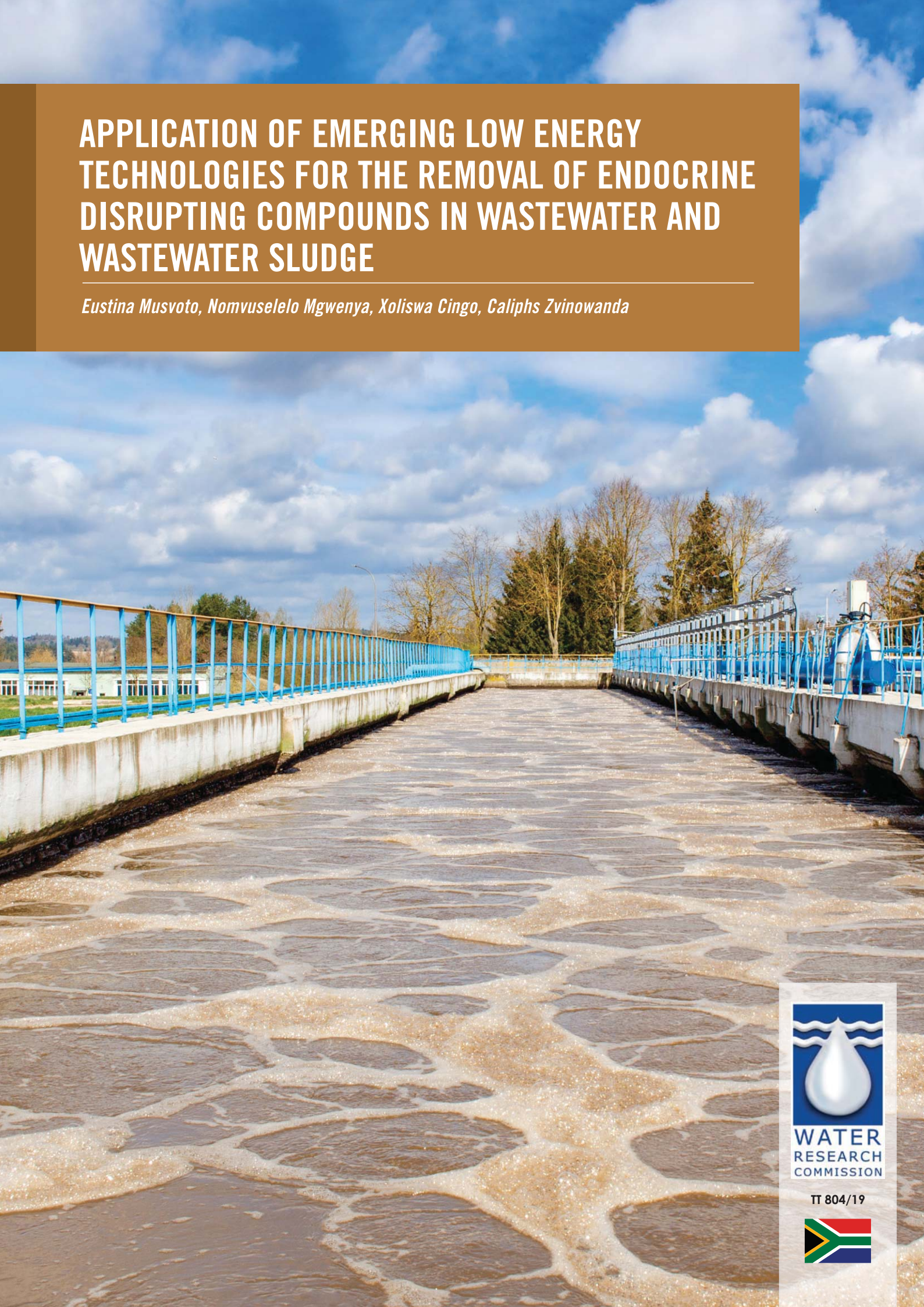
APPLICATION OF EMERGING LOW ENERGY TECHNOLOGIES FOR THE REMOVAL OF ENDOCRINE DISRUPTING COMPOUNDS IN WASTEWATER AND WASTEWATER SLUDGE

Eustina Musvoto, Nomvuselelo Mgwenya, Xoliswa Cingo, Caliphs Zvinowanda



WATER RESEARCH COMMISSION

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Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

To date, only a handful of studies have been undertaken on monitoring and removal of endocrine disrupting compounds (EDCs) from both wastewater and sludge in South Africa. The sludge management regulations in South Africa advocate beneficial utilization and most of the sludge generated at municipal wastewater treatment plants (WWTPs) is disposed on land and also reused for agriculture. Global research has indicated increased concerns over the risks potential leaching of EDCs from sludge disposed on land into groundwater and uptake by plants pose to the environment and human health. In view of this, it is thus important for the South African wastewater sector to understand the levels of EDCs in sludge, the associated risks as well as measures to lower them. This project was therefore funded by the Water Research Commission (WRC) to address the gaps in knowledge on processes and technologies that remove EDCs from wastewater sludge, as part of the ongoing South African research programme on EDCs. The main objectives of the project were to:

- Evaluate at pilot scale, the efficiency of an emerging sludge treatment technology in removing selected EDCs from various types of sludge generated at a local WWTP
- Compare the results from the pilot study with established technologies generally applied for sludge treatment in South Africa

The emerging polymeric carbon solid (PCS) process that demonstrated effective removal of some EDCs from sludge at laboratory scale in previous research was selected for evaluation. A 60 litre pilot reactor was installed at the City of Tshwane's Daspoort WWTP. Batches of primary sludge (PS), waste activated sludge (WAS), mixed PS and WAS (PS & WAS) and anaerobically digested sludge (DS) from the plant were processed in the pilot reactor. Both the sludge feedstock and process products (hydrochar and supernatant) were analysed for the following selected EDCs:

- Pharmaceuticals: acetaminophen (APAP), bezafibrate and carbamazepine (CBZ)
- Estrogens: oestrone (E1)
- Per-polyflucroalkyl substances (PFAS): perfluorooctanoic acid (PFOA), perfluorohexanoic acid (PFHxA), perfluoro-1 octanesulfonate (PFOS) and perfluorodecanocic acid (PFDA)

The EDCs were selected based on previous research at Daspoort WWTP as well as compounds of concern identified by the Global Water Research Coalition (GWRC).

Apart from PFHxA and PFDA, all EDCs were above the limit of detection in all sludge types. A mass balance approach taking into account EDCs in both the solid and liquid portions of the sludge feedstock and process products was applied in calculating the EDCs removal efficiencies of the PCS process. The results were then compared with the efficiency of a laboratory scale conventional MAD that processed sludge from Daspoort WWTP in a previous project. A comparison with the efficiency of the full-scale MAD at Daspoort WWTP that treats combined PS & WAS was also made. The removal efficiencies for EDCs that were above the limit of detection are given in Table 1.

Table 1: Summary of EDCs Removal Efficiencies in the PCS Pilot Reactor and Conventional MAD

Sludge/Technology	APAP	Bezafibrate	CBZ	E1	PFOA	PFOS
PS						
% Removal PCS	91	82	86	93	96	69
% Removal Lab Scale MAD	27	61	16			55
WAS						
Overall Removal	97	74	94	96	93	97
% Removal Lab Scale MAD	43	33	33			91
PS & WAS						
% Removal PCS Process	98	73	86	91	94	63
% Removal Lab Scale MAD	34	66	20			89
% Removal Full Scale MAD	41	17	38	93	44	-17
DS						
% Removal PCS Process	98	88	93	93	99	64
Average Untreated Sludge (PS, WAS, PS & WAS)						
Average % Removal PCS	95	77	89	94	94	76
Average % Removal MAD (Lab Scale)	35	53	23			78
Average % Removal MAD (Lab & Full scale)	36	44	27	93	44	72

The key findings from the project were as follows:

Pharmaceuticals

The average removal from untreated sludge (average removal from PS, WAS and combined PS & WAS) by the PCS process was 95%, 77% and 89% for acetaminophen, bezafibrate and carbamazepine respectively. The laboratory scale MAD average removal was much lower at 35%, 53% and 23% for the same compounds. Thus the average removal from untreated sludge in the PCS process was 174, 44, and 285% higher for acetaminophen, bezafibrate and carbamazepine than on the laboratory scale MAD. The PCS process also had higher removal efficiency from combined PS & WAS (98, 73 and 86%) compared to the full-scale MAD (41, 17 and 38%) for acetaminophen, bezafibrate and carbamazepine respectively. Removal in the PCS process was therefore 136, 331 and 129% higher than the full-scale MAD at Daspoort WWTP. The PCS process also removed 98, 88 and 93% of residual acetaminophen, bezafibrate and carbamazepine respectively from DS from the full-scale MAD

Estrogens

The average removal of oestrone from untreated sludge in the PCS process was 94%. Oestrone was not analysed in the laboratory scale MAD study. The PCS process removed 91% of oestrone from combined PS &WAS. The full-scale MAD had a slightly higher removal efficiency of 93%. Removal of residual oestrone from DS was 93% in the PCS process.

PFAS

The average removal of PFOA and PFOS from untreated sludge in the PCS process was 94% and 76% respectively. PFOA was not analysed in the laboratory scale MAD. The laboratory scale MAD achieved slightly higher PFOS average removal of 78%. The percentage removal for both PFOA and PFOS from combined PS & WAS by the PCS process was 94% and 65% respectively. The full-scale MAD achieved 45% removal for PFOA and there appeared to be a 17% increase in PFOS after full-scale MAD. The removal efficiency of residual PFOA and PFOS in DS were 99% and 64% respectively in the PCS process.

The results from this study indicate that apart from oestrone and PFOS, the emerging PCS technology has significantly higher removal efficiency for the selected EDCs than conventional MAD that is

commonly applied for sludge treatment at most South African WWTPs. The investigation therefore concluded the PCS process is a feasible technology for treating sludge to a higher quality than conventional processes and is better positioned to meet the requirements of future legislation on EDCs if implemented.

