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Biochar for the removal of detected micropollutants in South African domestic wastewater: a case study from a demonstration-scale decentralised wastewater treatment system in eThekwini

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The presence of micropollutants, such as pharmaceuticals and personal care products, in surface and ground water has escalated globally, leading to adverse effects on aquatic organisms in receiving waters. Untreated or inadequately treated wastewater is the main source of micropollutants entering the environment. In South Africa, the consumption of antibiotics and antiretroviral drugs is relatively higher than other nations; however, little data exists on the identification and remediation of micropollutants in domestic wastewater. In this study, a novel method to detect and measure 71 micropollutants using online solid phase extraction liquid chromatography coupled to tandem mass spectrometry was developed. To test the method in the South African context, grab samples of the influent and anaerobically treated effluent (AF effluent) from a demonstration-scale decentralised wastewater treatment system in eThekwini (Durban) were taken over 3 consecutive days at 2 time points. The presence of 24 micropollutants was detected in the raw wastewater, with analgesics/anti-inflammatory drugs, antiretrovirals, and antibiotics showing the highest concentrations and with the majority of compounds still present in the AF effluent. One antibiotic, ciprofloxacin, exceeded its predicted no-effect concentration in all influent and AF effluent samples. This suggests that the anaerobic treatment of the raw wastewater was not effective in removing micropollutants. Preliminary data from lab-scale adsorption experiments using biochar produced from a set of 4 feedstocks – olive residues, tomato residues, rice husks, and the African palm tree *Raphia farinifera* – showed average removal rates for 4 compounds of up to 62%. The application of biochar is thus recommended as a secondary treatment step in decentralised wastewater treatment for the removal of micropollutants in South Africa.

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INTRODUCTION

Inward migratory patterns from rural areas into the cities for better livelihoods and employment opportunities occurs at a much faster rate than anticipated in developing countries, especially South Africa. In eThekwini, KwaZulu-Natal, rapid urbanisation has resulted in the formation of densely populated informal settlements within the urban edge. These communities are largely lacking societal infrastructure, including sewerage systems, which leads to poor living conditions and environmental pollution. The eThekwini Water and Sanitation (EWS) unit has provided provisional services in the form of community ablution blocks with washing, toilet, and shower facilities. However, the wastewater generated is routed to the sewer, adding a burden to already over-capacity conventional wastewater treatment works (WWTWs) with ageing infrastructure. Furthermore, water security is challenged by prolonged periods of drought and wasteful expenditure of potable water in agriculture, waterborne sanitation, leaks, etc. Dry sanitation seems like the feasible option. However, user experience has revealed that it is not always acceptable or appropriate as dry toilets are often associated with blockages and thus uncleanliness and bad odours (Roma et al., 2013). To prevent housing development delays and ensure user satisfaction, EWS has opted for waterborne sanitation in dense social housing schemes within the urban edge.

Extending the sewer network, which is accompanied by high capital costs, is not practical. The decentralised approach to sanitation offers more affordable solutions. The technologies used in these systems usually do not require any electrical or chemical input, lowering operating costs. To determine the feasibility of this approach, EWS, with the aid of the Bremen Overseas Research and Development Association (BORDA: https://www.borda.org/), constructed a demonstration-scale decentralised wastewater treatment system (DEWATS) in Durban, South Africa. The DEWATS has been operational since 2010 with a design flow of 41.6 m^3/d. Wastewater is generated from 84 households, designed to serve individuals who are unable to qualify for state-subsidised housing or personal home loans (GCIS, 2017). Treatment is anaerobic, at which stage the effluent, which is relatively high in ammonium and phosphate ions but low in suspended solids and organic matter compared to the raw wastewater, can be reused in agriculture (Odindo et al., 2016). If local agriculture is not possible and the effluent needs to be discharged to the aquatic environment, the anaerobically treated wastewater undergoes further treatment for nitrogen, suspended solids and pathogen removal.

More recently, emerging contaminants from anthropogenic activities also require monitoring in WWTPs. Antibiotic consumption in South Africa is one of the highest worldwide (Van Boeckel et al., 2014), while almost 7.9 million people live with HIV, 18.1% of which reside in KwaZulu-Natal (Simbayi et al., 2019). More than 60% of HIV-infected individuals are on antiretroviral treatment (UNAIDS, 2021) suggesting a high probability of wastewater contamination with these pharmaceuticals.

DEWATS in eThekwini are aimed to fill the gap in urban sanitation and serve communities arising from previously disadvantaged backgrounds. Since the prevalence of HIV, for example, is higher than in more affluent groups (Simbayi et al., 2019), it is expected that these treatment systems may be the source of elevated levels of pharmaceuticals. There will, of course, also be other micropollutants (MPs) present, arising from the usage of personal care products, various household chemicals, as well as pesticides and herbicides. Despite being present in very low concentrations (some in pg/L), the harmful effects of MPs on aquatic life include feminization of fish, caused by endocrine disrupting compounds (EDCs), oxidative stress of freshwater mussels and behaviour alteration in fish exposed to anxiolytics (Brodin et al., 2013; Margot et al., 2015).

Although the number of served households in DEWATS are limited, the concentration of MPs in treated effluents can be high (∑MPs > 150 ng/L) and will vary in concentration according to the diurnal flow rate of each system (Gago-Ferrero et al., 2017). Therefore, it is essential to thoroughly assess the MP load and removal efficiency of individual systems and find add-on treatment solutions to mitigate the load to receiving waters. Generally, MPs are removed in WWTWs by either adsorption to the organic (lipophilic) layer of primary sludge or biodegradation in the secondary treatment step (Luo et al., 2014). Removal of MPs in WWTWs will depend on their physico-chemical properties but also differences in operational conditions, seasonal effects, etc., and for several MPs the overall removal will be inadequate (Luo et al., 2014; Lindberg et al., 2014; Yang et al., 2017; K'oreje et al., 2020). Tertiary treatment with, e.g., ozone or activated carbon, will increase the reduction of the MP load but comes with high costs and energy requirements (Hollender et al., 2009; Reungoat et al., 2012). A more cost-efficient option gaining interest is the application of biochar. Biochar, traditionally used for soil remediation, is produced from biomass by carbonization and can function as an adsorption material for various types of pollutants (Mohan et al., 2014). However, very little research has been done on the use of biochar for the removal of MPs from wastewater (Kyzas et al., 2015; Thompson et al., 2016; Weidemann et al., 2018; Oyjang et al., 2020).

While efforts to minimize and control the risks associated with MPs in the aquatic environment have been implemented in Europe, limited data are available on the detection and occurrence of MPs in South African wastewater. Olujimi et al. (2012) studied the occurrence and removal of 11 phenols and 6 phthalate esters in conventional WWTP influent and effluents. In KwaZulu-Natal, various pharmaceuticals, including antibiotics and antipyretics, were found in the Msunduzi River and Umgeni River (Agunbiade and Moodley, 2014; Matongo et al., 2015a,b), while Wanda et al. (2017) identified 6 MPs, such as carbamazepine and bisphenol A, in drinking and wastewater samples from Gauteng, Mpumalanga and the North West Province. Abafe et al. (2018) and Faleye et al. (2019) studied the occurrence of antiretroviral drugs and antibiotics in wastewater treatment plants and receiving waterbodies in Durban. To date, no studies have been conducted on the detection of MPs, especially pharmaceuticals, in DEWATS in South Africa.

This study aimed to evaluate the occurrence of MPs in the demonstration-scale DEWATS in eThekwini using online solid phase extraction liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS); determine the current removal rates of the identified compounds by the treatment process; and explore the potential for enhancing the removal efficiency with biochar. The investigated compounds included several antibiotics, antiretrovirals, analgesics/anti-Inflammatory drugs, hormonal contraceptives, and herbicides/pesticides.

METHODS

Site and sampling methodology

The Newlands Mashu decentralised wastewater treatment system (NM DEWATS) is situated in Newlands East, KwaZulu-Natal (29° 46' 25. 648" S, 30° 58' 28. 329" E). Raw wastewater from the 84 households is diverted from the main trunk sewer, passing through a stormwater overflow before entering the system. Primary treatment is in a 2-chambered settler, a 3-trained anaerobic baffled reactor (ABR) followed by a 2-chambered anaerobic filter (AF) (Fig. 1). The anaerobically treated effluent (AF effluent) from Train 1 of the ABR undergoes further treatment in a hybrid subsurface flow constructed wetland (CW) system consisting of a vertical down-flow CW (VFCW) and a horizontal flow CW (HFCW), while flow from Trains 2 and 3 are used for agricultural trials, on site.

Figure 1. Aerial view of the Newlands Mashu decentralised wastewater treatment system (taken September 2019) ABR = anaerobic baffled reactor; AF = anaerobic filter; HFCW = horizontal flow constructed wetland; SC = siphon chamber; TS = trunk sewer; VFCW = vertical flow constructed wetland. Black arrows denote the direction of flow. Flow from Train 1 of the ABR is further treated in a hybrid subsurface flow constructed wetland system.

For this study, only the inlet and the AF effluent from Train 1 were sampled. Influent samples were taken directly at the inflow while the AF effluent samples were taken from the siphon chamber, which houses a mechanical dosing device (siphon) for the intermittent feeding of the VFCW. Composite samples at both sampling points were collected in 500 mL pre-rinsed PET bottles, as grab samples, over 3 consecutive days (29–31 March, 2016) at 2 time points (morning, 07:30–08:00 and evening, 18:00–18:30), and thereafter stored in the dark at −20°C until analysis. Only one influent sample was taken on Day 2 (at 7:30). It is of course of great interest to also evaluate the performance of the wetland sections; however, due to the intermittent flux and the complexity of this part of the system, this aspect was omitted from this study. It should also be noted that not all DEWAT facilities are connected to a CW.

All samples were transported frozen to Umeå University, Sweden, for MP identification and quantification, chemical analysis and biochar production.

