lagoon

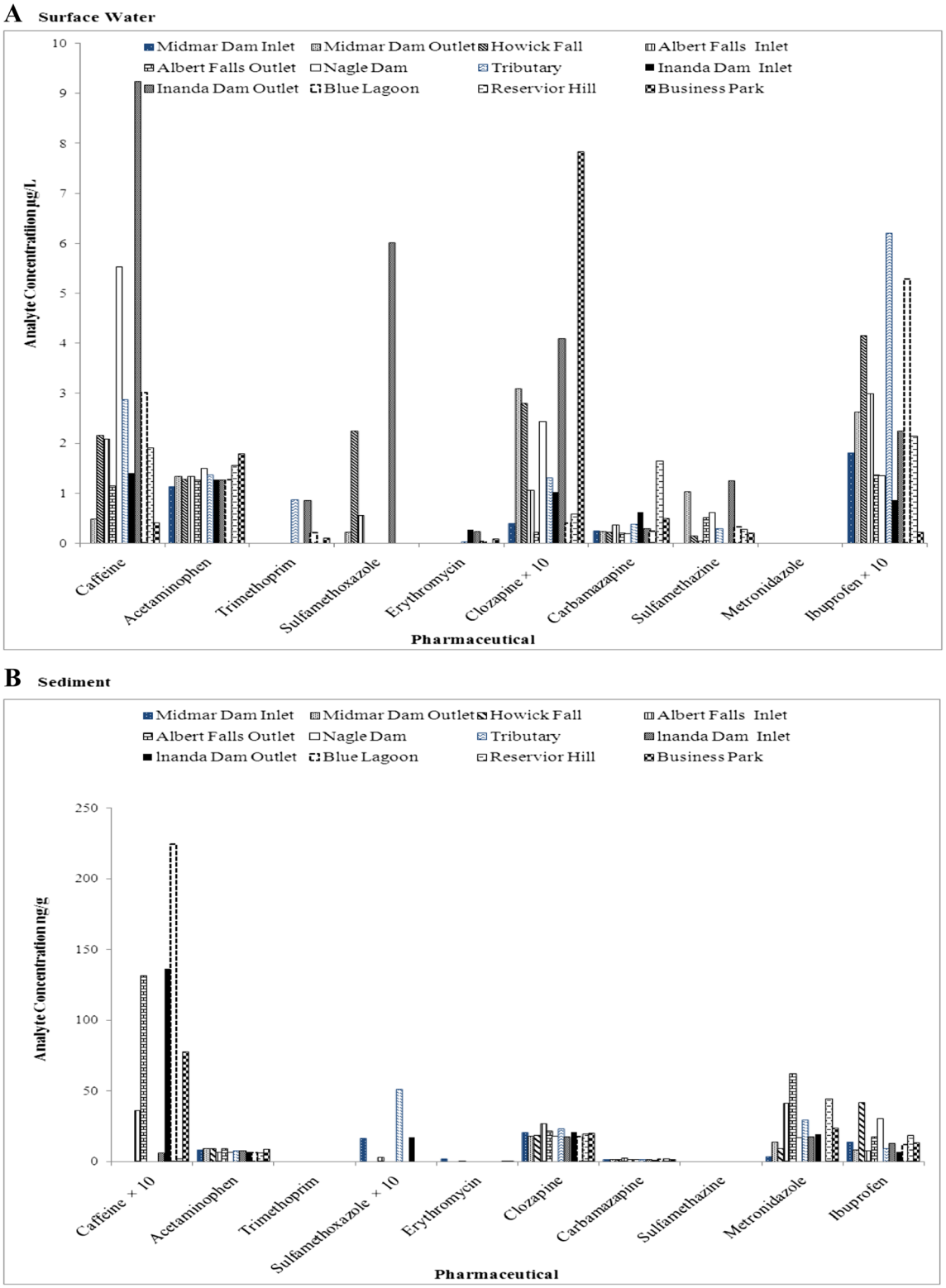

Fig. 5 Selected pharmaceutical residues in surface water and sediment along the Umgeni River

Carbamazepine was detected at low concentrations of 0.38–1.65 µg/L in all the Umgeni sampling sites. This is a prescription drug, and therefore, we expected low amounts since access is restricted. The low concentration observed in all sites is similar to data from Europe and North America where carbamazepine has been one of frequently detected pharmaceutical in river water (Clara et al. 2004).

Clozapine was detected in an appreciable concentration in both surface water and sediment. A higher concentration was observed in surface water compared to sediment with the highest concentration of ~78 μg/L detected at the business park sampling point. It is important to note that the business park sampling point is located close to the WWTP as shown in Fig. 2 and data from the wastewater treatment (Fig. 4) indicated incomplete removal of clozapine by the treatment at northern water works. Since the business park has a high population, this high concentration of clozapine may be attributed to the contribution from human activity and wastewater. High concentrations were also observed at the Midmar Dam, Howick Falls, Nagle Dam, Msunduzi Tributary, and Blue Lagoon associating its presence with human activity.

Caffeine was detected in about half of the sites sampled (Albert Falls, Inanda Dam, Blue Lagoon, Reservoir Hills and the business park) in both surface water (~0.4–9.25 μg/L) and sediment in high concentrations (187–22, 435 ng/g). The amount in the sediment was much higher than in the surface water at the same sites. Caffeine with a log K_{OW} of −0.07 tends to adsorb on organic matter hence the possible reason for its occurring at a higher concentration in the sediment compared to surface water. The highest was observed at the blue lagoon sampling site. This is the point where the Umgeni River pours it water into the Indian Ocean. This part is at the receiving end but is also associated with human activity as there are several recreational facilities near this site.

Conclusion

Selected pharmaceuticals were detected in wastewater, surface water, bio-solids and sediments along the Umgeni River in KwaZulu-Natal. The results indicate that while WWTPs contribute pharmaceutical loading to surface water, anthropogenic activities along the river also contribute greatly.

Higher concentrations of pharmaceuticals were generally observed at the point where Msunduzi Tributary joins the Umgeni River implying that it contributes to the observed pharmaceuticals in that river. This calls for investigation of the Msunduzi to determine its contribution to polluting the Umgeni.

Furthermore, the current wastewater treatment at the sites investigated during our study period was insufficient for removal of pharmaceutical contaminants. In future, we will investigate seasonal variation and fate of the pharmaceuticals detected in this study.

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Conflict of interest The authors declare no conflict of interest

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