In order to continue building the body of knowledge on the removal of EDCs in wastewater sludge in South Africa, the following is recommended based on the findings from this project:

- Development of a unified approach to analytical methods for detection of EDCs in liquid wastewater and sludge with the objective of increasing laboratory capabilities in South Africa.
- Continued qualitative and quantitative monitoring of target EDCs that are considered at a national level to be of concern in sludge to build a comprehensive national database
- Investigation and mathematical modelling of the mechanisms for removal of target EDCs in conventional MAD, emerging technologies such as the PCS process as well as other sludge treatment technologies most likely to be implemented in South Africa. The research needs to also focus on those aspects that were not adequately addressed in this project, e.g.
    - detailed evaluation of degradation pathways as well as analysis of any possible transformational compounds formed during processing of sludge
    - detailed monitoring and quantitative analysis of PFAS since some compounds that were not targeted in this project were detected in the sludge samples
- Comprehensive research on the fate of EDCs in treated sludge applied to land both for non-agricultural and agricultural purposes to fully understand the potential risks to the environment and human health
- Investigation of application of hydrochar generated from processing sludge in the PCS process as adsorption media to remove EDCs from wastewater effluent, thus advancing the principles of converting WWTPs into resource recovery facilities within a circular economy

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The Reference Group responsible for this project consisted of the following persons:

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Dr Caitlin Swiegelaar
Dr Maria Fernandes-Whaley

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LIST OF ABBREVIATIONS

AAF	average annual flow
APAP	acetaminophen
AOX	Adsorbable organic halogenated substances
AOPs	advanced oxidation processes
ASE	Accelerated solvent extractor
ASP	activated sludge plan
BaP	Benzo[a]pyrene
BNR	biological nutrient removal
BPA	bisphenol A
$Ca(OH)_2$	calcium hydroxide
CBZ	carbamazepine
Cd	cadmium
CO_2	carbon dioxide
CHP	combined heat and power
CH_4	methane
COD	chemical oxygen demand
Cr	chromium
Cu	copper
DAF	dissolved air flotation
DBP	di-n-butyl phthalate
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DEHP	di-(2-ethylhexyl) phthalate
DPCP	1.2-dibromo-3-chloropropane
DS	digested sludge
DWSV	drinking water screening values
E1	oestrone
E2	17β-oestradiol
EDC	endocrine disrupting compound
EDM	endocrine-disruptive metals
EE2	17α-ethinyloestradiol
EHTP	enhanced hydrothermal polymerization
EPA	Environment Protection Agency (USA)
ERWAT	East Rand Water Care Company
FOGs	fats, oils and greases

GAC	granular activated carbon
GHG	greenhouse gas
GWRC	Global Water Research Coalition
Hg	mercury
HTC	hydrothermal carbonization
H_2O_2	hydrogen peroxide
IWA	International Water Association
LAS	linear alkylbenzene sulphonates
MAD	mesophilic anaerobic digester
MLSS	mixed liquor suspended solids
MS	mixed sludge
N	nitrogen
NP	nonylphenol
NPE	nonylphenol ethoxylates
NPnEOs	nonylphenol polyexothylates
O_3	ozone
PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCB	polychlorinated biphenyl
PCDD/F	polychlorinated dibenzodioxins dibenzofurans
PCI	pulverised coal injection
PCS	polymeric carbon solid
PFAS	per - polyflucroalkyl substances
PFCS	perfluorinated chemicals
PFD	process flow diagram
PFDA	perfluorodecanocic acid
PFHxA	perfluorohexanoic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluoro-1 octanesulfonate
p-NP	p-nitrophenol
POP	persistent organic pollutant
PPCPs	pharmaceuticals and personal care products
PS	primary sludge
PST	primary settling tank
SAS	surplus activated sludge
Se	selenium
SRT	sludge retention time

SST	secondary settling tank
TiO_2	titanium dioxide
TPT	triphenyltins
TrOCs	trace organic contaminants
TSS	total suspended solids
UCT	University of Cape Town
UV	ultraviolet
VFA	volatile fatty acids
VSS	volatile suspended solids
WAS	waste activated sludge
WRC	Water Research Commission (South Africa)
WWTP	wastewater treatment plant
Zn	zinc

Chapter 1. Project Background

1.1 REMOVAL OF ENDOCRINE DISRUPTING COMPOUNDS IN WASTEWATER SLUDGE – OVERVIEW

Wastewater (both municipal and industrial) contains a wide range of endocrine disrupting compounds (EDCS) that are discharged into the sewers by households, industries as well as through stormwater runoff. Most wastewater treatment plants (WWTPs) apply biological wastewater treatment processes (e.g. activated sludge, biofilters and ponds) that are not capable of removing most EDCs. Residual EDCs therefore end up in the final effluent and are also adsorped onto sludge. Although regulations require that sludge be stabilized to remove pathogens prior to disposal or beneficial use, most commonly applied conventional sludge stabilization methods like aerobic and anaerobic digestion, composting and addition of alkalis have also been found to be ineffective in removing most EDCs (Ifelebuegu, 2011; Songca, 2012; LRCS, 2016; Coetzee et al., 2018). Thus, EDCS of concern (e.g. estrogen hormones, pharmaceuticals and personal care products, per- and polyfluoroakyl substances, plasticisers, surfactants) have been detected in both final effluent and sludge from conventional WWTPs and therefore enter the environment through effluent discharge into surface water and stabilized sludge disposal onto land. As a result, WWTPs are identified as one of the main pathways of EDCs into the aquatic environment.

EDCs can modulate or disrupt the function of the endocrine system in wildlife and humans with potential adverse impacts on health. There is a large body of corroborative evidence on the adverse impacts of EDCs on aquatic organisms including populations of fish (Mills and Chichester, 2005; Tetreault et al., 2011). There is still no scientific consensus on the severity of adverse effects on humans of EDCs through general environmental contamination or ingestion of food and water. However, the ubiquitous occurrence of EDCs in the water cycle (wastewater-aquatic system-drinking water), persistence and bioaccumulation has increased public concern over the long-term effects of even trace EDCs on health (LRCS, 2016; Wee and Aris, 2019).

Globally most of the sludge produced at WWTPs ends up on land. Historically this has been through disposal in landfills and lagoons. However, in recent years factors such as increased sludge quantities and associated sludge management costs, environmental concerns and impacts of climate change on resources have resulted in more regulations on sludge disposal routes. As a consequence, beneficial use of sludge is now the de facto sludge management strategy internationally. Land application for both agricultural and non-agricultural purposes is the most widely adopted beneficial use route because it is cost effective, recycles nutrients and conditions the soil. Studies have shown that EDCs in sludge can potentially leach into both ground water and soil and/or get taken up by plants, ending up in drinking water and the food chain (Wu et al., 2015; LCRS, 2016; Dodgen, 2018). Although risk studies to date have shown no concrete evidence of the risks to human health of EDCs from sludge, the public has become increasingly concerned about exposure to trace EDCs from sludge that is

disposed on land (Herbert 2007; Lovingood et al., 2018; Wee and Aris, 2019). This concern is influencing the public's decision to accept wastewater and sludge reuse initiatives in their communities. To allay public concerns regarding EDCs in wastewater and wastewater by-products; the wastewater sector has increased research efforts in this area in recent years. The research and studies have focused mainly on reduction of EDCs discharged into wastewater, EDC removal processes and technologies, monitoring and analytical technologies as well as legislation and regulations.

Historically research into EDC removal technologies has mostly focused on tertiary treatment of effluent due to higher concern over the impacts of wastewater effluent on aquatic organisms and drinking water sources. Removal of EDCs from sludge has therefore lagged behind. However, the promotion of sludge reuse, particularly through land application, has increased studies on removal of EDCs from sludge in recent years. The majority of the research has focused on the efficiency of conventional anaerobic digestion in the removal of mostly estrogens as well as certain (pharmaceuticals and personal care products) PPCPs and plasticers of concern. Significant research has also been undertaken at laboratory and pilot scale on application of other technologies to remove EDCs from sludge such as:

- Advanced anaerobic digestion using various disintegration techniques for pre-treatment (e.g. thermal hydrolysis, ultrasonication, ozonation)
- Alkali stabilization
- Composting
- Advanced oxidation processes (AOPs) such as ozonation, hydrogen peroxide (H_2O_2), ultra violet (UV)
- Coupled AOPs
- Thermal treatment (pyrolysis, hydrothermal carbonization)

The studies have reported varied removal efficiencies depending on the type of EDCs and technology. Often conflicting removal efficiency results have been reported for the same EDCs using the same technology. Investigations into these technologies have only been carried out at laboratory and pilot scale thus both efficacy in EDCs removal and economic viability have not been proven at full-scale. Research has also been fragmented resulting in some EDCs and technologies being better studied than others. For example, estrogens, plasticisers, surfactants and certain PPCPs have been extensively researched while there are barely any studies on other EDCs with proven higher toxicity. Technology research has also focused mostly on anaerobic digestion and AOPs with very little done on thermal treatment processes. Monitoring and analytical methods for EDCs in sludge as well as associated costs continue to be a challenge and this has significantly impacted the progress in implementing environmental quality regulatory standards for EDCs for both sludge and wastewater effluent.

Historical data thus indicates that more work still needs to be done to develop processes and technologies that can be reliably implemented at full-scale to remove EDCs of concern from

wastewater sludge. In particular, research into and development of alternative low emissions sludge treatment technologies that can recover energy and other useful resources while reducing EDCs to acceptable levels would result in a net environmental benefit which is very important in this era of climate change.

1.2 PROJECT CONTEXTUALISATION AND OBJECTIVES

In 2001, the South African Water Research Commission (WRC) launched the EDC Research Programme to coordinate local research undertaken on this subject and also to involve other role-players such as government departments, industry and water suppliers in the research (Burger, 2010). Being a member of the Global Water Research Coalition (GWRC), the WRC has guided research into EDCs in the water environment taking cognisance of the activities as well as recommendations of the GWRC. At a workshop held in Pretoria in 2002 the GWRC agreed on a list of 34 priority substances (Table 1-1) to be targeted as part of the global efforts on EDCs (AwwARF, 2006).

Table 1-1: Priority List of EDCs agreed by GWRC Members (Pretoria Workshop 2002)[1]

Confirmed Chemicals		Possible Candidates
Hormones 17β-Estradiol Estriol Estrone 17a-Ethinylestradiol **Pesticides and Herbicides** DDT, DDE, DDD Dieldrin, Aldrin, Endrin, Isodrin A-Endosulphan, β-Endosulphan Endosulphan-sulphate Heptachlor, Heptachlor epoxide Lindane (?-BHC) Vinclozolin Parathion Atrazine Simazine Terbutylazine 2.4-D Metoxychlor Tributylin Cyhexitin	**Heavy Metals:** Cadmium **Industrial Chemicals** PCB (total) Glycol ethers *p*-Nonylphenol *p*-Octylphenol Phthalates: DEPH, DBP Bisphenol A	Glyphosate 2.4-dichlorophenol DPCP (1.2-dibromo-3-chloropropane) Chlordecone Arsenic Amitrole Kepone B-BHC Chrome VI

Notes:

1. Since then more trace organic contaminants (TrOCs) have been added to the priority list of EDCs of concern (e.g. certain pharmaceuticals and PFAS)

The workshop also identified research needs/knowledge gaps and then developed seven project proposals listed below for collaboration to address the research gaps:

- Public Health Impacts – Continuing Literature Surveillance and Reporting
- Ecological Impact of selected EDCs on Aquatic Organisms

- Evaluation and testing of chemical and biological analytical methods for EDC in the water system
- Sources of EDCs in the water cycle
- Occurrence and Fate of EDCs in surface water
- Fate and behaviour of EDCs in Wastewater Treatment (including sludge)
- Fate and behaviour of EDCs in Drinking Water Treatment

Between 2005 and 2010 four projects aimed at providing strategic guidance to the EDC Research Programme, were completed by the WRC (Burger 2010). To date more than 50 studies and projects (some funded by the WRC) have been undertaken in South Africa as part of this programme. Most of the projects fell into the following targeted aims of the research programme (i) strategic planning and management (ii) data acquisition and analytical method development and (iii) risk assessment model development focused on water resources and drinking water. Very few studies have been undertaken on monitoring EDCs in conventional WWTPs and efficiency of conventional WWTPs and sludge stabilization technologies as well as alternative technologies to reduce EDCs discharged into the environment via wastewater effluent and sludge disposed on land. The few studies identified in these subject areas include:

- Olujini et al. (2013) investigated the levels of nonylphenol (NP) and Bisphenol A in WWTP effluent, sludge and leachate at Cape Flats WWTP
- Archer et al. (2017) monitored about 90 emerging contaminants in the influent, effluent and water in the river downstream of a WWTP in Gauteng with the aim of determining the fate of the EDCs during wastewater treatment as well as the impact on the receiving water bodies
- Coetzee et al. (2017) investigated the efficiency of various wastewater treatment plants in Gauteng as well as mesophilic anaerobic digestion (at pilot scale) in removing selected PPCPs, PFAS and estrogen from liquid wastewater and sludge

The above analysis shows that minimal research has been carried out in South Africa on EDCs in wastewater and sludge as well as associated technologies that can enhance EDC removal at conventional WWTPs. Considering that the sludge management regulations in South Africa advocate beneficial utilization including land disposal and reuse for agriculture, understanding the levels of EDCs in treated sludge and measures to lower them is important. To address some of the research gaps the WRC funded this project as part of the EDC Research Program.