Analytical methods

Due to the lack of prescription data for pharmaceuticals in South Africa, the pharmaceuticals selected were based on the World Health Organisation (WHO) national list of essential medicines for South Africa (DOH, 2014). Compounds not compatible for LC-MS/MS analysis were excluded. Additionally, commonly used herbicides/pesticides in the region were selected. An analytical method was developed for a total of 72 selected analytes, divided into 18 different categories, including: antibiotics (12), analgesics/anti-inflammatory drugs (9), antiretrovirals (8), psycholeptics/antidepressants (7), antihistamines (4), anticonvulsants (4), antihypertensives (4), hormonal contraceptives (4), anticholinergics (3), herbicides/pesticides (2), antiarrhythmics (2), antidiabetics (2), antimycotics (2), antivirals (2), antidotes (1), antiparasitics (1), decongestants (1) and stimulants (1).

The methanol used for the standard solutions was of HPLC grade and purchased from Fisher Chemicals (Loughborough, UK). Hyper grade acetonitrile and methanol (LiChrosolv) for LC-MS were both purchased from Merck (Darmstadt, Germany). Formic acid (Fluka) as eluent additive was purchased from Sigma-Aldrich (Steinheim, Germany). Ultrapure Milli-Q water was produced from a Merck Millipore Advantage A10 system equipped with a Q-Pod unit. All standards and labelled standards were of analytical grade (above 95%). Details of the CAS number, formula and supplier are given in Table A1 (Appendix).

Samples were thawed at room temperature and filtered through a 0.45 µm Filtropur S membrane filter (Sarstedt, Nürnberg, Germany). After filtration, 10 mL of each sample was spiked with 5 ng of each internal standard and 10 µL of formic acid (98%).

On-line SPE was carried out by a Dionex UltiMate 3000 UHPLC system consisting of 2 LC pumps (Ultimate LPG 3400SD quaternary pump and HPG 3400RS binary UHPLC pump) with an Accela Open autosampler (Thermo Scientific), an on-line SPE column (Waters, Oasis HLB, 2.1 x 20 mm, 15 µm), and an analytical column (Thermo Scientific Hypersil GOLD, 50 x 2.1 mm, 5 µm) equipped with a precolumn (Hypersil GOLD, 10 x 2.1 mm, 3 µm). The column compartment was kept at 25°C. Chromeleon Xpress (Thermo Scientific) was used to control the UHPLC system. Samples were injected onto a 1 mL loop and transferred to the online SPE column by quaternary pump using 0.1% formic acid in acetonitrile as eluent. After 60 s, the autosampler valve switched and the binary pump started the elution from the on-line SPE column through the analytical column using a gradient of 0.1% formic acid in Milli-Q water and 0.1% formic acid in acetonitrile as mobile phase. Gradients for both pumps are shown in Table A2 (Appendix).

The UHPLC system was connected to a TSQ Quantiva triple quadrupole mass spectrometer (Thermo Scientific) equipped with a heated-electrospray ionization ion source operating in positive mode. The resolution for both quadrupoles was 0.7 FWHM. Spray voltage was 3 500 V, sheath gas 40 arbitrary units, sweep gas 0 arbitrary units, ion transfer tube temperature 350°C, and vaporizer temperature 338°C. For control of the mass spectrometer and data analysis, an Xcalibur (Thermo Scientific) was used.

Two MS/MS transitions – one for quantification, one for qualification – were monitored for all analytes. MS/MS transitions, corresponding collision energies and tube lens voltages, associated internal standards, and retention times for each analyte are shown in Table A3 (Appendix).

Identification and quantification of micropollutants

Compounds were identified based on retention time matching and the ratio of quantifier and qualifier ion. Internal standard calibration was used for quantification. Internal standards were assigned to the analytes according to the best match in terms of recovery: 10 mL of AF effluent and influent was spiked with 10 ng of analytes and 5 ng of internal standards and analysed in the same way as the samples. The internal standard that resulted in a recovery of a compound closest to 100% was selected (blank areas were subtracted). Assigned internal standards are shown in Table A3 (Appendix).

An 8-point standard curve was prepared in 10 mL Milli-Q water ranging from 20–10 000 ng/L. Calibration standards were prepared and analysed in the same way as the samples.

Method validation

The method was validated by spiking analytes into 3 matrices (Milli-Q water, AF effluent, and influent) and determining the following parameters: linearity, limit of quantification (LOQ), precision, accuracy, and filter recovery. Since several of the analytes were present in the AF effluent and influent, its areas in the non-spiked matrices were subtracted. Eight standard curve points (20–10 000 ng/L) were prepared in triplicate and analysed as described above. Linearity was expressed as R^2. LOQs were calculated using Eq. 1.

$$\mathbf{LOQ} = 10 \times \frac{\mathbf{STDEV}}{\mathbf{slope}} \quad (1)$$

where: STDEV is the standard deviation of the triplicates of the last visible standard curve point with S/N above 10.

To determine precision and accuracy, Milli-Q water, AF effluent, and influent were spiked with 10 ng of analytes and 5 ng of internal standards. Triplicates of each sample were prepared and analysed together with a calibration curve on 3 consecutive days. The concentration was determined by using the calibration curve analysed on the respective day. Intra-day precision was calculated as the ratio between standard deviation and average of the triplicates of the first day (x 100). Inter-day precision was calculated as the ratio between standard deviation and average of the triplicates on all 3 days (x 100). Instrument precision was assessed by a triple injection of one sample on the first day. Accordingly, inter-day, intra-day, and instrument accuracy were determined by comparing average values with expected values.

Filter recovery was assessed by spiking AF effluent and influent before and after filtering through a 0.45 µm Filtropur S membrane filter (Sarstedt, Nürnberg, Germany).

Removal efficiencies

Removal efficiencies (REs) of the identified MPs in the decentralised wastewater treatment system were calculated according to Eq. 2:

$$RE_i = [1 - (C_{eff} / C_{inf})] \times 100 \quad (2)$$

where: RE_i is the removal efficiency for compound *i*, C_{eff} the concentration in AF effluent, and C_{inf} the concentration in influent.

When a compound was not detected in at least 60% of the influent and AF effluent samples, no RE was calculated.

Biochar adsorption

The biochars used were produced from a set of 4 feedstocks: olive residues, tomato residues, rice husks, and the African palm tree *Raphia farinifera* (RF), by torrefaction at 260°C for 3 h in a rotating furnace (Nordin et al., 2013). Torrefaction is a slow pyrolysis operated under mild conditions, at temperatures ranging between 200°C and 350°C, ambient pressure, and with an inert atmosphere to avoid oxidation and combustion of the starting material (Nordin et al., 2013; Van der Stelt et al., 2011). Additional information about the biochar, including surface area, pore volume and surface characteristics, is given in Tables A4 and A5 (Appendix). Addition of biochar as remediation would most likely occur in the siphon, which is located after the ABR treatment. Wastewater influent and effluent (from the NM DEWATS in eThekwini) were therefore pooled in a ratio of 1:1, to take the variability of the concentrations of MPs into account and produce more robust results. 300 mg of biochar was added to 30 mL of wastewater and each sample was shaken for 24 h. Triplicates were prepared for each biochar, as well as biochar blanks (i.e. wastewater without char) (n = 4), and water blanks (Milli-Q water). After centrifugation, samples were filtered and analysed as described above.

RESULTS AND DISCUSSION

In all samples, MPs were successfully analysed with no carry-over effects observed. R^2 values for all compounds were above 0.99 in Milli-Q water, AF effluent, and influent. Average LOQs were 21 ng/L (with a range of 2–200 ng/L) in Milli-Q water, 100 ng/L (with a range of 4–500 ng/L) in the AF effluent, and 170 ng/L (with a range of 7–1 000 ng/L) in the influent, respectively. Inter-day, intra-day, and instrument precision for all matrices was below 20% (maximum 18%), and accuracy between 51 and 150%. Filter recoveries in both AF effluent and influent were very low (0–14%) for carvedilol, clotrimazole, etravirine, and saquinavir. Therefore, these compounds were excluded, and the filtration step retained to reduce the matrix effects and extend instrument performance. Average recoveries for the remaining 67 compounds were 90% and 110% for the AF effluent and influent, respectively. A summary of the method validation parameters is shown in Tables A6 and A7 (Appendix).

Determination of MPs in the influent and AF effluent

Micropollutants from 10 out of 18 compound classes targeted in this study were detected. In total, 24 MPs were present in at least one sample, of which 20 were present in all samples. The sum of all MPs detected was 287 µg/L and 179 µg/L in the influent and AF effluent, respectively, which correlates to a removal of 38%. Average concentrations, based on 2 daily samples for 3 consecutive days, ranged from 25–140 µg/L in the influent and 22–130 µg/L in the treated AF effluent (Table 1). Twelve compounds were detected at elevated concentrations (>1 µg/L) in the influent and AF effluent. Paracetamol (140 µg/L), followed by the antiretroviral drug lamivudine (74 µg/L) and caffeine (22 µg/L), were the highest average concentrations in the influent, while in the AF effluent the antiretroviral drug darunavir (10 µg/L) and the antihypertensive enalapril (8.1 µg/L) were the highest, besides lamivudine (130 µg/L). None of the 7 psycholeptics targeted were found in any of the samples. Coefficients of variation (CVs) between sampling points were between 3 and 39% in the AF effluent and 0–46% in the influent, with the exception of abacavir and clindamycin which showed much higher CVs (100% and 110%, respectively). This variability in MP composition was likely to be caused by fluctuations in consumption, due to changes in number of people served each day (refer to Table A8, Appendix).