The project investigated application of the emerging catalysed enhanced hydrothermal polymerisation Polymeric Carbon Solid (PCS) process for removal of EDCs from various types of sludge. The PCS process is a subcritical water thermochemical conversion process that converts a wide range of biomass into a sterile hydrochar that has various uses including as a biofuel or a soil conditioner in agriculture. Unlike other thermal processes (e.g. incineration, gasification, pyrolysis, torrefaction) that operate at high temperatures, the catalyst applied in the PCS process significantly reduces the

required operating temperatures and pressures. As a result, the process has lower capital and operating cost and no greenhouse gas emissions. A previous study by Musvoto et al. (2018) at laboratory scale showed that the PCS technology is capable of achieving 67-100% removal of some EDCs (carbamazepine, methylparaben, Bisphenol A and chloramphenicol) from various sludge types. This project built on these findings and investigated application of the PCS process at pilot scale as a possible emerging low energy thermal treatment technology for the removal of EDCs in wastewater sludge.

The main objectives of the project were to:

- Conduct a literature review of established and emerging technologies that remove EDCs from wastewater sludge including legislation and regulations for EDCs in wastewater sludge
- Carry out pilot scale experiments using the PCS technology and assess the removal of targeted EDCs from various types of sludge generated at a local WWTP
- Compare the results from the pilot study with other technologies and processes that remove EDCs from wastewater sludge
- Prepare a report in line with the requirements of the WRC

The pilot plant was located at the City of Tshwane's Daspoort WWTP. Primary sludge (PS), waste activated sludge (WAS), mixed PS and WAS (MS) and anaerobically digested sludge (DS) from the plant were processed in the PCS pilot plant. Table 1-2 gives the EDCs that were targeted for study under this project. The EDCS were selected based on previous research at Daspoort WWTP (Coetzee et al., 2017) as well as compounds of concern identified by the GWRC

Table 1-2: EDCs Selected for Analysis in this Project

Class of EDC	Compounds	Abbreviation
per - polyflucroalkyl substances (PFAS)	Perfluorodecanoic acid	PFDA
	Perfluorooctanoic acid	PFOA
	Perfluorohexanoic acid	PFHxA
	Perfluoro-1-octanesulfonate	PFOS
Oestrogens	Oestrone	E1
	17β-oestradiol	E2
	17α-ethinyloestradiol	EE2
Pharmaceuticals	Bezafibrate	
	Acetaminophen	
	Carbamazepine	CBZ

Chapter 2. Literature Review

2.1 OVERVIEW OF EDCS

Endocrine disrupting compounds encompass a variety of chemical classes, including drugs, pesticides, compounds used in the plastics industry and in consumer products, industrial by-products and pollutants, and even some naturally produced botanical chemicals. Some are pervasive and widely dispersed in the environment and may bio-accumulate. Some are persistent organic pollutants (POP's), that can be transported long distances across national boundaries and have been found in virtually all regions of the world, including even concentrating near the North Pole, due to weather patterns and cold conditions (Visser, 2007). Others are rapidly degraded in the environment or human body or may be present for only short periods of time (Damstra, 2002).

Research over the past three decades has shown that EDCs imitate natural hormones of the endocrine system and display either oestrogenic or androgenic activities. They therefore can have adverse effects by either unnaturally inhibiting or stimulating the endocrine system and/or hormonal production in animals including humans. Health effects attributed to EDCs include a range of reproductive problems (reduced fertility, male and female reproductive tract abnormalities, and skewed male/female sex ratios, loss of foetus, menstrual problems), changes in hormone levels; early puberty; brain and behaviour problems; impaired immune functions; and various cancers (Harrison et al., 1995; Diamanti-Kandarakis et al., 2009; Schug et al., 2011; Marques-Pinto et al., 2013; WHO, 2013). Adverse effects of EDCs on aquatic species as well as on invertebrates and wildlife populations have also been documented (Matthiessen et al., 1998; Soares et al., 2008; Flint et al., 2012).

The Endocrine Society released a scientific statement outlining mechanisms and effects of endocrine disruptors on “male and female reproduction, breast development and cancer, prostate cancer, neuroendocrinology, thyroid, metabolism and obesity, and cardiovascular endocrinology,” and showing how experimental and epidemiological studies converge with human clinical observations “to implicate EDCs as a significant concern to public health.” The statement noted that it is difficult to show that endocrine disruptors cause human diseases, and it recommended that the precautionary principle should be followed (Short, 1999) A concurrent statement expresses policy concerns Diamanti-Kandarakis et al., 2009). Thus due to these potential adverse impacts EDCs are considered priority pollutants and worldwide research is ongoing to develop strategies to remove EDCs from the environment.

2.2 TYPES OF EDCS

Numerous compounds are suspected to interact with endocrine systems in humans and animals Currently, more than 38, 000 pharmaceutical compounds are identified as endocrine disrupting and more than 87 000 new chemicals have not been tested yet (Tijani et al., 2013; Coetzee et al., 2017).

These compounds can be natural or synthesised. Since these compounds are part of modern existence more and more organic compounds with potential endocrine disrupting effects will therefore continue to be manufactured.

There are several ways to classify EDCs. One of the most convenient ways is according to their origins (Caliman and Gavrilescu, 2009) as follows:

(i) Natural and artificial hormones (e. g., Phytoestrogens, 3-omega fatty acids, contraceptive pills and thyroid medicines)
(ii) Drugs with hormonal side effects (e. g., naproxen, metoprolol and clofibrate)
(iii) Industrial and household chemicals (e. g., phthalates, alkylphenol etoxilate detergents, fire retardants, plasticizers, solvents, 1,4-dichloro-benzene and polychlorinated bis-phenols (PCBs)
(iv) Side products of industrial and household processes (e. g., polycyclic aromatic hydrocarbons (PAHs), dioxins, pentachlorobenzene).

Table 2-1: Some well-known EDCs and their Origins

Category/Use	Example EDCs
Pesticides	DDT, endosulfan, chlorpyrifos, atrazine, 2,4-D, glyphosate, triphenyltins (TPT), vinclozolin
Children's products	Lead, phthalates, cadmium
Food contact materials	BPA, phthalates, phenol, organotin compounds
Electronics and Building materials	Brominated flame retardants, PCBs
Personal care products, medical tubing	Phthalates
Antibacterial	Triclosan
Textiles, clothing	Perfluorochemicals
Product Cleaner	Fragrances, cyclosiloxanes
Surfactants-certain kinds of detergents used for removing oil and their metabolites	Nonylphenol (alkylphenols)
Contraceptives	17-alpha ethinylestradiol
Natural hormones	Oestrogens, genistein, zearalenone
Food Packaging, fire retardants, fabric protectors, waxes, paints	Per- and Polyfluoroalkyl Substances (PFAS)

Per - and Polyflucroalkyl Substances (PFAS)[1] are a group of group of emerging compounds that have raised concern recently. PFAS are organic compounds in which the hydrocarbons of the compound are substituted with fluorine (Stahl et al., 2011). They are commonly used as fabric protectors (stain and water repellent), packaging of foodstuffs and in firefighting materials, paints, non-stick products, cleaning (Sciences, 2016; EPA, 2019).

[1] PFAS is a term that is now applied by the US EPA as a substitute for Perfluorinated Chemicals (PFCs) to collectively describe perfluorooctanoic Acid (PFOA), perfluorooctanesulfonic acid (PFOS) and other chemicals in this group

2.3 SOURCES, PATHWAYS AND FATE OF EDCS IN THE ENVIRONMENT

The presence of pharmaceuticals, endocrine disruptors and degradation by-products in the environment has continued to increase due to urbanisation and rapid population growth rate (Kolpin et al., 2002). Discharge of effluents from wastewater treatment plants after incomplete removal, and disposal of sludge onto land are one of the main routes of entry for EDCs into the environment (Figure 2-1). Due to the low concentrations of these compounds in wastewaters and general sludge, as well as the complexity and diversity of chemical structures, conventional technologies used in wastewater and drinking water treatment plants are not highly efficient in removing EDCs. Thus several classes of potential EDCs such as PPCPs, alkylphenols, PAHs, PFAS, triclosan, bisphenol A, musks and pesticides have been detected in WWTP effluent and sludge.

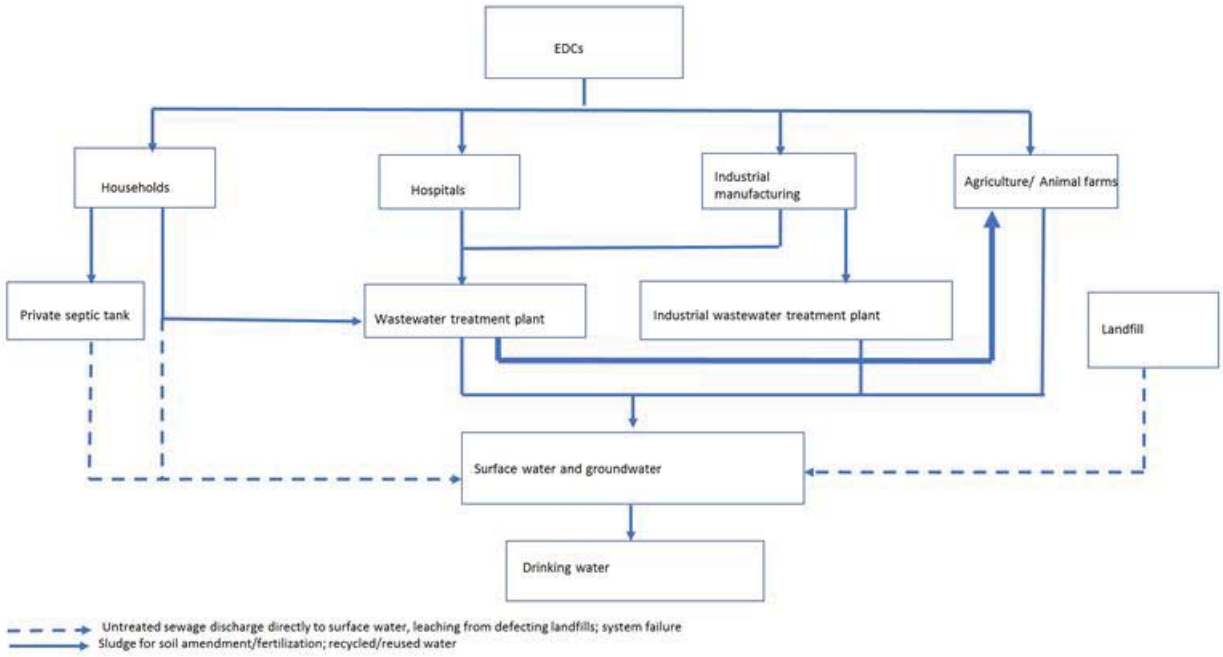


Figure 2-1: Source of EDCs in the Environment

Other known secondary sources of EDCs include landfill leachate, confined animal feeding operations and aquaculture. In addition, combustion waste management technologies and practices like incineration of municipal waste and backyard burning of household trash can release dioxins and furans into the atmosphere. Intentional use, as with agricultural and household pesticides and pharmaceuticals and personal care products (PPCPs), is another important source of EDCs in the environment. EDCs can also be volatile and distributed through long-range atmospheric transport.

The fate of EDCs in the environment depends on the molecular structure of a particular chemical. Some may be completely broken down, changed only slightly, or remain unaltered in the environment for a very long time. Chemicals that are classified as POPs (e.g. PCBs) are extremely resistant to

degradation and are still present many years after being released into the environment. Because of their persistence, POPs have the potential for bioaccumulation and long-range transportation causing extensive environmental contamination. The pesticide DDT has not been used in the U.S. and other countries for over 30 years but it is still present in the environment along with its partial degradation products DDE and DDD. Also, PCBs and organochlorine pesticides have been detected in remote arctic regions where deposition from the atmosphere is the only likely source (Ritter, 1995; Stockholm Convention, 2001; USA EPA, 2019). Since the initial Stockholm Convention in 2001, 16 new POPs of global concern have been added to the original list of 12 (Stockholm Convention, 2017).

2.4 FATE OF EDCS IN CONVENTIONAL MUNICIPAL WASTEWATER TREATMENT PLANTS

2.4.1 Overview

Municipal wastewater treatment plants are not specifically designed to handle the trace levels of EDCs found in wastewater and many EDCs pass through conventional treatment systems without being degraded. Furthermore, EDC compounds belong to different classes of organic compounds and have a variety of functional groups which can make them less amenable to removal by established treatment techniques (sedimentation, biology, filtration, flocculation/precipitation, etc.) used in conventional municipal WWTPs.

The fate of EDCs in wastewater is determined by the physicochemical properties of the different organic compounds (Sawyer et al., 1994; Birkett and Lester, 2003) and based on the properties removal of EDCs can be achieved via the following mechanisms (Birkett and Lester, 2003):

- Adsorption onto suspended solids, fats and oils
- Biological degradation
- Chemical transformations: hydrolysis, photolysis, and oxidation and reduction reactions
- Volatilization

The most important properties are the octanol/water partition coefficient (K_{OW}), Henry's law constant (H), the organic carbon to water partition coefficient (K_{OC}), and the solubility of the organic compound in water (Caliman and Gavirlescu, 2009; Coetzee et al., 2017). Possible removal mechanisms can be predicted by using the coefficients and constants of a specific organic compound.

2.4.2 EDCs Removal Efficiency of Conventional Wastewater Treatment Plants

Range of EDCs removal in conventional WWTP through biological processes, combined with absorption and adsorption mechanisms can achieve up to 99% removal of EDCs. Processes such as primary sedimentation that remove EDCs through adsorption onto primary sludge and fats, oils and greases (FOGs) has been shown to remove the lowest quantity of EDCs. Removal is dependent on the physico-chemical properties of the compound, characteristics of the wastewater as well as retention time (Hamid and Eskicioglu, 2012; Kohl et al., 2008). Data observed on PSTs indicates a wide variation in removal rates (0-46%) depending on EDC type (Coetzee et al., 2017). The bulk of EDCs is removed

through biological treatment, and the following key factors have been observed (Caliman and Gavrilescu, 2009; Ifelebuegu, 2010; Coetzee et al., 2017):

- Compounds with high pseudo first order biodegradation constants (k_{biol}) and low sludge water distribution coefficients (K_{OC}) such as ibuprofen are efficiently transformed independently of sludge retention time (SRT) or hydraulic retention time (HRT)
- Compounds with low k_{biol} and high K_{OC} values, such as musks, are retained in the aeration tank by sorption and significantly transformed at sufficient SRT
- Compounds with low k_{biol} and medium K_{OC} values, such as E1 and E2, are moderately transformed independently of HRT and slightly dependent of hydraulic retention
- Compounds with low k_{biol} and K_{OC} values, such as carbamazepine, are neither removed nor bio-transformed no matter which SRT and HRT is used.

Among all conventional wastewater treatment processes, the activated sludge process has been found to be the most efficient in EDCs removal. Since the proportion of removal by adsorption in primary setting, chemical precipitation, aeration volatilization and WAS absorption is small, the majority of EDCs in wastewater is removed by biodegradation. Factors that have a significant impact on removal efficiency are the type of activated sludge process (aerobic, nitrification, denitrification, phosphorus removal) and sludge age. Long sludge ages increase the removal efficiency of most EDCs.

Activated sludge plant configured for biological nutrient removal have generally shown better removal of EDCs compared to conventional activated sludge plant effluents. A comparison of removal technologies by Ifelebuegu (2010) indicated that the removal efficiency of the treatment processes were in the order activated sludge > oxidation ditch > biofilter > rotating biological contactors.

Coetzee et al. (2017) carried out the most extensive study on EDC removal in South Africa. The study compared the removal efficiency of a range of oestrogens, PFAS and pharmaceuticals at three full scale WWTPs (Daspoort, Zeekoegat and Phola). The removal efficiencies in each EDC group varied from, 'not removed' to >99% removal. Removal efficiencies also varied with the different treatment technologies. The Integrated Ponds system at Phola achieved better removals of the oestrogens and PFCs, with PFOS as the exception. Comparison of the two activated sludge plants indicated that for most of the EDCs the removals were better in the Zeekoegat plant than at Daspoort. Factors that could have contributed to the improved removals at Zeekoegat were the longer SRT, higher MLSS content and the improved oxygen transfer rate in the aeration zone. The removal efficiencies for the three plants are summarised in Table 2-2.

Table 2-2: Comparison of EDCs Removal Efficiency at three WWTPs in Gauteng (Coetzee et al., 2017)

	Zeekoegat PS + AS (%)	Daspoort PS + AS (%)	Phola AP + BF (%)
PFCs:			
PFBA	38	-13	17
PFDA	27	44	35
PFOA	63	54	63
PFHxA	43	45	68
PFOS	94	85	76
PFPeA	23	23	55
PFHxS	75	17	74
Total PFCs	**84**	**75**	**75**
Oestrogens:			
E1	44	28	61
E2	12	34	76
EE2	61	55	65
Total Oestrogens	**47**	**33**	**70**
Pharmaceuticals:			
Nalidixic acid	-1.2	13	35
Bezafibrate	94	90	88
Acetaminophen	87	76	94
Carbamazepine	58	56	41
Stavudine	72	41	74
Lamivudine	100	100	52
Total Pharmaceuticals	**78**	**56**	**87**

Note: AS – Activated Sludge BF – Biofilter/Trickling filter AP – Anaerobic Pond
PS – Primary Settling

The above review has shown that the removal efficiency of EDCs from conventional WWTPs varies considerably depending on the type of compound and removal process. Advanced treatment processes like activated carbon adsorption processes have been found to be more effective in removing EDCs in the aqueous phase. However, since this project investigated removal of EDCs from sludge advanced technologies that remove EDCs from wastewater effluent were not removed. Rather a detailed review of technologies and processes that remove EDCs from sludge is given below.

2.5 REVIEW OF ESTABLISHED AND EMERGING TECHNOLOGIES FOR REMOVAL OF EDCS FROM WASTEWATER SLUDGE

EDCs have been shown to be persistent during conventional biological processes that are widely applied at WWTPs. Due to their hydrophobicity, EDCs end up being adsorped into sludge. Since most of the sludge ends up in land through disposal or beneficial use, there are potential risks associated with the presence of contaminants in sludge. Of particular concern is EDCs leaching into ground water, being taken up by plants and crops and ending up in the human food chain. There are also potential adverse impacts on terrestrial animals. With the drive-in recent years towards beneficial utilization of sludge in agriculture the public has become increasingly concerned about consuming trace elements of EDCs from sludge applied on land. To mitigate these concerns efforts are being made in the wastewater sector to research and develop efficient methods to remove EDCs from sludge. Due to the complex composition of sludge and associated matrix interferences during quantitative analysis, it should be noted though that most of the studies in removal of EDCs have mainly focused on elimination from wastewater and drinking water. Thus studies on sludge are limited. A review of the available literature on removal of EDCs from wastewater sludge using established as well as emerging technologies is outlined below.

2.5.1 Established Sludge Treatment Technologies

Conventional Aerobic and Anaerobic Digestion

Digestion (both aerobic and anaerobic) is the most commonly used sludge stabilization method with anaerobic digestion more widely used applied than anaerobic. Results of some studies on the fate of EDCs groups selected for this study during anaerobic and aerobic digestion are summarised below.

Estrogens

- Earlier studies by Holbrook et al. (2002) on full scale sludge treatment facilities showed an increasing trend of estrogenicity during both mesophilic anaerobic (35 ± 2^{o}C) and thermophilic aerobic stages (55 ± 2^{o}C). Only mesophilic aerobic treatment showed a slight decrease in estrogenicity. An increase in estrogenity in the sludge dewatering liquors that contributed about 5-10% of influent estrogenicity when the liquors were recycled to the influent was also observed.
- Carballa et al. (2006) reported high removal rate (75-90%) of the three natural hormones (E1[2]+E2[3]+EE2[4]) in both mesophilic and thermophilic anaerobic digestion pilot scale studies. The study also concluded that digester operating parameters (temperature and SRT) had no effect on removal rates. In contrast, a study by Muller et al. (2010) on a full-scale anaerobic digester with similar feed (65:35, v/v, PS: WAS) found only around 30-40% removal of the three natural hormones. Also, an increase in EE2 concentration from below detection limit in the feed sludge to > 2 ng/gdw in the digested sludge was observed. A study by Czajka and

[22] E1 - Estrone
[3] E2 - 17β-estradiol
[4] EE2 - 17α-ethynlestradiol

Landry (2012) also found that EE2 degradation was minimal during extended anaerobic digestion of sludge (271 days).

- Furlong et al. (2010) suggested aerobic digestion removed most of the natural and synthetic estrogenic compounds successfully, corresponding to 18% reduction of estrogenicity observed in the YES bioassay. In contrast, thermophilic and mesophilic anaerobic digestion resulted in a net increase in estrogenicity as measured by YES bioassay and the contribution of estrogenic hormones to total estrogenicity more than doubled after anaerobic digestion.
- Ifelebuegu (2011) analyzed undigested and anaerobically digested mixed primary sludge and WAS sludge at two activated sludge plants in the UK. The average removal efficiencies for E1, E2 and EE2 were 24%, 25% and 12% respectively.
- Anderson et al. (2003) investigated the effect on estrogens of mesophilic anaerobic digestion SRT ~ 20 days in full-scale plants in Germany. They concluded that E1 increased from feed MS to digested sludge.
- Similar to the findings of Furlong et al. (2010) a study by Sarkar (2013) on the removal of three types of oestrogens (E1, E2 and E3[5]) using laboratory scale anaerobic digesters and inoculated sludge concluded that there was no anaerobic digestion of estrogenic compounds under any circumstances and the estrogenicity of the sludge measured by YES assay increased during digestion. The increase was attributed to part reduction of E1 to E2 which has higher estrogenicity. No E3 was found in the sludge during anaerobic digestion of E1 and E2.
- In South Africa, Coetzee et.al (2017) investigated the removal of three classes of EDCs; oestrogens (EE2), pharmaceuticals (carbamazepine, acetaminophen and bezafibrate), and PFAS (PFOS and PFDA) from PS, WAS, and mixed PS & WAS using small laboratory batch-scale mesophilic anaerobic digesters. The digesters were operated at 20 days SRT and 36˚C. The sludge was obtained from Daspoort WWTP. Percentage removals of EE2 from WAS, PS and mixed sludge were found to be 0%, 93% and 78% respectively.