Antibiotics

Of the 12 antibiotics included in this study, 5 were found in all influent and AF effluent samples, with the lowest average concentrations for levofloxacin (25 and 22 ng/L in the influent and AF effluent, respectively) while the highest was sulfamethoxazole (12 and 2.5 µg/L in the influent and AF effluent, respectively). The presence of ciprofloxacin, clindamycin, and levofloxacin in South African wastewater has not been reported previously. Ciprofloxacin concentration was much higher than Swedish wastewater, where Lindberg et al. (2005) found concentrations up to 300 and 60 ng/L in the influent and effluent, respectively. Clindamycin and levofloxacin concentrations were similar to that detected in German wastewater (Rossmann et al., 2014). Compared to conventional South African WWTPs, Archer et al. (2017) detected sulfamethoxazole at lower concentrations of 2.6 and 1.6 µg/L in the influent and effluent, respectively, and trimethoprim at higher concentrations of 6.2 and 1.5 µg/L, respectively). Antibiotics are known to promote antimicrobial resistance in exposed bacteria and therefore their presence in effluent poses a certain risk. Bengtsson-Palme and Larsson (2016) reported on predicted no-effect concentrations (PNEC) in terms of antibiotic resistance for 111 antibiotics. Comparing the PNEC with concentrations determined in this study, ciprofloxacin exceeds the PNEC of 64 ng/L in all influent and AF effluent samples, trimethoprim exceeds the PNEC of 500 ng/L in all influent samples and sulfamethoxazole the PNEC of 16 µg/L in one of the influent samples.

Antiretrovirals

Six of the eight targeted antiretrovirals were found in all influent and AF effluent samples, varying in average concentrations from a few hundred ng/L for abacavir and nevirapine up to several thousand ng/L for darunavir and lamivudine (Table 1). Concentrations of atazanavir, darunavir, and raltegravir were similar to concentrations measured previously at the NM DEWATS as well as at 2 conventional WWTPs in eThekwini (Abafe et al., 2018). Abacavir was found in German WWTP influent at similar concentrations while lamivudine and nevirapine were found at much lower concentrations than in South African wastewater (Prasse et al., 2010). Lamivudine and nevirapine were detected in both waste- and surface water in Kenya (K'Oreje et al., 2012; Wooding et al., 2017, K'Oreje et al., 2018, Muriuki et al., 2020), which implies that these antiretrovirals are semi-persistent.

Other MPs

The non-steroidal anti-inflammatory drug (NSAID), diclofenac, and the anticonvulsant, carbamazepine, are included in the European Commission's first watchlist. Bouissou-Schurtz et al. (2014) estimated PNECs for several pharmaceuticals according to the EU guideline. The average concentration of diclofenac in the AF effluent (2.1 µg/L) exceeds their proposed PNEC of 0.05 µg/L (for rainbow trout *Oncorhynchus mykiss*) and proposes a possible risk. The concentration of carbamazepine (280 ng/L) is below the PNEC of 2.5 µg/L (for zebrafish *Danio rerio*) (Bouissou-Schurtz et al., 2014).

Table 1. Average concentrations (ng/L) of the identified micropollutants in influent and AF effluent samples of the Newlands Mashu decentralised wastewater treatment system, eThekwini, South Africa

Compound	Influent AV[a]	RSD[b]	*n*[c]	AF effluent AV[a]	RSD[b]	*n*[c]
Analgesics/anti-inflammatory drugs						
Diclofenac	2 300	13	5	2 100	7	6
Paracetamol	140 000	21	5	4 600	39	6
Tramadol	330	34	5	400	7	6
Antibiotics						
Ciprofloxacin	1 300	27	5	1 600	13	6
Clindamycin	270	100	5	270	12	6
Levofloxacin	25	4.7	3	22	13	6
Sulfamethoxazole	12 000	36	5	2 500	19	6
Trimethoprim	1 400	34	5	290	14	6
Anticonvulsants						
Carbamazepine	480	22	5	480	3	6
Lamotrigine	240	0	2	0	-	0
Antidiabetics						
Gliclazide	-	-	0	44	8	6
Antihypertensives						
Atenolol	-	-	0	580	-	1
Enalapril	7 600	16	5	8 100	7	6
Antimycotics						
Fluconazole	730	32	5	1 800	5	6
Antiretrovirals						
Abacavir	100	110	5	540	4	6
Atazanavir	3 100	14	5	3 000	12	6
Darunavir	14 000	21	5	10 000	11	6
Lamivudine	74 000	23	5	130 000	15	6
Nevirapine	350	13	5	350	16	6
Raltegravir	4 100	46	5	3 500	10	6
Antivirals						
Aciclovir	3 000	42	5	1 900	29	6
Herbicides/Pesticides						
Tebuthiuron	96	22	5	110	14	6
Terbuthylazine	41	31	4	53	15	5
Stimulants						
Caffeine	22 000	22	5	7 500	19	6

[a]average concentration; [b]relative standard deviation; [c]number of detects

The antimycotic fluconazole was present in both influent and AF effluent samples at average concentrations of 730 ng/L and 1.8 µg/L, respectively (Table 1). These concentrations exceed the PNEC for fluconazole of 250 ng/L (Bengtsson-Palme and Larsson, 2016).

The herbicide tebuthiuron was detected in all samples at average concentrations of 96 and 110 ng/L in the influent and AF effluent, respectively (Table 1). This report appears to be the first finding of tebuthiuron in domestic wastewater and could be due to exposure of clothing and/or ingestion during usage. It has been found at high concentrations in waters connected to sugarcane production in China (7–22 µg/L) (Qian et al., 2017) and in the Pardo River, São Paulo, Brazil (1 µg/L) (Machado et al., 2016). Another herbicide, terbuthylazine, was found in the samples from Days 2 and 3 (at 41 ng/L in the influent and 53 ng/L in the AF effluent, respectively). It has been detected in South African surface water associated with corn production and other agricultural use at concentrations ranging from 1.04 to 4.2 µg/L (Du Preez et al., 2005). It has also been found in ground and surface water in Slovenia (Koroša et al., 2016), Germany (Christoffels et al., 2016) and Spain (Robles-Molina et al., 2014), among others, all associated with agricultural run-off. Terbuthylazine is widely used in European countries and South Africa as a replacement for atrazine (Heri et al., 2008) and, as such, atrazine was not found in any of the samples investigated in this study.

Caffeine is naturally occurring in various plant species and used as a constituent in food, beverages, and an additive in common pain relievers. Due to its widespread consumption, caffeine is used as an anthropogenic marker for wastewater pollution (Buerge et al., 2003). Caffeine was present at average concentrations of 22 and 7.5 µg/L in all influent and AF effluent samples, respectively (Table 1). Similar concentrations were found in conventional WWTP influent (15 µg/L); however, AF effluent concentrations were about 10-fold lower (0.8 µg/mL) (Archer et al., 2017).

Removal efficiencies

On average, the compound class of antibiotics and analgesics/anti-inflammatory drugs were most efficiently removed (31% and 29%, respectively). It is noteworthy that antiretrovirals, the second-most abundant class in influent, showed very poor REs (Table A9, Appendix).

Six compounds were removed with REs ranging from < 25 to 97%, and four compounds had REs that were larger than 60%. These compounds include paracetamol (97%), the two antibiotics sulfamethoxazole (79%) and trimethoprim (79%), and caffeine (66%). Similar REs were reported for another decentralised system consisting of a septic tank and a drain field, with the exception of sulfamethoxazole which had a lower RE of 40% (Schaider et al., 2017). Comparable removal of MPs for DEWATS and conventional WWTPs has been reported previously (Blum et al., 2017; Gros et al., 2017).

No removal was observed for 15 compounds, or an increase in concentration was found in the AF effluent (negative REs). An increase in MP concentration through a treatment system has been widely reported. It is assumed to be associated with the biological and non-biological deconjugation of metabolites during wastewater treatment and the release of compounds accumulated in aggregates (Blair et al., 2015; Stadler et al., 2012; Verlicchi et al., 2012). In addition, our sampling strategy, grab sampling at set time-points, could be heavily influenced by a high variability in the system.

A majority of compounds with low or negative REs were reported to be more efficiently removed by other OWTS and WWTPs (comparison shown in Table A6, Appendix). This can partly be explained by the short retention time in this system. However, it should be noted that removal of MPs in this study was only evaluated from the AF effluent and not the final effluent (i.e., secondary treatment of the AF effluent in the hybrid subsurface flow CW system) (Fig. 1).

Removal of MPs using biochars

Twenty-four identified compounds present in the wastewater were used for the biochar removal tests. None of the compounds were detected in Milli-Q-blanks. As the internal standard ketoprofen-D3 was not visible in the biochar-treated water samples, fluconazole-D4 was instead used for the respective compounds.

Overall, all biochars were able to remove some of the targeted MPs (Table A9, Appendix) with the highest average REs of 62% for biochar produced from olive residues, followed by RF (53%), tomato (46%), and rice husks (44%). Depending on the biochar, some compounds showed varying REs, with the widest range observed for clindamycin from 70% (olive) to −73% (RF).

In total, 14 compounds had REs higher than 60% for olive biochar (8, 8, and 7 for rice husk, RF, and tomato, respectively). Compounds with high REs for most biochars were the antibiotics ciprofloxacin, sulfamethoxazole, and trimethoprim, as well as terbuthylazine. It is noteworthy that for the two most dominant compound classes – antibiotics and antiretrovirals – olive biochar had the greatest average removal of 87 and 63%, respectively, compared to tomato (87 and 46%), rice husk (76 and 39%) and RF (55 and 55%). Apart from clindamycin, for all antibiotics, REs of 100% could be achieved by at least one of the biochars. Therefore, by introducing biochar adsorption as an additional treatment step, the posed risk of antimicrobial resistance by ciprofloxacin, that by far exceeded its PNEC in DEWATS effluent, could be significantly decreased.

Negative removal was only observed for a few compound/char combinations (2 for rice husk, 1 for olive, tomato, and RF, respectively). In total, only 2 compounds had a maximum removal lower than 30%, namely, fluconazole (29%) and enalapril (20%) (Table A10, Appendix).

In conclusion, the implementation of a biochar filter in DEWATS would significantly decrease the total concentration of MPs in the AF effluent, especially the load of critical antibiotics and antiretrovirals, thus decreasing the risks to the receiving environment. To maximize the removal, it is anticipated that applying a mix of different biochars would be a suitable approach and should be assessed in future studies. Depending on the respective micropollutant pattern, combining biochar with different physical and chemical properties would allow for a wastewater treatment approach that meets the demands of the diversity of MP properties.