In general the majority of studies indicate that estrogens are recalcitrant to conventional aerobic and anaerobic digestion and bioassay analysis (YES tests) have indicated an increase in estrogenicity after digestion.

Pharmaceuticals

The few studies found in the literature indicate variable removal of the pharmaceuticals selected for this study during conventional anaerobic digestion. Carballa et al. (2006) reported no removal of carbamazepine during pilot scale mesophilic and thermophilic anaerobic digestion of mixed PS & WAS. However variable removal rates of 50-59% for mesophilic and 48-61% for thermophilic anaerobic digestion of WAS in laboratory scale anaerobic digesters were reported by Zhou et al. (2015). The study also showed that increasing the SRT time improved removal efficiency of carbamazepine under both mesophilic and thermophilic digestion. Selcen (2012) studied the removal of both

[5] E3 - Estriol

acetaminophen and carbamazepine from WAS in laboratory scale mesophilic anaerobic digesters. Removal rates of 30% and 50% were observed for carbamazepine and acetaminophen respectively. Martin et al. (2015) investigated the removal of acetaminophen, carbamazepine and bezafibrate during anaerobic digestion of mixed sludge. Acetaminophen was present, but below the detection limit in both WAS and the digested sludge and both carbamazepine and bezafibrate were reportedly removed to a significant extent.

In South Africa the laboratory study by Coetzee et al. (2017) under mesophilic conditions showed carbamazepine removal rates of 33%, 20% and 16% for WAS, MS and PS respectively. Acetaminophen removal rates of 43%, 34% and 27% were observed for of WAS, MS and PS respectively. The removals obtained for bezafibrate were 33%, 66% and 61% from WAS, MS and PS respectively.

Most of the literature data indicates low removal efficiencies of the selected pharmaceuticals by conventional anaerobic digestion. Carbamazepine removal was lower than acetaminophen but both were on average < 50% for all sludge types. Improved removal was observed with increase in temperature (thermophilic digestion) and increased SRT. Of the three selected pharmaceuticals, bezafibrate had the best removal rates with > 50% for PS and MS.

PFAS

Very few studies are available on the removal of PFAS from sludge. Schultz et al. (2006) conducted a field study at a full-scale municipal WWTP and determined the removal of various PFAS including PFOS, PFOA and PFDA during mesophilic anaerobic digestion of MS at 30 days HRT. An increase in both PFOS and PFOA were observed after anaerobic digestion while there was no change in the concentration of PFDA after anaerobic digestion. PFOS had the highest concentration in all sludge types. The authors attributed the increase in PFOS to either the differences in HRTs between the thickener and anaerobic digester or to the degradation of precursors to PFOS.

Other studies on full-scale plants also observed that PFOS had the highest concentration in all sludge types. An increase in PFOS and PFOA during digestion (both anaerobic and aerobic) of MS was also observed (Gómez-Canela et al., 2012; Guerra et al., 2014; Yu et al., 2009). Possible reasons given for the increase include degradation of precursor compounds, decrease of volatile solids during digestion and increased sorption capacity of the digested sludge (Guerra et al. 2014).

In South Africa, Coetzee et al. (2017) also found that PFOS had the highest concentration in all sludge types with the concentration in PS almost double that in WAS. Contrary to the full-scale observations mentioned above, Coetzee et al. (2017) observed removals of both PFOS and PFDA in their laboratory scale mesophilic anaerobic digestion study. PFOS achieved the highest removal efficiency (64%) for PS, followed by WAS at 56% and MS at 44%. PFDA removals were 91%, 89% and 55% for WAS, PS and MS respectively.

Advanced Anaerobic Digestion

Advanced anaerobic digestion involves pre-treatment of sludge to disintegrate sludge cells and to improve hydrolysis rates and consequently increase VFA production and methane production during anaerobic digestion. Sludge pre-treatment not only increases biogas generation but also produces less digested sludge with improved characters thereby enhancing subsequent stabilisation, conditioning, dewatering and final disposal processes. Recent studies have also shown that some sludge pre-treatment processes improve the removal of TrOCs including EDCs of concern during anaerobic digestion.

Methods that can be employed for sludge pre-treatment fall into the following categories:

- Thermal (thermal hydrolysis, autoclaving)
- Mechanical (ultrasound, grinding, high pressure homogenisation)
- Chemical (acid, alkali, oxidant addition (ozonation, peroxidation))
- Electrical (focused high voltage pulses)
- Biological (enhanced enzyme hydrolysis)

Literature reported studies on the impact of applying some of these pre-treatment methods on EDCs removal in the downstream anaerobic digestion process are discussed in the relevant technology sections below.

Composting

The efficiency of composting in removing EDCs is variable depending on types of EDCs as well as composting conditions. Composting can be applied for either primary treatment of untreated sludge or enhanced treatment of sludge that has already been stabilised by other means. The process is aerobic and often the sludge is mixed with a carbon-rich bulking agent, (e.g. straw, wood chips, sawdust) to achieve a C:N ratio that favours microbial processes. Due to its aerobic nature and high microbial activity, that accelerate the degradation of organic matter, composting has been viewed as having a high potential to remove EDCs and several studies that have been carried out mostly focused on the removal of NP/ NPnEOs, phthalates, sulfonamides and some pharmaceuticals. Both significant (>60%) and low removals of these EDCs (e.g. nonylphenol, Ibuprofen, triclosan, doxycline) have been reported (Citulski et al., 2010; Semblate, 2015; Haiba and Nei, 2017;)

To date, the removal of a large group of EDCs of concern including the ones selected for this project is poorly studied. One of the available few studies by Martin et al. (2015) investigated the occurrence of twenty two EDCs including carbamazepine, acetaminophen, bezafibrate and estrogens (E1, E2, E3 and EE2) in sludge from a full scale composting facility that composted anaerobically digested MS. Composting of the detectable EDCs selected for this study appeared to increase the concentration of E3 and carbamazepine. There was slight removal (~20%) of bezafibrate.

Alkaline Stabilisation

Alkaline treatment involves the addition of an alkali to raise sludge pH to at least 12 for a contact time for at least 2 hours. The contact time can be increased and supplemental heating applied depending on the required sludge quality (EPA, 2000). Materials that may be used for alkaline stabilisation include lime, fly ash, or cement kiln dust are used. Conceptually, the increase in pH alters the sorption behaviour of some ionisable TrOC causing desorption into the aqueous phase thus potentially increasing their bioavailability in further sludge treatment (e.g. digestion) or enhancing their removal from the sludge matrix after dewatering (Semblante et al., 2015; Venkatesan and Halden, 2016). Traditionally the objective for alkaline stabilization is pathogen reduction. However, the secondary benefit of alkaline stabilization is potential to remove trace organic contaminants (TrOC).

Despite alkaline treatment being a common well established sludge stabilization method, very few studies are available in the literature on the impact of the process on EDCs. The few available studies have investigated removal of EDCs when alkali is added for sludge pre-treatment prior to anaerobic digestion, primary sludge stabilization and post stabilisation of digested sludge.

Alkaline Pre-treatment followed by Anaerobic Digestion

Carballa et al. (2006) used quick lime (CaO) to pre-treat MS prior to feeding into pilot scale mesophilic and thermophilic anaerobic digesters. The study compared the removal efficiencies of 13 PPCPs including carbamazepine and estrogens (E1, E2 and EE2). The study found that alkaline pre-treatment did not significantly influence the removal efficiencies of the PPCPs including the EDCs selected for this study (carbamazepine and estrogens) during both mesophilic and thermophilic anaerobic digestion.

Primary Alkaline Stabilization

Ivashechkin et al. (2010) investigated at laboratory scale, the impact on EDCs of sludge conditioning using hydrated lime (calcium hydroxide; $Ca(OH)_2$). They found that estrogens (E1 and E2) and other similar EDCs like NP and BPA desorbed from sludge during lime stabilization. Further studies on the impact of disposal of lime stabilized sludge onto land found that desorption increased leaching rates and also altered the degradation pathways of certain EDCs in the soil (Semblante, 2015). Thus primary lime stabilization increases the potential for soil groundwater contamination with EDCs if the stabilized sludge is applied on land.

2.5.2 Advanced and Emerging Sludge Treatment Technologies

Advanced Oxidation Processes

Ozonation

Ozone is a strong oxidant that has been used extensively for disinfection of water and wastewater effluent. In sludge treatment the interest in ozonation has mostly been as a pre-treatment method prior to anaerobic digestion. Numerous studies have shown that ozone has high cell lysis efficiency that increases sludge solubilisation and biodegradability and consequently biogas generation in subsequent anaerobic digestion. In recent years, studies have also explored the impact of sludge

ozonation on EDCs. Most of the studies have focused on the impact of ozone pre-treatment of sludge on the efficiency of EDCs removal during anaerobic digestion. Apart from increasing sludge solubilisation and biodegradability, ozone being a powerful oxidant, can also oxidize soluble and particulate compounds. Studies have shown that during sludge treatment ozone rapidly decomposes into radicals and the produced radicals affect oxidation of both particulate and soluble organics. Thus it has been demonstrated that ozone can potentially remove EDCs from sludge primarily through degradation by chemical oxidation; by either direct ozone (O_3) oxidation or indirect hydroxyl radical (OH) oxidation which is formed from O_3 decay (Qiang et al., 2013).

Ozone Pre-treatment followed by Anaerobic Digestion

Bernal-Martinez et al. (2007) reported that ozone pre-treatment of sludge (dose of 100 mg O_3/g TSS) increased poly aromatic hydrocarbons (PAHs) removal by up to 68% during mesophilic anaerobic digestion. A study by Carballa et al. (2007) on the effect of ozone pre-treatment of MS (dose 20 mg/of TSS) on the removal of a range of PPCPs during mesophilic and thermophilic anaerobic digestion concluded that ozonation did not affect the removal efficiencies of all PPCPs except for carbamazepine. Whereas anaerobic digestion without pre-treatment had no effect on carbamazepine, pre-ozonation stimulated removal rates of 17% and 60% during mesophilic and thermophilic anaerobic digestion respectively. The authors attributed this to the tendency of carbamazepine to stay primarily in the aqueous phase, and thus being available for a direct ozone attack. The PPCPs included estrogens (E1, E2 and EE2) selected for this project, whose removal efficiencies were also not impacted by ozone pre-treatment.

In a laboratory scale study Selcen (2012) applied ozone (at three different dosage rates and times) to pre-treat WAS prior to MAD. The ozone was applied at three different dosage rates (0.66, 1.33 and 2.65 mgO_3/TSS). Removal rates of various EDCs were significantly increased compared to removal with conventional MAD. Acetaminophene removal increased from 50% with conventional MAD to 59-90% with ozonation pre-treatment while removal for carbamazepine increased from 30% with conventional MAD to 68-82% with ozonation pre-treatment. The removal of E1 also increased significantly from 55% without pre-treatment to 88-98% with ozonation pre-treatment. Removal rates were found to increase with ozone dose and duration of ozonation. Removal of other EDCs (Benzyl butyl phthalate, diltiazem and progesterone) was also significantly increased with ozone pre-treatment of sludge prior to anaerobic digestion.