CONCLUSIONS

In this study, MP detection was done in the influent and AF effluent of a demonstration-scale DEWATS using a novel method LC-MS/MS. Of 71 MPs detectable with this method, 24 MPs belonging to 10 compound classes were found in at least one sample. These MPs were generally detected at high concentrations, some of them exceeding those measured in other parts of the world. Highest concentrations were observed for analgesics/anti-inflammatory drugs, antiretrovirals, and antibiotics. Two compounds, the antibiotic ciprofloxacin and the antimycotic fluconazole, exceeded their PNEC in AF effluent. This may lead to antibiotic resistance.

This study showed that primary anaerobic treatment DEWATS is not effective in removing the identified MPs and that alternative measures need to be adopted to reduce the environmental concerns of discharging AF effluent without adequate MP removal. Future DEWATS in eThekwini are planned to be combined with flushing urine diversion (UD) toilets at the household level. Urine separation will prevent most of the MPs from entering the DEWATS.

In existing DEWATS, biochar may be a promising filter media to remove MPs from wastewater. In this study, the biochar from 4 different feedstocks was found to be able to efficiently remove a majority of the compounds (REs up to 100%), with a maximum average removal of 62%, concluding that biochar adsorption is a suitable option to enhance MP removal from anaerobically treated domestic wastewater.

However, the performance of the hybrid subsurface flow CW system for MP removal must be evaluated. Constructed wetlands are a common treatment option in DEWATS due to its buffering capacity to filter suspended solids and biologically reduce the nutrient content (especially nitrogen) through microbial degradation (nitrification/denitrification) and plant assimilation (Kadlec and Wallace, 2009; Stefanakis et al., 2014; Vymazal, 2010). More recently, CWs were found to be effective in the removal of antibiotics in China (Dan et al., 2020).

The performance of the CWs at the NM DEWATS has been evaluated. In their study, Arumugam and Buckley (2020) found that only nitrate was poorly removed from the CW system operating in series due to the lack of available biodegradable COD (bCOD) as a carbon source for denitrification in the HFCW. As a low-cost alternative, they suggested using plant-based carbon sources to aid in total nitrogen removal.

As for the selection of feedstock, as well as the technique used to produce the biochar, much more research is needed. Interestingly, the giant reed, *Arundo donax*, which is characterised as a Category 1b invasive species in South Africa (implying that the plant must be removed and destroyed immediately) (DEA, 2016) is abundant on site at the NM DEWATS. Considered a waste biomass due to the large size of the species, *A. donax* has been used as a

plant-based biochar in CWs for improved nitrogen removal (Li et al., 2018). Li et al. (2018) observed higher nitrate and total nitrogen removal in surface-flow CWs with a 20% plant-derived biochar than in those with 10% or no biochar.

Additional research is needed to ensure that DEWATS can produce fully compliant effluent for safe discharge to the environment, providing a sustainable option for non-sewered urban sanitation.

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This paper is dedicated to the memory of the late Prof. Chris Buckley.

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APPENDIX

Table A1. CAS number, formula, and supplier for all analytes and internal standards

Compound	CAS	Formula	Supplier
Analgesics/anti-inflammatory drugs			
Betamethasone	378-44-9	$C_{22}H_{29}FO_5$	Sigma-Aldrich
Betamethasone-17,21-dipropionate	5593-20-4	$C_{28}H_{37}FO_7$	Sigma-Aldrich
Betamethasone-17-valerate	2152-44-5	$C_{27}H_{37}FO_6$	Sigma-Aldrich
Budesonide	51333-22-3	$C_{25}H_{34}O_6$	Sigma-Aldrich
Codeine	76-57-3	$C_{18}H_{21}NO_3$	Sigma-Aldrich
Diclofenac	15307-79-6	$C_{14}H_{10}Cl_2NNaO_2$	Sigma-Aldrich
Ketoprofen	22071-15-4	$C_{16}H_{14}O_3$	Sigma-Aldrich
Paracetamol	103-90-2	$C_8H_9NO_2$	Sigma-Aldrich
Tramadol	36282-47-0	$C_{16}H_{25}NO_2$	Sigma-Aldrich
Antiarrhythmics			
Carvedilol	72956-09-3	$C_{24}H_{26}N_2O_4$	Sigma-Aldrich
Lignocaine	137-58-6	$C_{14}H_{22}N_2O$	Sigma-Aldrich
Antibiotics			
Amoxicillin	26787-78-0	$C_{16}H_{19}N_3O_5S$	Sigma-Aldrich
Ciprofloxacin	85721-33-1	$C_{17}H_{18}FN_3O_3$	Sigma-Aldrich
Clindamycin	21462-39-5	$C_{18}H_{33}ClN_2O_5S$	Sigma-Aldrich
Erythromycin	114-07-8	$C_{37}H_{67}NO_{13}$	Sigma-Aldrich
Flucloxacillin	1847-24-1	$C_{19}H_{17}ClFN_3O_5S$	Sigma-Aldrich
Levofloxacin	100986-85-4	$C_{18}H_{20}FN_3O_4$	Sigma-Aldrich
Linezolid	165800-03-3	$C_{16}H_{20}FN_3O_4$	LGC Standards
Nalidixic acid	389-08-2	$C_{12}H_{12}N_2O_3$	Sigma-Aldrich
Sulfamethazine	57-68-1	$C_{12}H_{14}N_4O_2S$	Sigma-Aldrich
Sulfamethoxazole	723-46-6	$C_{10}H_{11}N_3O_3S$	Riedel-de Haen
Trimethoprim	738-70-5	$C_{14}H_{18}N_4O_3$	Sigma-Aldrich
Virginiamycin	21411-53-0	$C_28H_{35}N_3O_7$	Sigma-Aldrich
Anticholinergics			
Atropine	51-55-8	$C_{17}H_{23}NO_3$	Sigma-Aldrich
Biperiden	1235-82-1	$C_{21}H_{30}ClNO$	Sigma-Aldrich
Orphenadrine	83-98-7	$C_{18}H_{23}NO$	LGC Standards
Anticonvulsants			
Acetazolamide	59-66-5	$C_4H_6N_4O_3S_2$	Sigma-Aldrich
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	Sigma-Aldrich
Lamotrigine	84057-84-1	$C_9H_7Cl_2N_5$	Sigma-Aldrich
Phenytoin	57-41-0	$C_{15}H_{12}N_2O_2$	Sigma-Aldrich
Antidiabetics			
Glibenclamide	10238-21-8	$C_{23}H_{28}ClN_3O_5S$	Sigma-Aldrich
Gliclazide	21187-98-4	$C_{15}H_{21}N_3O_3S$	Sigma-Aldrich
Antidotes			
Naloxone	465-65-6	$C_{19}H_{21}NO_4$	Sigma-Aldrich
Antihistamines			
Antazoline	2508-72-7	$C_{17}H_{19}N_3$	Sigma-Aldrich
Cetirizine	83881-52-1	$C_{21}H_{25}ClN_2O_3$	Sigma-Aldrich
Chlorpheniramine	113-92-8	$C_{16}H_{19}ClN_2$	Sigma-Aldrich
Cimetidine	51481-61-9	$C_{10}H_{16}N_6S$	Sigma-Aldrich
Promethazine	58-33-3	$C_{17}H_{20}N_2S$	Sigma-Aldrich
Antihypertensives			
Atenolol	29122-68-7	$C_{14}H_{22}N_2O_3$	Sigma-Aldrich
Bezafibrate	41859-67-0	$C_{19}H_{20}ClNO_4$	Sigma-Aldrich
Enalapril	84680-54-6	$C_{18}H_{24}N_2O_5$	LGC Standards
Nifedipine	21829-25-4	$C_{17}H_{18}N_2O_6$	Sigma-Aldrich
Antimycotics			
Clotrimazole	23593-75-1	$C_{22}H_{17}ClN_2$	Sigma-Aldrich
Fluconazole	86386-73-4	$C_{13}H_{12}F_2N_6O$	Sigma-Aldrich
Antiparasitics			
Albendazole	54965-21-8	$C_{12}H_{15}N_3O_2S$	Sigma-Aldrich

Table A1 continued. CAS number, formula, and supplier for all analytes and internal standards

Compound	CAS	Formula	Supplier
	Antiretrovirals		
Abacavir	188062-50-2	$C_{28}H_{36}N_{12}O_2$	Sigma-Aldrich
Atazanavir	229975-97-7	$C_{38}H_{52}N_6O_7$	Sigma-Aldrich
Darunavir	206361-99-1	$C_{27}H_{37}N_3O_7S$	Sigma-Aldrich
Etravirine	269055-15-4	$C_{20}H_{15}BrN_6O$	LGC Standards
Lamivudine	134678-17-4	$C_8H_{11}N_3O_3S$	Sigma-Aldrich
Nevirapine	129618-40-2	$C_{15}H_{14}N_4O$	Sigma-Aldrich
Raltegravir	871038-72-1	$C_{20}H_{20}FKN_6O_5$	Sigma-Aldrich
Saquinavir	149845-06-7	$C_{38}H_{50}N_6O_5$	Sigma-Aldrich
	Antivirals		
Aciclovir	59277-89-3	$C_8H_{11}N_5O_3$	Sigma-Aldrich
Famciclovir	104227-87-4	$C_{14}H_{19}N_5O_4$	Sigma-Aldrich
	Decongestants		
Oxymetazoline	1491-59-4	$C_{16}H_{24}N_2O$	Sigma-Aldrich
	Herbicides/pesticides		
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	Sigma-Aldrich
Tebuthiuron	34014-18-1	$C_9H_{16}N_4OS$	Sigma-Aldrich
Terbuthylazine	5915-41-3	$C_9H_{16}ClN_5$	Sigma-Aldrich
	Hormonal contraceptives		
Levonorgestrel	797-63-7	$C_{21}H_{28}O_2$	LGC Standards
Medroxyprogesterone	520-85-4	$C_{22}H_{32}O_3$	Sigma-Aldrich
Norgestrel	6533-00-2	$C_{21}H_{28}O_2$	Sigma-Aldrich
Progesterone	57-83-0	$C_{21}H_{30}O_2$	Sigma-Aldrich
	Psycholeptics/antidepressants		
Amitriptyline	549-18-8	$C_{20}H_{23}N$	Sigma-Aldrich
Clozapine	5786-21-0	$C_{18}H_{19}ClN_4$	Sigma-Aldrich
Diazepam	439-14-5	$C_{16}H_{13}ClN_2O$	LGC Standards
Fluoxetine	56296-78-7	$C_{17}H_{18}F_3NO$	Sigma-Aldrich
Haloperidol	52-86-8	$C_{21}H_{23}ClFNO_2$	Sigma-Aldrich
Lorazepam	846-49-1	$C_{15}H_{10}Cl_2N_2O_2$	BP Laboratory
Oxazepam	604-75-1	$C_{15}H_{11}ClN_2O_2$	Sigma-Aldrich
	Stimulants		
Caffeine	58-08-2	$C_8H_{10}N_4O_2$	Sigma-Aldrich
	Internal standards		
Atazanavir-D5	1132747-14-8	$C_{38}H_{47}D_5N_6O_7$	Toronto Research Chemicals
Carbamazepine-D10	132183-78-9	$C_{15}D_{10}H_2N_2O$	Sigma-Aldrich
Clindamycin-D3	1356933-72-6	$C_{18}H_{30}D_3ClN_2O_5S$	LGC Standards
Codeine-D6	1007844-34-9	$C_{18}H_{15}D_6NO_3$	Sigma-Aldrich
Darunavir-D9	1133378-37-6	$C_{27}H_{28}D_9N_3O_7S$	Toronto Research Chemicals
Fluconazole-D4	1124197-58-5	$C_{13}D_4H_8F_2N_6O$	Sigma-Aldrich
Ketoprofen-D3	159490-55-8	$C_{16}D_3H_{11}O_3$	Sigma-Aldrich
Oxazepam-D5	65854-78-6	$C_{15}H_6D_5ClN_2O_2$	Sigma-Aldrich
Sulfamethoxazole-D4	1020719-86-1	$C_{10}H_7D_4N_3O_3S$	LGC Standards
Tramadol-13C-D3	NA	$^{13}CC_{15}D_3H_{22}NO_2$	Sigma-Aldrich
Trimethoprim-13C-D3	NA	$^{13}C_{13}CH_{15}D_3N_4O_3$	Cambridge Isotope Laboratories

Table A2. Gradient program for on-line SPE and LC

Time (min)	A (%)	B (%)	Flow (mL/min)
	On-line SPE		
0.00	100	0	0.00
0.01	100	0	1.00
2.00	100	0	1.00
2.10	0	100	2.00
4.00	0	100	2.00
4.10	100	0	1.00
7.00	100	0	1.00
	LC		
0.00	90	10	0.20
3.00	90	10	0.20
6.00	0	100	0.25
8.00	0	100	0.25
8.01	90	10	0.20
10.00	90	10	0.20

Table A3. MS/MS transitions, collision energies, tube lenses, associated internal standards, and retention times for all analytes

Compound	Internal standard	Precursor (m/z)	Product ion (m/z) 1	Collision energy (V) 1	RF Lens (V) 1	Product ion m/z) 2	Collision energy (V) 2	RF Lens (V) 2	Retention time (min)
Analgesics/anti-inflammatory drugs									
Betamethasone	Codeine-D6	393.2	355.2	10	37	373.2	10	37	6.2
Betamethasone-17, 21-dipropionate	Codeine-D6	505.3	279.1	16	52	411.2	10	52	5.5
Betamethasone-17-valerate	Codeine-D6	477.3	279.2	17	47	355.2	10	47	6.1
Budesonide	Tramadol-13C-D3	431.2	323.1	10	46	413.2	10	46	5.9
Codeine	Codeine-D6	300.2	165	39	80	215.1	25	80	4
Diclofenac	Codeine-D6	296	215	19	47	214	35	47	6.1
Ketoprofen	Ketoprofen-D3	255.1	105.1	22	56	209	13	56	5.8
Paracetamol	Codeine-D6	152.1	93.06	23	46	110.1	15	46	3.5
Tramadol	Tramadol-13C-D3	264.2	246.1	10	44	58.1	17	44	5
Antiarrhythmics									
Carvedilol	Tramadol-13C-D3	407.2	222.1	24	81	224.1	21	81	5.4
Lignocaine	Codeine-D6	235.2	58.17	32	48	86.1	17	48	4.8
Antibiotics									
Amoxicillin	Codeine-D6	381.1	255	21	75	349.1	13	75	4.7
Ciprofloxacin	Clindamycin-D3	332.1	314.1	21	71	288	17	71	4.8
Clindamycin	Clindamycin-D3	425.2	377.2	18	83	126.2	28	83	5.1
Erythromycin	Tramadol-13C-D3	716.4	158.1	27	89	558.3	16	89	5.4
Flucloxacillin	Tramadol-13C-D3	486.1	454.1	16	74	160.1	18	74	5.8
Levofloxacin	Oxazepam-D5	362.1	261.1	26	73	318.1	18	73	4.8
Linezolid	Tramadol-13C-D3	338.2	195	23	83	296.1	17	83	5.1
Nalidixic acid	Ketoprofen-D3	233.1	187	25	57	215.1	14	57	5.6
Sulfamethazine	Codeine-D6	279.1	124	25	65	186	16	65	4.9
Sulfamethoxazole	Sulfamethoxaxole-D4	254	108.1	24	54	156	16	54	5.2
Trimethoprim	Trimethoprim-13C-D3	291.1	261	24	79	230.1	24	79	4.8
Virginiamycin	Ketoprofen-D3	526.2	355.1	17	68	508.3	11	68	5.6
Anticholinergics									
Atropine	Codeine-D6	290.2	93.04	29	73	124.1	23	73	4.9
Biperiden	Tramadol-13C-D3	312.2	294.2	15	58	98.1	21	58	5.5
Orphenadrine	Tramadol-13C-D3	270.2	165	46	34	181	10	34	5.4
Anticonvulsants									
Acetazolamide	Codeine-D6	223	163.9	21	47	180.9	13	47	3.9
Carbamazepine	Carbamazepine-D10	237	192.1	23	60	194.1	19	60	5.5
Lamotrigine	Carbamazepine-D10	256	159	29	82	210.9	26	82	5
Phenytoin	Tramadol-13C-D3	253.1	171	16	51	182.1	17	51	5.5
Antidiabetics									
Glibenclamide	Codeine-D6	494.1	169	32	55	369.1	13	55	6
Gliclazide	Tramadol-13C-D3	324.2	110.1	22	62	127.1	18	62	5.9
Antidotes									
Naloxone	Codeine-D6	328.1	212	39	66	310.1	18	66	3.9
Antihistamines									
Antazoline	Tramadol-13C-D3	266.2	91.04	27	53	196.1	15	53	5.3
Cetirizine	Codeine-D6	389.2	166.1	39	54	201	17	54	5.5
Chlorpheniramine	Codeine-D6	275.1	167	40	42	230.1	17	42	5.1
Cimetidine	Codeine-D6	253.2	117	16	48	159	15	48	3.2
Promethazine	Tramadol-13C-D3	285.1	198	25	41	86.11	16	41	5.4
Antihypertensives									
Atenolol	Codeine-D6	267.2	190	18	63	145	26	63	3.2
Bezafibrate	Codeine-D6	362.1	139	25	59	316	13	59	5.8
Enalapril	Clindamycin-D3	349.2	303.1	16	57	206	17	57	4.9
Nifedipine	Tramadol-13C-D3	329.1	270.1	15	65	284.1	21	65	5.8
Antimycotics									
Clotrimazole	Codeine-D6	277.1	241.1	26	73	165	22	73	5.6
Fluconazole	Fluconazole-D4	307.1	238	15	57	220	18	57	5
Antiparasitics									
Albendazole	Codeine-D6	266.1	191	33	67	234	19	67	5.4

Table A3 continued. MS/MS transitions, collision energies, tube lenses, associated internal standards, and retention times for all analytes

Compound	Internal standard	Precursor (m/z)	Product ion (m/z) 1	Collision energy (V) 1	RF Lens (V) 1	Product ion m/z) 2	Collision energy (V) 2	RF Lens (V) 2	Retention time (min)
Antiretrovirals									
Abacavir	Codeine-D6	287.2	150	30	64	191	19	64	4.4
Atazanavir	Atazanavir-D5	705.2	534.3	26	110	335.2	27	110	5.6
Darunavir	Darunavir-D9	548.2	436.2	10	62	392.2	12	62	5.8
Etravirine	Tramadol-13C-D3	437.1	273	29	150	306	38	150	6.2
Lamivudine	Trimethoprim-13C-D3	230	94.99	35	31	112.1	11	31	2.9
Nevirapine	Oxazepam-D5	267.1	198.1	36	82	226.1	25	82	5.1
Raltegravir	Ketoprofen-D3	445.2	109.1	31	73	361.1	17	73	5.6
Saquinavir	Codeine-D6	671.2	433.2	30	110	570.3	30	110	5.6
Antivirals									
Aciclovir	Codeine-D6	226.1	135.1	28	31	152.1	12	31	2.8
Famciclovir	Codeine-D6	322.2	280.1	17	87	136.1	27	87	4.7
Decongestants									
Oxymetazoline	Tramadol-13C-D3	261.2	135.1	34	75	205.1	24	75	5.3
Herbicides/pesticides									
Atrazine	Codeine-D6	216.1	132	23	49	174.1	17	49	5.7
Tebuthiuron	Tramadol-13C-D3	229.1	116	27	55	172.1	17	55	5.3
Terbuthylazine	Tramadol-13C-D3	230.1	167	33	61	174.1	17	61	6
Hormonal contraceptives									
Levonorgestrel	Ketoprofen-D3	313.2	185.1	19	57	245.1	17	57	6.1
Medroxyprogesterone	Tramadol-13C-D3	345.2	327.2	15	63	123	24	63	6.1
Norgestrel	Codeine-D6	313.2	295.2	14	59	245.2	17	59	6.1
Progesterone	Tramadol-13C-D3	315.2	97.04	21	63	109	25	63	6.4
Psycholeptics/antidepressants									
Amitriptyline	Tramadol-13C-D3	278.2	191.1	26	100	233	18	100	5.5
Clozapine	Tramadol-13C-D3	327.1	192.1	43	75	270	22	75	5.1
Diazepam	Codeine-D6	285.1	154.1	26	76	193.1	31	76	5.9
Fluoxetine	Tramadol-13C-D3	310.1	148.1	10	41	44.22	10	41	5.5
Haloperidol	Tramadol-13C-D3	376.1	123	39	130	165	24	130	5.4
Lorazepam	Tramadol-13C-D3	321	303	14	67	275.1	21	67	5.6
Oxazepam	Oxazepam-D5	287	269	13	66	241	22	66	5.6
Stimulants									
Caffeine	Codeine-D6	195.1	110	23	63	138.1	18	63	4.5
Internal standards									
Atazanavir-D5		710.2	340.2	29	120	539.3	27	120	5.6
Carbamazepine-D10		247.1	204.1	21	69	202.1	34	69	5.5
Clindamycin-D3		428.2	129.2	27	86	380.2	19	86	5.1
Codeine-D6		306.2	218.1	26	81	165.1	40	81	3.9
Darunavir-D9		557.2	401.2	13	65	445.2	10	65	5.8
Fluconazole-D4		311.1	223	18	63	242.1	16	63	5
Ketoprofen-D3		258.1	212.1	14	57	105	23	57	5.8
Oxazepam-D5		292.1	246.1	23	66	274	14	66	5.6
Sulfamethoxazole-D4		258.1	160	16	54	112	25	54	5.3
Tramadol-13C-D3		268.2	58.1	18	46	250.1	10	46	5
Trimethoprim-13C-D3		295.1	230.1	23	79	123.1	25	79	4.7