Ozonation as Primary Sludge Treatment

Qiang et al. (2013) investigated the removal efficiencies of several typical EDCs (NP, BPA as well as estrogens E1, E3 and EE2) during WAS ozonation at three dosage rates (29, 64 and 100 mgO_3/g TSS). Significant reduction of all estrogens was achieved with >90% removal at ozone dose of 64 mgO_3/gTSS. Complete removal of E3 and EE2 and near complete removal of E1 were achieved at ozone dose of 100 mgO_3/g TSS ozone dose. The removal rates for NP and BPA (that indicated lower desorption rates) were much lower at 40% and 65% respectively. Removal rates increased with increase in ozone dose

while increase in pH increased the removal of all EDCs except NP. The authors concluded that EDCs present in WAS could be effectively removed by ozonation. However, optimal control of the ozone dose is required to ensure effective removal of all EDC groups.

Ozonation as Post Treatment of Digested Sludge

A study by Vranitzky and Lanizter (2009) on the removal of various EDCs from anaerobically digested sludge using ozone, showed that removal rates for NPE ranged from 34-71% and PAH 18-81% depending on ozone dose. The study also reported that removal rates increased with ozone dose. Ozonation had no significant impact on alkylbenzene sulfonates (LAS) and di-ethylexyl phthalate (DEPH). Selcen (2012) also ozonated anaerobic digester sludge (2.65 mg ozone/gTSS for 45 minutes) and found no significant reduction of the EDCs under investigation that included estrogens, acetaminophen and carbamazepine.

Fenton Treatment

In the Fenton reaction ferric (Fe^{2+}) is oxidized by hydrogen peroxide (H_2O_2) to generate OH that serves as the primary oxidant of organic contaminants. Studies on the removal of EDCs from sludge using Fenton treatment have investigated both application for pre-treatment prior to anaerobic digestion and primary treatment. Most reported studies have focused on removal of phthalates and PAHs (e.g. Zheng et al., 2007, Pham et al., 2011). One study that investigated removal of EDCs selected for this project was by Li and Zhang (2014). The removal of four estrogens (E1, E2, E3 and EE2) from WAS treated with Fenton oxidation was investigated. Removal efficiencies of 70%, 90%, 84% and 98% for E1, E2, EE2, and E3 respectively (under the following reaction conditions: H_2O_2 dosage = 15.62 mmol/g, initial pH = 3, reaction time = 60 min, Fe(II) to H_2O_2 molar ratio = 0.167) were reported.

Ultra Violet Irradiation

Recent studies have also investigated applying UV irradiation to remove EDCs from sludge through oxidation. Salihoglu et al. (2014) investigated the removal of 16 targeted PAHs from sludge using UV light. The total amount of PAHs decreased by 21% after UV application. Removals rates increased to 63-77% when titanium dioxide TiO_2 photocatalyst was added during UV exposure. The study also found that total PAHs removal rates increased with temperature although some removal rates for individual compounds decreased with temperature increase. Conversely removal rates were found to decrease with increase in TiO_2 dose. It was hypothesised that this was due to titanium particles causing the UV light to scatter, decreasing the absorption of light in the UV reactor.

Zhang and Li (2014) tracked the removal of six EDCs (E1, E2, EE2 E3, bisphenol A, and 4-NP) from WAS using UV light. Removal rates of about 64% for E1, 67% for E2, 49% for EE2, 54% for E3, 29% for BPA and 13% for NP were achieved at a UV concentration of 0.1-0.2 mg/gdw and 2 hours of irradiation. Increasing irradiation rate to 5 hours increased the removal rates to about 81% of E1, 95% of E2, 73% of EE2, 72% of E3, 59% of BPA, and 34% of NP.

Coupled Advanced Oxidation Processes

In order to improve the efficiency of EDCs removals, various studies have investigated coupled AOP processes. Combinations such as UV plus H_2O_2, ozone plus H_2O_2, and UV plus ozone are powerful oxidation processes that effectively oxidize contaminants. These combinations are designed specifically to increase the concentration of OH radicals formed, since OH radicals have less selectivity as oxidants.

Ultraviolet/Hydrogen Peroxide

In addition to investigating UV irradiation on its own, Zhang and Li ((2014) also investigated the removal of the six EDCs using combined UV/H_2O_2. Compared to sole UV irradiation or H_2O_2 oxidation, combined UV/H_2O_2 treatment was much more effective for both EDC degradation and WAS solubilisation. Removal efficiencies with the combined process for E1, E2, EE2, E3, BPA, and NP were 97%, 92%, 95%, 94%, 89%, and 67%, respectively (at reaction conditions of pH = 3, UV wavelength = 253.7 nm, UV fluence rate = 0.069 mW/cm^2, and H_2O_2 dosage = 0.5 mol/l and reaction time 2 minutes). The EDC degradation rate constants during UV/H_2O_2 oxidation were noted to be 45-197 times greater than those during UV irradiation and 11-53 times greater than those during H_2O_2 oxidation. The OH radical was proven to have the most important role in the removal of EDCs and high H_2O_2 doses and low pH were favourable for the degradation of EDCs.

Ozonation/Electrooxidation

De Leon-Condes et al. (2017) investigated the removal of BPA, NP and triclosan from WAS using ozonation and electrooxidation with boron-doped diamond electrodes. The results indicated removal rates for BPA, NP and triclosan of 86%, 68% and 67%. The combined process was also found to reduce the sludge quantity as well as decrease the COD, colour and turbidity of the supernatant. The authors also reported no generation of secondary pollutants from the combined process.

2.5.3 Thermal Treatment

Thermal treatment of sludge has been applied as a means to reduce potential toxicity and to generate energy and stable solid by products that can be applied to land. Since thermal treatment is heat driven the processes can potentially destroy most organic contaminants and hence EDCs. This potential combined with energy generation that can replace fossil fuels enhances the net environmental benefits of thermal treatment making it particularly attractive for EDCs removal compared to other sludge treatment methods. In addition to established technologies like incineration, gasification, pyrolysis and torrefaction, research and development continues to bring innovative and improved thermal treatment technologies to the market (e.g. thermal hydrolysis, hydrothermal carbonization, catalysed hydrothermal polymerisation). Very limited amount of work on the impact of thermal treatment on EDCs has been carried out. The few studies have investigated thermal treatment both as a sludge pre-treatment disintegration method prior to anaerobic digestion and as primary treatment. Varying impacts on EDCs removal have been reported.

Thermal Pre-treatment Prior to Anaerobic Digestion

McNamara et al. (2012) investigated the impact of thermal hydrolysis (150°C, 510 kPa, 2 hours) pre-treatment on NP and short-chain nonylphenol ethoxylates (NPEs) during subsequent anaerobic digestion. The results showed that during thermal hydrolysis, the high temperature and pressure alone did not directly destroy NPE and NP. An increase in the ratio NP:NPE following MAD was observed (average ~ 25%) indicating deterioration in NPE removal in anaerobic digestion due to pre-treatment by thermal hydrolysis. Carballa et.al (2012) found that autoclave pre-treatment of mixed sludge (130°C for 1 hour) had no impact on the removal of various PPCPs (that included E1, E2, E3 and carbamazepine) in subsequent mesophilic and thermophilic anaerobic digestion.

Hamid and Eskiciouglu (2013) studied the impact of advanced anaerobic digestion (both mesophilic and thermophilic) on detectable steroidal hormones (E1, E2, Ad and Pr) using microwave pre-treatment (2.45 GHz, 1,200 W, 3.5 MPa) at varying temperature (80, 120 and 160°C). The anaerobic digester SRT was varied at 20, 10 and 5 days. The results showed that microwave pre-treatment decreased the hormone concentration after mesophilic anaerobic digestion. At SRT of 20 days, mesophilic supernatants contained 42%, 52%, 78% less hormones at microwave pre-treatment temperatures of 80, 120 and 160°C, compared to conventional MAD. On the other hand, the thermophilic control contained more or less the same concentrations of hormones in its supernatant as the pretreated digesters.

Primary Thermal Treatment

Pyrolysis

Pyrolysis is a thermal process that occurs in the absence of oxygen and is gaining interest for biosolids management. The process produces a beneficial soil conditioner as well as pyrolysis-gas and pyrolysis-liquid (bio-oil), both of which can be used as fuel. Ross et al. (2016) investigated the impact of pyrolysis on the removal of triclocarban, triclosan and NP from a mixture of heat dried WAS and digested primary sludge. Triclocarban and triclosan were removed to below quantification limit (200°C and 300°C, reaction time 60 minutes). Significant removal (>90%) of NP was achieved at 300°C as well, but 600°C was required to remove NP to below the quantification limit. At 500°C, the pyrolysis reaction time to remove >90% of micro-constituents was less than 5 minutes. Removal of EDCs was attributed to both volatilization and thermochemical transformation during pyrolysis with higher vapor pressures compounds more likely to volatilize and leave the pyrolysis reactor before being transformed than compounds with lower vapor pressures. The study detected reductive dehalogenation products of triclocarban and suspected dehalogenation products of triclosan in the pyrolysis gas. The authors concluded that pyrolysis could be added as a biosolids processing step that reduces the amount of organic micro-constituents discharged to the environment provided that the combustion of pyrolysis oil and pyrolysis gas is appropriately management to avoid release of the trapped EDCs into the atmosphere.

Hydrothermal Carbonization

Von Eyser et al. (2016) investigated the removal of diclofenac from sludge in a laboratory scale HTC reactor operated at a temperature of >190˚C, pressure ~1.5 MPa and duration of 4 hours. A removal

of 56% was achieved. The study also detected six compounds from the transformation of diclofenac during HTC treatment. These transformation compounds had been reported from other EDCs treatment processes like advanced oxidation. The authors concluded that the removal of diclofenac was through degradation via HTC reactions such as dehydroxylation and decarboxylation.

Bioaugmentation

Bioaugmentation is a treatment procedure that involves the addition of exogenous microorganisms to enhance the biodegradation of contaminants. So far, only a few studies have investigated TrOC removal from sludge by bioaugmentation with different organisms such as bacteria, yeast, and fungi.

2.5.4 Comparison of EDCs Removal Efficiencies by Various Processes and Technologies and Processes

A comparison of the efficiency of the reviewed technologies in removing the EDCs targeted in this project is given in Table 2-3. Where multiple data on removal efficiencies is available, studies that have results that contradict the majority of findings have not been taken into consideration.

Table 2-3: Comparison of Literature Reported Removal Efficiencies of some of the Targeted EDCs by Various Processes and Technologies

Compounds/Removal (%)	PFDA	PFOA	PFOS	E1	Bezafibrate	APAP	CBZ
Conventional Anaerobic Digestion							
MAD		Increase	Increase	24-40		30-50	0-59
TAH							0-61
MAD (Coetzee et al., 2018)	55-91		44-64		33-61	27-43	16-33
Composting					20		Increase
Advanced MAD							
Ozonation						59-90	68-92
Microwave				42			
Advanced Oxidation Processes (AOPs)							
Ozonation				90-100			
Fenton				70			
UV				64-81			
UV/H_2O_2				97			

Data from the literature indicate inconsistent removal efficiency of the same EDC by the same technology. Most of the literature reported studies were at laboratory and small pilot scale particularly for the AOPs. Additional research using full-scale demonstrations is therefore required in order to compare the efficiency of the various technologies at a practical level.