Table A4. Temperature, reaction time, yield, surface area and pore volume of the biochars

Feedstock	CT	RT	Yield	CSA	PV
	(°C)	(h)	(%)	(m^2/g)	(cm^3/g)
Olive residues	260	3	56	0.1	0.02
Tomato residues	260	3	50	0.6	0.05
Rice husks	260	3	59	3.6	0.07
African palm tree	260	3	60	0.5	0.07

CT – combustion temperature; RT – reaction time, yield; CSA – char surface area; PV – pore volume

After the carbonization process the yield of the chars were calculated with the equation:

Yield (%) = $(m/m_{biomass})$ x 100

where 'm' is the dry mass of the char and '$m_{biomass}$' is the initial dry mass of the biomass before the carbonization. The dry mass of the biomass was analysed by placing samples of biochar in an oven at 105°C, when the sample weight was stable the dry weight was obtained. Surface area and pore volume were determined using Nitrogen adsorption and are presented in Table A4. This analysis was performed with a TriStar 3000. Prior to analysis the chars were degassed, with a micromeritics SmartPrep degasser, at 120°C with N2 (g) for approximately 2 h. Subsequently, the chars were cooled to 77K with N2 (l) and the surface area was determined under vacuum.

Table A5. Atomic concentration of carbon functional groups in percentage for the C1s spectra from the XPS analysis. Five distinct functional groups are derived from the binding energy measured in eV

Feedstock	C-C sp2	C-C line	C-OH	C=O	COOH
	(%)	(%)	(%)	(%)	(%)
Olive residues	71	9	6	-	4
Tomato residues	66	14	2	-	3
Rice husks	53	-	12	3	4
African palm tree	59	10	7	3	5

T C-C sp2 (286.4 eV), C-C line (285.3 – 285.9 eV), C-OH (285.9 – 286.6 eV), C=O (287.0 – 287.9 eV) and COOH (288.3 – 289.2 eV)

The surface functionalities of the biochars was analysed using X-ray photoelectron spectroscopy (XPS), to obtain both qualitative and quantitative data for all elements, except for H and He. It also provides specific information about functional groups present in the top surface layer (3-5 nm). The XPS analysis was performed using an AXIS Ultra DLD with the lens in hybrid mode, pass energy 160 was used for the resolution, and an acquisition time of 330 seconds was applied. Five sweeps were performed with a dwell time of 60 ms. The charge nebuliser was on.

Table A6. Linearity (R2), limit of quantification (LOQ, in pg on column), and filter recovery

	Linearity			LOQ			Filter recovery		
Compound	**mq**	**eff**	**inf**	**mq**	**eff**	**inf**	**MQ**	**eff**	**inf**
Analgesics/anti-inflammatory drugs									
Betamethasone	0.9985	0.9987	0.9979	20	80	300	130	110	140
Betamethasone-17, 21-dipropionate	0.9955	0.9964	0.998	50	100	400	16	25	21
Betamethasone-17-valerate	0.9983	0.9988	0.998	60	200	100	36	45	41
Budesonide	0.9987	0.9983	0.9982	40	300	500	52	45	120
Codeine	0.9994	0.9992	0.9991	10	100	200	120	90	100
Diclofenac	0.9988	0.9976	0.9987	40	60	90	51	80	82
Ketoprofen	0.9988	0.9976	0.9952	20	200	300	110	75	96
Paracetamol	0.9999	0.9973	0.9975	30	10	200	150	96	110
Tramadol	0.9914	0.9978	0.9973	20	300	100	110	94	100
Antiarrhythmics									
Carvedilol	0.9991	0.9976	0.9996	30	100	200	0	0	0
Lignocaane	0.9995	0.9992	0.9972	7	100	60	140	99	130
Antibiotics									
Amoxicillin	0.9986	0.9983	0.9947	20	100	40	210	110	180
Ciprofloxacin	0.9979	0.9971	0.9955	9	200	200	77	110	67
Clindamycin	0.9991	0.9989	0.9993	10	100	40	120	100	130
Erythromycin	0.9987	0.9984	0.9986	10	90	40	78	100	100
Flucloxacillin	0.9968	0.9987	0.9972	10	100	100	98	110	120
Levofloxacin	0.9994	0.9993	0.9955	8	10	20	90	85	60
Linezolid	0.9984	0.9993	0.9994	8	30	100	85	98	140
Nalidixic acid	0.9994	0.9938	0.9982	10	60	40	140	90	130
Sulfamethazine	0.9961	0.9924	0.9984	30	50	20	150	110	140
Sulfamethoxazole	0.9988	0.9969	0.9987	6	200	300	110	100	130
Trimethoprim	0.9994	0.999	0.9992	4	20	50	120	100	110
Virginiamycin	0.9952	0.999	0.9942	200	100	200	110	100	130
Anticholinergics									
Atropine	0.9989	0.9989	0.9984	8	10	8	170	98	150
Biperiden	0.9984	0.999	0.9993	4	10	7	87	100	120
Orphenadrine	0.999	0.9989	0.999	8	5	10	94	98	110
Anticonvulsants									
Acetazolamide	0.9983	0.9988	0.9979	7	300	700	170	100	99
Carbamazepine	0.9993	0.9984	0.9996	10	200	60	110	110	110
Lamotrigine	0.999	0.9974	0.9978	10	500	200	170	110	100
Phenytoin	0.9978	0.9963	0.9966	50	200	600	94	100	120
Antidiabetics									
Glibenclamide	0.993	0.9988	0.9979	40	100	200	0	51	79
Gliclazide	0.999	0.9977	0.9982	9	20	10	90	100	120

Table A6 continued. Linearity (R2), limit of quantification (LOQ, in pg on column), and filter recovery

	Linearity			LOQ			Filter recovery		
Compound	**mq**	**eff**	**inf**	**mq**	**eff**	**inf**	**MQ**	**eff**	**inf**
Antidotes									
Naloxone	0.9983	0.9987	0.9988	10	30	300	92	110	130
Antihistamines									
Antazoline	0.9963	0.9985	0.9975	4	20	20	97	100	110
Cetirizine	0.9992	0.9972	0.9987	30	100	300	120	97	110
Chlorpheniramine	0.9979	0.9965	0.998	30	10	10	110	93	130
Cimetidine	0.9973	0.9986	0.9988	20	10	20	140	110	140
Promethazine	0.9982	0.9984	0.9934	20	4	20	62	85	80
Antihypertensives									
Atenolol	0.9977	0.9981	0.9976	3	200	200	150	97	100
Bezafibrate	0.9992	0.9989	0.9982	20	200	200	90	81	97
Enalapril	0.9989	0.9982	0.9987	9	30	200	140	110	110
Nifedipine	0.9988	0.9994	0.9979	20	6	40	61	83	72
Antimycotics									
Clotrimazole	0.9966	0.9987	0.9982	3	90	100	42	2.8	11
Fluconazole	0.9993	0.9986	0.9996	2	50	100	120	100	110
Antiparasitics									
Albendazole	0.9988	0.9984	0.9965	20	10	20	91	49	65
Antiretrovirals									
Abacavir	0.9952	0.9978	0.9989	10	9	20	140	100	140
Atazanavir	0.9993	0.9977	0.9981	30	70	70	63	60	73
Darunavir	0.9982	0.9931	0.9976	40	300	400	77	57	80
Etravirine	0.9992	0.9993	0.9978	20	70	200	0.53	0	10
Lamivudine	0.9997	0.9992	0.9987	5	60	50	95	120	130
Nevirapine	0.999	0.9981	0.998	3	20	10	100	100	140
Raltegravir	0.9979	0.9987	0.9964	10	50	200	130	97	100
Saquinavir	0.9977	0.9984	0.9995	20	40	60	18	7.7	14
Antivirals									
Aciclovir	0.9998	0.9984	0.9972	4	300	700	180	92	110
Famciclovir	0.9988	0.9993	0.9971	2	10	9	180	100	150
Decongestants									
Oxymetazoline	0.9992	0.9993	0.9987	6	20	8	110	100	120
Herbicides/pesticides									
Atrazine	0.9973	0.9974	0.9983	3	8	20	150	110	130
Tebuthiuron	0.9987	0.9984	0.9984	5	10	30	120	110	120
Terbuthylazine	0.9972	0.9986	0.9981	3	7	20	100	87	110
Hormonal contraceptives									
Levonorgestrel	0.9982	0.9983	0.9956	100	200	300	80	63	70
Medroxyprogesterone	0.995	0.999	0.9975	20	100	100	67	67	77
Norgestrel	0.9984	0.9954	0.997	40	300	1000	73	110	150
Progesterone	0.9951	0.9956	0.9965	30	200	100	44	35	37
Psycholeptics/antidepressants									
Amitriptyline	0.9986	0.9991	0.9987	8	40	100	52	80	76
Clozapine	0.9988	0.9996	0.9995	50	50	20	48	68	84
Diazepam	0.9995	0.9981	0.9958	6	20	40	83	79	130
Fluoxetine	0.9983	0.9983	0.9985	20	30	30	32	69	74
Haloperidol	0.9992	0.999	0.9993	10	20	30	48	80	57
Lorazepam	0.9973	0.9983	0.9981	5	200	90	110	93	100
Oxazepam	0.9995	0.9995	0.9996	9	200	200	100	100	100
Stimulants									
Caffeine	0.9989	0.9986	0.9978	9	30	800	140	100	81

Table A7. Method (1), intraday (2), and interday (3) precision and accuracy

	Precision									Accuracy								
	mq			eff			inf			mq			eff			inf		
Compound	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Analgesics/anti-inflammatory drugs																		
Betamethasone	1.3	4.5	4.8	3.1	5.4	7.4	6.9	6.7	7.7	110	110	89	94	94	89	90	96	99
Betamethasone-17,21-dipropionate	6.8	5.7	5.1	13	8.7	10	16	14	11	140	140	110	140	140	140	130	140	150
Betamethasone-17-valerate	8.1	6.1	4.9	2.7	7.2	7.8	10	7.7	6.9	85	88	80	94	92	90	89	97	110
Budesonide	5.1	4.9	7.1	10	9.2	13	15	11	9.8	82	81	73	85	85	88	84	83	99
Codeine	3.1	2	2.4	0.92	5.4	5.1	1.3	5.1	4.7	97	97	89	110	100	98	110	120	110
Diclofenac	7	6.5	6.2	14	11	8.6	0.43	5.4	10	110	100	97	86	82	78	110	120	93
Ketoprofen	3.8	3.4	3.7	11	11	8.9	6.3	6.7	8	110	110	96	95	100	99	110	110	96
Paracetamol	2.2	1.4	1.9	2	3.5	3.8	7.1	5.5	5.7	100	100	91	120	120	110	110	110	97
Tramadol	3.8	2.9	3.9	2.8	1.8	7.4	2.3	5.1	6.1	85	86	120	87	86	82	58	62	72
Antiarrhythmics																		
Carvedilol	6	4	4.6	3	3.7	5	9.9	9.1	9.4	89	88	72	77	77	77	67	73	84
Lignocaine	1.8	2.2	2.9	3.5	4.6	6.4	2.4	3.7	4.3	98	96	90	89	89	91	84	92	88
Antibiotics																		
Amoxicillin	3.3	2.6	3.3	5.3	5.9	4.6	2.6	4.6	5	86	86	76	100	100	89	100	110	87
Ciprofloxacin	4.2	3	3	4.8	4.9	3.8	6.9	7.8	7.3	88	89	78	83	83	89	66	72	74
Clindamycin	0.56	0.98	1.7	3.3	3.1	2.1	2.3	2.1	2.4	110	110	100	110	110	100	110	110	100
Erythromycin	4.4	4.1	4.5	4.5	5.9	10	12	6.5	7.4	90	87	73	63	64	60	58	62	62
Flucloxacillin	7.4	4.2	5	2.4	4.3	6.8	9.2	7	7	71	70	66	95	94	91	97	100	110
Levofloxacin	3.3	2.8	3.1	5.9	4.9	6.6	4.9	6.1	6	110	110	92	95	95	90	100	110	90
Linezolid	1.3	0.98	1.9	1	1.2	3.2	7.7	4.7	4.2	91	90	86	110	110	100	80	84	77
Nalidixic acid	3.6	4.1	3.4	8.4	6	7	6.9	4.3	4.9	110	110	110	110	110	110	99	100	100
Sulfamethazine	4.6	4.6	6.5	11	15	15	8.6	9.7	11	110	110	110	86	95	97	110	120	98
Sulfamethoxazole	2.6	2.9	3.7	18	12	12	6	6.5	5.7	110	110	98	100	100	95	100	110	110
Trimethoprim	2.9	3.4	3.7	5.8	3.4	3.2	5.6	4.2	3.7	100	100	98	120	120	110	120	120	110
Virginiamycin	1.6	3.6	6.3	15	11	11	9	7.4	6.5	140	140	130	120	120	110	90	97	90
Anticholinergics																		
Atropine	5	4.2	3.2	3.2	3.4	3.2	1.2	2.7	2.7	97	96	89	110	110	110	120	120	110
Biperiden	1.7	1.7	2.8	0.32	3.3	5.1	3.7	1.7	3.6	120	120	110	75	77	69	73	75	72
Orphenadrine	2.4	2.1	2.5	2.7	3.7	6	3.3	2.4	3.4	110	110	96	96	98	89	94	97	91
Anticonvulsants																		
Acetazolamide	5	2.9	2	1.9	4.2	4	2	5.5	4.2	83	81	72	74	72	69	63	68	61
Carbamazepine	1	2	2	5	4.2	4.1	2.7	2.7	2.8	120	120	110	110	110	110	110	110	100
Lamotrigine	3.6	3.9	4.1	1.7	4	7	7.2	7.5	8.7	91	87	74	89	88	93	100	100	95
Phenytoin	4.5	7.6	7.2	3.7	3.3	8.4	12	9.6	10	83	79	68	63	62	65	66	69	72
Antidiabetics																		
Glibenclamide	5.2	5.1	3.6	12	6	5.8	6.4	5	5.5	110	110	110	83	80	86	78	84	89
Gliclazide	2.7	2.7	2.9	3.8	4.9	6.9	5.2	2.6	3.5	93	91	85	120	120	110	100	110	120
Antidotes																		
Naloxone	3	2.5	2.6	6.4	4.8	4.5	1.4	4.2	5	120	120	120	120	120	110	120	130	110
Antihistamines																		
Antazoline	0.13	1.7	2.1	2.5	2	3.4	3.9	3.5	3.7	120	120	110	120	120	110	110	110	110
Cetirizine	3.1	2.5	3.7	5.1	7.2	9.8	6.6	8.4	7.8	100	100	85	130	140	120	98	100	110
Chlorpheniramine	4.1	1.9	2.6	4.1	2.7	3.7	6.1	4.9	4.7	82	79	100	77	78	110	68	71	96
Cimetidine	1.9	2.7	1.8	1.9	2.7	3.8	3.5	3.2	3.8	130	130	110	120	120	110	120	130	110
Promethazine	2	3.1	3.1	5.4	5.8	7.7	7.9	5.2	4.9	120	120	110	66	66	64	60	66	62

Table A7 continued. Method (1), intraday (2), and interday (3) precision and accuracy

	Precision									Accuracy								
	mq			eff			inf			mq			eff			inf		
Compound	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Antihypertensives																		
Atenolol	5.9	5.1	4.8	4.4	9.3	12	5	9.6	11	100	110	100	86	86	87	100	110	90
Bezafibrate	1.6	5.1	4.9	9.1	7.8	10	3.8	4.8	6.5	94	94	99	100	97	90	96	96	94
Enalapril	2.5	2.7	2.8	3.3	2.4	3.2	9.8	6.5	4.2	110	110	100	130	130	120	120	130	120
Nifedipine	2	2.1	2.8	3.6	4.3	7.1	5.3	4.6	4.6	100	100	100	81	80	85	51	53	69
Antimycotics																		
Clotrimazole	5.8	3.1	3.5	4.4	4.8	6.5	9.2	6	5.8	130	130	110	110	110	96	78	84	83
Fluconazole	3	1.8	2.5	3	3.1	3	4.6	4.2	4	110	110	100	110	110	100	110	110	110
Antiparasitics																		
Albendazole	1.7	2.5	3.1	6.1	7.9	6.3	5	6.1	6.2	110	110	97	120	120	110	120	120	99
Antiretrovirals																		
Abacavir	1.6	1.3	2.2	5.1	4.2	3.4	4.3	3.7	4	140	140	120	130	130	120	110	120	100
Atazanavir	8.6	4.2	6.2	5.1	6	7.2	6	7.1	5.5	110	110	91	110	110	92	110	110	96
Darunavir	0.6	4	5.8	13	12	16	3.6	9.1	9.1	91	93	91	87	97	97	92	100	100
Etravirine	1.4	3.4	3.9	3.5	5.4	6.5	8.4	11	8.4	91	92	71	99	100	97	97	100	96
Lamivudine	2.4	3	3.6	2.6	5.1	4.2	7.8	4.4	4.5	100	110	100	81	81	70	110	120	100
Nevirapine	1.6	2.3	4.3	4.1	3.5	6.1	1.6	2.5	3.3	120	120	110	110	110	99	90	95	79
Raltegravir	0.64	2.1	3.5	7.6	7.7	7.2	7.4	8	7.5	120	120	110	100	110	110	84	88	82
Saquinavir	5.8	4.7	3.8	7.7	5.4	6	5.5	7.1	6.7	88	86	72	77	76	76	67	74	85
Antivirals																		
Aciclovir	1.8	2.3	2.1	9	7.8	5.9	6.1	7.1	6.2	110	110	96	86	86	82	97	110	92
Famciclovir	3.1	3.4	3.3	2.5	3.6	6.4	0.96	3.8	5.1	100	110	110	110	110	100	120	120	100
Decongestants																		
Oxymetazoline	1.3	2.3	2.3	1.7	2.5	3.3	2.3	2.9	3.5	100	98	90	100	100	100	120	130	120
Herbicides/pesticides																		
Atrazine	1.4	0.93	2.8	2.3	3.4	4.9	5	4.6	5	120	120	110	120	120	110	100	110	110
Tebuthiuron	4.1	2.8	3	1.8	3.7	4.1	5.2	4.3	4.3	86	86	78	130	130	120	130	140	130
Terbuthylazine	1.8	2.1	2.6	1.3	3.8	7.2	5.7	3.1	4.3	74	73	67	97	94	95	88	91	110
Hormonal contraceptives																		
Levonorgestrel	6.9	5.7	8.3	17	13	12	13	13	10	85	87	80	95	99	92	86	89	90
Medroxyprogesterone	4.1	5.7	5.4	3.6	4.9	6.3	3.4	4.8	7.1	69	67	61	84	84	81	90	91	100
Norgestrel	1.1	6.3	5.4	7.5	6.4	8.4	6.7	11	8.7	88	83	74	130	140	130	110	120	140
Progesterone	7.5	8.3	7.3	7.5	11	8.9	5.7	8	8.1	66	65	63	81	85	77	89	98	100
Psycholeptics/antidepressants																		
Amitriptyline	3.2	3.6	3.2	2.9	6.5	8.5	2.8	2.5	5.1	120	110	97	73	74	65	66	72	72
Clozapine	3.7	4	2.7	2.6	3.1	3.9	4.2	2.8	2.6	120	120	110	99	100	100	110	120	110
Diazepam	7.5	5.1	5.5	3.3	4.4	7.7	6.4	8.1	7.9	110	110	90	140	140	120	140	140	120
Fluoxetine	3.5	3.3	3.6	5.5	6.4	9.3	5.5	3.2	5.5	81	81	65	64	64	56	59	62	61
Haloperidol	2	2.3	2.8	1.7	4.5	8.2	7.1	3	5.4	99	97	82	74	77	68	70	73	74
Lorazepam	3.1	2.7	3.5	4	5	7.2	3.4	4.5	4.9	80	79	72	110	120	110	110	120	130
Oxazepam	1.7	1.7	2.4	0.71	2.4	3.4	5.2	2.4	4.7	110	110	100	110	110	110	110	110	100
Stimulants																		
Caffeine	2.1	1.8	2.5	2.4	2.6	3.1	6.3	6.4	12	87	85	76	130	120	110	120	120	110

Table A8. Concentrations (ng/L) of micropollutants in influent and effluent samples of the demonstration-scale decentralised wastewater treatment system in eThekwini

	Influent					Effluent					
	Day 1		Day 2	Day 3		Day 1		Day 2		Day 3	
Compound	**07:30**	**18:00**	**07:30**	**07:30**	**18:00**	**07:30**	**18:00**	**07:30**	**18:00**	**07:30**	**18:00**
Analgesics/anti-inflammatory drugs											
Betamethasone	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Betamethasone-17,21-dipropionate	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Betamethasone-17-valerate	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Budesonide	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Codeine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Diclofenac	2 100	2 300	2 400	2 000	2 800	1 900	2 300	2 100	1 900	2 100	2 100
Ketoprofen	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Paracetamol	150 000	110 000	120 000	120 000	180 000	7 400	4 600	3 600	2 600	5 900	3 400
Tramadol	520	300	310	290	220	430	430	390	390	360	390
Antiarrhythmics											
Carvedilol	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Lignocaine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Antibiotics											
Amoxicillin	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Ciprofloxacin	1 400	780	1 300	1 400	1 800	1 500	1 500	1 300	1 800	1 800	1 500
Clindamycin	760	230	120	150	110	230	250	230	290	290	300
Erythromycin	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Flucloxacillin	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Levofloxacin	< LOQ	< LOQ	24	26	24	26	21	20	20	25	20
Linezolid	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Nalidixic acid	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Sulfamethazine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Sulfamethoxazole	9 300	7 000	14 000	18 000	11 000	3 200	2 800	2 000	2 000	2 400	2 300
Trimethoprim	1 300	780	1 400	2 100	1 300	300	330	250	250	260	340
Virginiamycin	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Anticholinergics											
Atropine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Biperiden	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Orphenadrine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Anticonvulsants											
Acetazolamide	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Carbamazepine	410	450	420	660	440	490	470	500	470	470	480
Lamotrigine	240	< LOQ	< LOQ	240	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Phenytoin	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Antidiabetics											
Glibenclamide	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Gliclazide	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	46	38	48	42	46	46
Antidotes											
Naloxone	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Antihistamines											
Antazoline	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Cetirizine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Chlorpheniramine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Cimetidine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Promethazine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table A8 continued. Concentrations (ng/L) of micropollutants in influent and effluent samples of the demonstration-scale decentralised wastewater treatment system in eThekwini

	Influent					Effluent					
	Day 1		Day 2	Day 3		Day 1		Day 2		Day 3	
Compound	**07:30**	**18:00**	**07:30**	**07:30**	**18:00**	**07:30**	**18:00**	**07:30**	**18:00**	**07:30**	**18:00**
Antihypertensives											
Atenolol	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	580	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Bezafibrate	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Enalapril	8 300	6 500	6 300	9 200	7 800	8 800	8 400	8 100	8 100	7 000	8 100
Nifedipine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Antimycotics											
Clotrimazole	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Fluconazole	1 100	670	810	570	510	1 900	1 900	1 900	1 800	1 800	1 700
Antiparasitics											
Albendazole	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Antiretrovirals											
Abacavir	290	100	69	29	21	500	550	570	540	550	550
Atazanavir	3 400	3 100	2 400	3 500	2 900	2 700	2 900	3 500	3 200	2 600	3 300
Darunavir	16 000	10 000	14 000	17 000	12 000	9 200	10 000	9 100	9 700	12 000	10 000
Etravirine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Lamivudine	85 000	85 000	65 000	47 000	86 000	94 000	120 000	140 000	130 000	130 000	150 000
Nevirapine	340	320	310	420	370	280	310	330	360	390	440
Raltegravir	4 000	2 200	2 400	6 300	5 800	3 300	3 300	3 300	4 100	3 400	3 800
Saquinavir	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Antivirals											
Aciclovir	2 000	4 700	2 700	1 700	3 800	2 400	2 600	2 200	1 400	1 600	1 300
Famciclovir	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Decongestants											
Oxymetazoline	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Herbicides/pesticides											
Atrazine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Tebuthiuron	100	110	86	66	120	90	100	130	120	110	100
Terbuthylazine	< LOQ	56	25	41	43	< LOQ	43	62	59	46	53
Hormonal contraceptives											
Levonorgestrel	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Medroxyprogesterone	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Norgestrel	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Progesterone	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Psycholeptics/antidepressants											
Amitriptyline	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Clozapine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Diazepam	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Fluoxetine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Haloperidol	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Lorazepam	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Oxazepam	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Stimulants											
Caffeine	22 000	23 000	16 000	19 000	29 000	9 000	9 200	7 900	6 900	6 100	5 800

Table A9. Removal efficiencies (%) of Newlands Mashu decentralised wastewater treatment system (NM DEWATS); and other decentralised wastewater treatment systems (DEWATS) and conventional wastewater treatment plants (WWTP) reported in literature

Compound	NM DEWATS	DEWATS	WWTP	Reference
	this publication			
Analgesics/anti-inflammatory drugs				
Diclofenac	11	82[1]	24	Schaider et al., 2017
Paracetamol	97	99.8[1]	99.8	Schaider et al., 2017
Tramadol	–21	53[2]	50	Gomes et al., 2008; Vymazal et al., 2017
Antibiotics				
Ciprofloxacin	–17	-	69	Margot et al., 2015
Clindamycin	3	-	< 0	Gurke et al., 2015
Levofloxacin	11	-	75	Golovko et al., 2014
Sulfamethoxazole	79	40[1]	47	Schaider et al., 2017
Trimethoprim	79	60[1]	70	Schaider et al., 2017
Anticonvulsants				
Carbamazepine	0	8[1]	8.6	Schaider et al., 2017
Antihypertensives				
Enalapril	–6	-	> 60.7	Gurke et al. 2015
Antimycotics				
Fluconazole	–150	-	15	Margot et al., 2015
Antiretrovirals				
Abacavir	–430	62–100[3]	> 99	McCurry et al., 2014; Prasse et al., 2010
Atazanavir	1	-	-	
Darunavir	28	-	-	
Lamivudine	–73	90–100[3]	24–59, > 76	K'Oreje et al., 2016; McCurry et al., 2014; Prasse et al., 2010
Nevirapine	0	-	11–39, 0	K'Oreje et al., 2016; Prasse et al., 2010
Raltegravir	15	-	-	
Antivirals				
Aciclovir	36	94–96[3]	98	McCurry et al., 2014; Prasse et al., 2010
Herbicides/pesticides				
Tebuthiuron	–12	-	-	
Terbuthylazine	–28	-	24	Margot et al., 2015
Stimulants				
Caffeine	66	99.63[1]	80	Schaider et al., 2017

[1]septic tank, drainfield; [2]constructed wetland; [3]membrane bioreactor

Table A10. Average removal efficiencies (%) (n = 3) of micropollutants from South African wastewater using biochars produced from olive residues, tomato residues, rice husk, and Raphia farinifera

	Olive	Tomato	Rice husk	*Raphia farinifera*
Analgesics/anti-inflammatory drugs				
Diclofenac	31	9.7	5	23
Paracetamol	51	35	26	41
Tramadol	79	68	73	43
Antibiotics				
Ciprofloxacin	100	100	100	100
Clindamycin	70	40	34	–73
Levofloxacin	100	100	100	100
Sulfamethoxazole	63	100	53	63
Trimethoprim	100	93	92	83
Anticonvulsants				
Carbamazepine	61	1.3	38	50
Lamotrigine	100	19	100	100
Antidiabetics				
Gliclazide	45	6.1	–11	52
Antihypertensives				
Enalapril	20	–2.9	–13	20
Antimycotics				
Fluconazole	22	6.2	5.6	29
Antiretrovirals				
Abacavir	55	37	44	33
Atazanavir	76	38	63	60
Darunavir	75	51	57	48
Lamivudine	64	57	–21	74
Nevirapine	43	19	27	40
Raltegravir	63	76	61	75
Antivirals				
Aciclovir	–31	40	18	36
Herbicides/pesticides				
Tebuthiuron	75	36	36	56
Terbuthylazine	100	100	100	100
Stimulants				
Caffeine	53	37	34	58