2.6 EXISTING REGULATIONS GOVERNING EDCS IN WASTEWATER SLUDGE

Very few countries have implemented regulations governing EDCs in wastewater effluents, wastewater sludge and drinking water supplies. Some of the challenges in implementing regulations cited in the literature include limited sound and affordable evaluation and monitoring tools, poorly

understood and confounding factors on impacts of EDCs on natural aquatic ecosystems as well as limited understanding of the impact of various treatment processes on EDCs and transformational by-products (Eggen et al., 2014).The regions and countries that have implemented regulations are mostly in the developed world.

2.6.1 South Africa

South Africa has no regulations on EDCs from WWTPs and in water sources. A number of EDCs (e.g. oestrone, oestriol, estradiol, phthalates, atrazine, p-NP, DEHP, DBP, lindane, chlorpyrifos, PCBs and PFAS) have been detected in South African surface water sources (Burger, 2010; Heath et.al, 2013). Although WWTPs contribute as point sources for EDCs discharged into surface water sources no actual continued quantitative monitoring has been undertaken in the effluents discharged from WWTPs. No monitoring has also been undertaken in sewage sludge. Monitoring has been has been hampered by both excessive costs of analytical procedures as well as limited availability of laboratories in South Africa that are accredited to undertake the analysis of EDCs.

2.6.2 European Union

EU Directive 86/278/EEC regulates the use of sludge in agriculture. However, the directive only sets limits for heavy metals (Cd, Cr, Cu, Hg, N, Pb and Zn) but has no limits for organic contaminants and EDCs (EU, 1986). Rules for sampling and analysis, records keeping of the quantities of sludge produced at WWTPs, quantities used in agriculture, composition and properties of the sludge, the type of treatment and the sites where the sludge is finally applied are also set out in the directive.

A few countries in the EU (Germany, France, Denmark, Sweden, Austria and the Czech Republic) have national regulations on specific groups of organic contaminants and EDCs. In Germany the application of sewage sludge on land is regulated by the Sewage Sludge regulation of 15 April 1992. Limits are set for polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins and furans (PCDD/Fs) and adsorbable organic halogenated substances (AOX). The regulation has been updated over the years and the updates in 2007 included limits on PAH benzo(a)pyrene (BMU, 2007).

In France, agricultural use of sludge is regulated by the Decree No. 1133 of December 8, 1997 and by the Enforcement Order dated January 8, 1998. The decree has been updated over the years and sets limits for PAHs and PCBs, but not PCDD/Fs. The French legislation on the spreading of sewage sludge to land is globally more stringent than Directive 86/278/CEE.

Denmark, on the other hand has set limits on a range of EDCs including di(2-ethylhexyl) phthalate (DEHP), linear alkylbenzene sulphonate (LAS), NPs/NPEs and PAH (Smith, 2009). Sweden has limits on NP/NPE, PAH and PCB while the Czech Republic has limits on AOX and PCB. Austria limits AOX, PCB and PCDD/F (Milieu Ltd, 2010).

2.6.3 USA and Canada

USA and Canada have not imposed any limits on EDCs citing that research suggests concentrations present in sludge are not hazardous to human health, the environment or soil quality. Evaluation of EDCs of concern has however been carried out over the years with a view to inform any required legislation. For example, in British Columbia (BC) proposed changes to the regulation governing land application of biosolids suggest monitoring of dioxins/furans, phthalates, PAH, PCB, polybrominated diphenyl ethers, and select pharmaceuticals and personal care products in Class A biosolids and Class B biosolids (BC Ministry of Environmental Climate Change Strategy, 2018).

In the USA biennial reviews have been conducted over the years. The 2013 biosolids biennial review identified thirty-five new chemicals and six new microbial pollutants. Thirteen of the newly identified chemicals are PFAS. No human health toxicity data were identified for any of the 35 new chemicals or for chemicals identified in previous biennial reviews. However, the EPA is currently engaged in efforts around PFAS including developing toxicity values for certain PFAS. Ecological toxicity values were found for one chemical (triclosan) identified in previous biennial reviews. New physical-chemical properties were identified for 22 chemicals and new bioaccumulation factors were identified for five previously identified chemicals (U.S. EPA, 2013).

In the 2016-2017 biennial review, the EPA identified a further 28 new chemicals in biosolids. The chemicals included seven polybrominated diphenyl ethers (PBDEs), nine parabens and metabolites, five brominated flame retardants (BFRs), three other flame retardants, two PFAS and two triclosan transformation products. Human health toxicity values were found for three of the new chemicals (benzoic acid, 2,4-dichlorophenol and hexabromobenzene). Physical-chemical properties and bioaccumulation factors were identified for 22 and 23 of the new chemicals respectively. The identified chemicals require further evaluation for relevance for inclusion in risk assessments. The EPA is currently working on building capacity to assess new found pollutants by developing the necessary screening tools and data which will assist in the next phase of risk screening of pollutants found in biosolids (U.S. EPA, 2019).

A summary of the legislation and regulations governing EDCs in wastewater sludge in the different regions is given in Table 2-4.

Table 2-4: Legislation and Regulations on EDCs and other Emerging Contaminants from Different Regions

Country/Legislation	Description	Organic Compounds and Limits
Denmark Ministry of Environment and Energy Statutory Order No. 823 of September 16, 1996 on application of sludge, wastewater and compost for agricultural use	Regulations for metals and some organic compound in sewage sludge.	➢ di-(2-ethyhexyl) phthalate (DEHP) – 50 mg/kg DS) ➢ Nonylphenol (NP)/Nonyphenol Ethoxylates (NPE) – 10 mg/kg DS ➢ seven polychlorinated biphenyl congeners (PCB) ➢ polycyclic aromatic hydrocarbons (PAH) – 3[a] mg/kg dm and ➢ linear alkylbenzene sulphonates (LAS) are fixed
Germany German Fertilizer Act – The Ordinance on the Reform of Sewage Sludge Utilisation of 27 September	Regulate sewage sludge for agricultural use. The order only contains limits on metals and organic compounds.	➢ Polychlorinated biphenyl congeners (PCB) – 0.1b mg/kg TS) ➢ Dibenzofurans (PCDD/F) – 30 ng/kg DS (Fertilizer) ➢ Adsorbable organic halogenated substances) (AOX) – 400 mg/kg TS) ➢ Benzo[a]pyrene (BaP) – 1 mg/kg TS) ➢ Perfluorocarbon tracer (PFT) – 0.1 mg/kg TS (Fertilizer)
France 1992 Water Act and 1975 & 1992 Waste Act - Decree No. 97-1133 of the 8th December 1997	Technical specifications applicable to the spreading of sludge on agricultural land. The order constitutes the enactment of the previous decree of the 8th December 1997 and provides definitions of solid, stabilised and sanitised sludge.	➢ PAH, PCB (7 elements) – 0.8 mg/kg DS ➢ Fluoranthene – 4 mg/kg DS ➢ Benzo(b)fluoranthene – 2.5 mg/kg DS ➢ Benzo(a)pyrene – 1.5 mg/kg DS
Sweden Swedish Environmental Protection Agency (SEPA) Protection Order 1994:2 (SNFS 1994: 2)	The order contains regulations on the protection of the environment, in particular the soil, when sewage sludge is used in agriculture	➢ NP/NPE – 50 mg/kg DS ➢ PAH – 3.0 mg/kg DS ➢ PCB – 0.4 mg/kg DS
Upper Austria and Lower Austria Waste Act – Order No. 21/1993 Waste Act – Order No. 30/05/2000	Regulates the use of sewage sludge, compost, and composted waste on land Order on sewage sludge management	**Metals:** Cd, Cr, Cu, Hg, N, Pb and Zn **Organic Compounds:** ➢ AOX – 500 mg/kg DS ➢ PCB – 0.2 mg/kg DS ➢ PCDD/F – 100 ng/kg DS
Czech Republic Waste Act No. 185/2001 Coll. – Decree No. 382/2001 Coll.	Conditions of application of treated sludge on agricultural land, as amended	➢ AOX – 500 mg/kg DS ➢ PCB – 0.6 mg/kg DS

Notes:
[a]Sum of acenapthene, phenathrene, fluoranthene, pyrene, benzo(b+j+k) fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno (1,2,3-c, d) pyrene.
[b]Each of the six congeners PCB 28,52,101,138,153,180

Chapter 3. PCS Technology Pilot Scale Study

3.1 TECHNOLOGY FUNDAMENTALS

The PCS process is a catalysed wet sub-critical water thermochemical process that efficiently and effectively processes any type of biomass to produce a solid hydrochar. The process is similar to hydrothermal carbonization (HTC) except that catalysts are selected to reduce decarboxylation reactions and reduce carbon dioxide (CO_2) evolution. Thus, the process has been coined enhanced hydrothermal polymerization (EHTP). The process takes place in a sealed anaerobic tank that is heated to temperatures between 180-240°C for a reaction time of 1-2 hours depending on feedstock type and required product quality. At this temperature range, the generated autogenous pressure is less than 4 MPa. Under these conditions most organics remain as they are or are converted to liquid (~15% of solid feedstock). The amount of gas produced is relatively small (~5% of solid feedstock) and low in carbon dioxide (CO_2) with no methane (CH_4) generated. Thus the process has minimal greenhouse gas (GHG) effects. A schematic representation of the process is given in Figure 3-1.

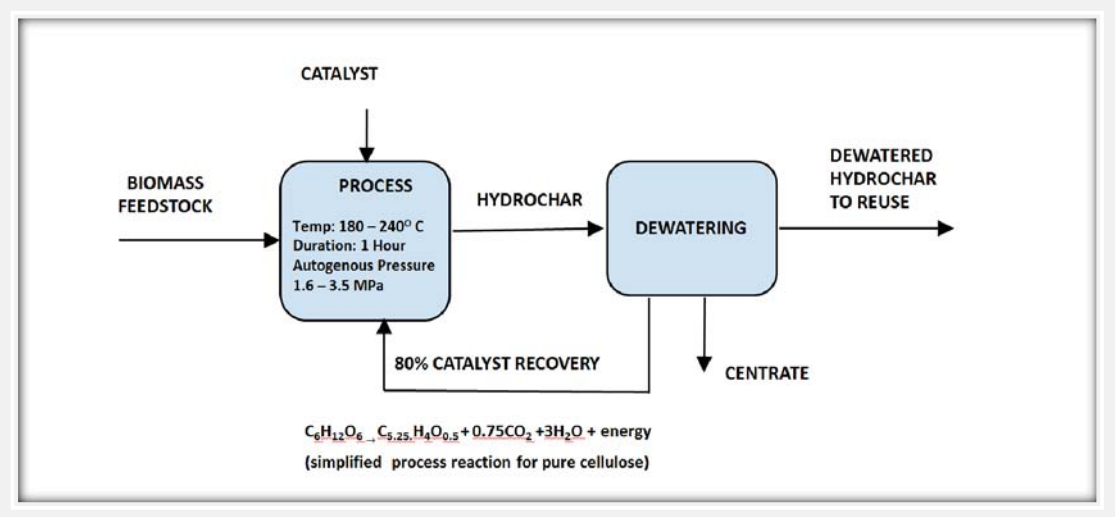


Figure 3-1: Schematic Representation of the PCS Process

To test the efficacy of the technology when processing wastewater sludge, Musvoto et al. (2018) conducted laboratory (using a 200 ml steel batch reactor) and pilot (using a 60 litre steel batch reactor) scale studies from 2016 to 2017. PS, WAS, combined PS & WAS and digested sludge were processed in the laboratory and pilot reactors. Sludge combined with inlet works screenings was also processed. During the laboratory study, four EDCs (methylparaben, chloramphenicol, Bisphenol A and carbamazepine) were analysed in both the sludge feedstock and the produced hydrochar and process supernatant. The analysis results showed removal rates of 65-100% for the four EDCs. The results from the pilot study showed that the hydrochar from the PCS process had a higher calorific value than the original sludge feedstock and was also completely sterile. Analysis of the hydrochar also showed that it has potential multiple uses, e.g.:

- Biofuel that can be used for combined heat and power (CHP) generation at WWTPs, co-combustion with coal or other green biofuel in power stations, as a substitute for coal in pulverised coal injection (PCI) processes and domestic use as a replacement for firewood and coal
- In agriculture as a fertilizer/soil conditioner
- Functionalised carbon microspheres that can be used as adsorption media for tertiary treatment of water/wastewater effluent instead of conventional granular activated carbon (GAC)

The study by Musvoto et al. (2018) therefore demonstrated that the PCS process is a feasible sludge treatment technology that can be applied as a substitute to conventional sludge treatment processes like anaerobic digestion. The technology not only produces a higher quality multi-use hydrochar, but also potentially destroys emerging contaminants of concern. Based on the laboratory scale study results, the technology was therefore selected to further investigate its effectiveness in destroying a wider range of EDCs at pilot scale in this project The 60 litre pilot scale batch reactor that was used in the previous study (Musvoto et al., 2018) was also used for this project.

3.2 APPROACH AND METHODOLOGY

3.2.1 Pilot Plant Location

The pilot scale study was conducted at the City of Tshwane's Daspoort WWTP. The plant has a design capacity of 38.3 Ml/d average annual flow (AAF) and has two liquid treatment modules. Module 1 consists of 4 primary settling tanks (PSTs), 16 trickling filters and 2 humus tanks. Module 2 consists of 6 PSTs, 3 separate individual biological nutrient removal (BNR) activated sludge bioreactors and 6 secondary settling tanks (SSTs). WAS is thickened in dissolved air flotation (DAF) thickeners and then combined with PS from the PSTs prior to anaerobic digestion in 6 conventional MAD. Digested sludge is discharged to sludge drying beds for dewatering and drying.

Sludge samples that were processed in the PCS reactor were collected at the following points (Figure 3-2):

- PS from the PST underflow sump
- Thickened WAS from the DAF units
- Digested sludge from the discharge pipeline from the anaerobic digester prior to discharge to the sludge drying beds

Raw influent and effluent liquid wastewater samples were also collected at the beginning of the project to track the variation of selected EDCs in the liquid treatment process.

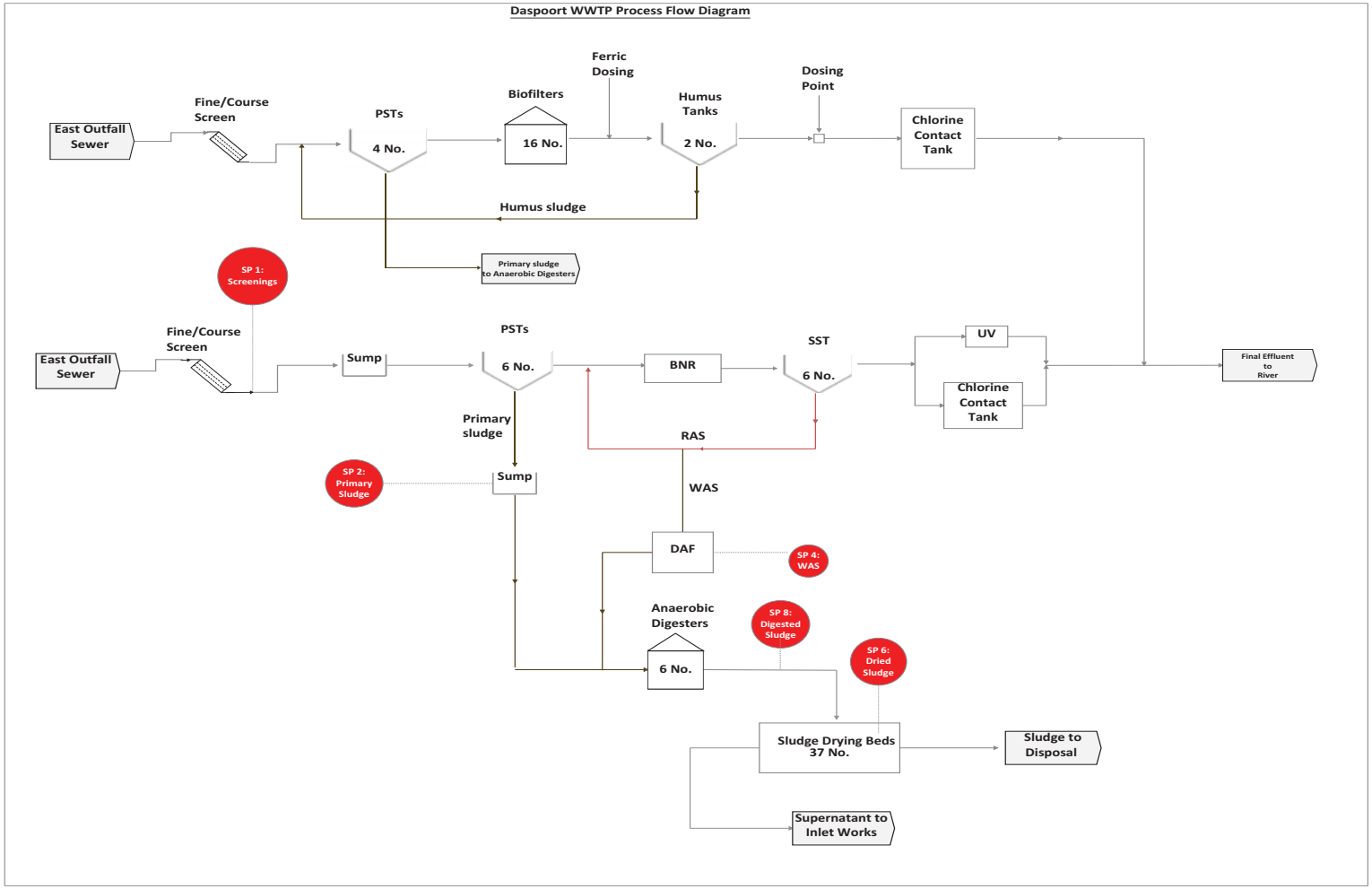


Figure 3-2: Sampling Points at Daspoort WWTP

3.2.2 PCS Pilot Plant Experimental Procedure

Sludge samples were processed in the 60 litre steel batch reactor. The reactor is designed to be heated by an inbuilt electrical element and can be heated to a maximum temperature of 300°C and withstand 5 MPa autogenous pressure. The reactor is equipped with a feedstock input valve, product output valve as well as various pressure relief and safety valves. Two temperature sensors monitored the temperature of the heating element as well as the contents inside the reactor. Reactor pressure was monitored by a pressure gauge. An energy meter was also connected to the reactor to monitor the energy used per batch experiment conducted.

Composite sludge samples were collected from the identified sampling points. Prior to adding the sludge feedstock to the reactor, the sample volume, mass, total suspended solids (TSS) and pH were measured. A portion of the feedstock sample was also retained and about 5 ml of dilute hydrochloric acid was added to the sample to stop biological activity. The retained sample was allowed to settle in a cylinder to separate the supernatant from the sludge. The supernatant and sludge samples were immediately stored in a freezer to preserve them prior to sending to the laboratory for analysis. A catalyst solution was then added to the feedstock sample and the volume of catalyst as well as mass and volume of the feedstock sample were recorded. The sample was then fed into the reactor which was then sealed and purged with nitrogen gas prior to heating the contents to a temperature of 190 ± 5^{o}C. The temperature was then held at the maximum value for 1 hour[6]. The maximum autogenous pressure achieved ranged from 3.6 to 3.8 MPa. Upon completion of the reaction, the reactor was cooled to room temperature and the product (hydrochar and supernatant) was discharged into a container. The mass, volume, TSS and pH of the product were recorded. A portion of the product sample was settled to separate the hydrochar and the supernatant and the samples were also stored in the freezer prior to sending to the laboratory for analysis.

3.2.3 Diurnal Variation Survey of EDCs in the Influent Raw Wastewater and Final Effluent

As part of the project, a survey of the variation of EDCs in the raw influent and final at Daspoort WWTP effluent EDCs was carried out. Grab samples were collected every hour (from 6 am to 6 pm) from the raw influent and effluent streams of both Modules 1 and 2. The samples were inactivated by adding dilute hydrochloric acid and stored in the fridge (4^{o}C) prior to analysis. The analysis results of the liquid samples are given in Appendix B.

3.2.4 Laboratory Analysis for Target EDCs

The liquid as well as sludge and hydrochar samples were sent to the laboratory for analysis of the target EDCs. The pharmaceuticals, oestrone and PFOA were analysed by the University of Johannesburg's Analytical Chemistry department and the other PFAS were analysed by the NMISA laboratory. The samples were also screened for other PFAS that were not targeted in this project. The University of Johannesburg used analytical procedures adapted from UKWIR (2006) and Zhao et al.

[6] Optimal operating parameters for processing wastewater sludge were determined in previous studies. Operating temperature 180-200˚C, Reaction time 1 hour; autogenous pressure 2.5-4 MPa (Musvoto et al., 2018)

(2009). NMISA used extraction procedures adapted from Yang et al. (2001) and Labadie & Chevrill (2011). The instrument optimisation was based on USEPA (2009) and Ballesteros-Gomez et al. (2010).-

3.3 RESULTS AND DISCUSSION

3.3.1 Concentration of EDCs in Untreated Sludge

Concentrations of EDCs per dry weight of untreated sludge feedstock (PS, WAS and combined PS & WAS) are given in Table 3-1. A graphical illustration of the concentrations is shown in Figure 3-3.

Table 3-1: EDC Concentrations in the Sludge Feedstock (concentrations in solid portions per kg dry weight)

Feedstock	EDC Concentration (µg/kgdw)							
	APAP	Bezafibrate	CBZ	E1	PFOA	PHxA[a]	PFOS	PFDA[a]
PS	26.9 ± 2.5	25.9 ± 0.5	29.9 ± 1.4	36.0 ± 0.8	25.9 ± 2.5	<LOD	17.4	<LOD
WAS	15.4 ± 0.9	12.4 ± 1.1	8.7 ± 1.1	21.0 ± 0.1	12.3 ± 0.9	<LOD	220	<LOD
PS & WAS	14.6 ± 2.0	5.3 ± 1.1	15.0 ± 1.7	9.3 ± 1.7	13.0 ± 2.0	<LOD	106	<LOD
DS	10.4 ± 1.0	15.2 ± 0.5	23.4 ± 0.6	0.6 ± 0.4	11.5 ± 1.0	<LOD	49.3	<LOD

Notes:
a. LOD – Limit of Detection from NMISA laboratory : PFHxA = 1.46 µg/kgdw and PFDA = 6.12 µg/kgdw

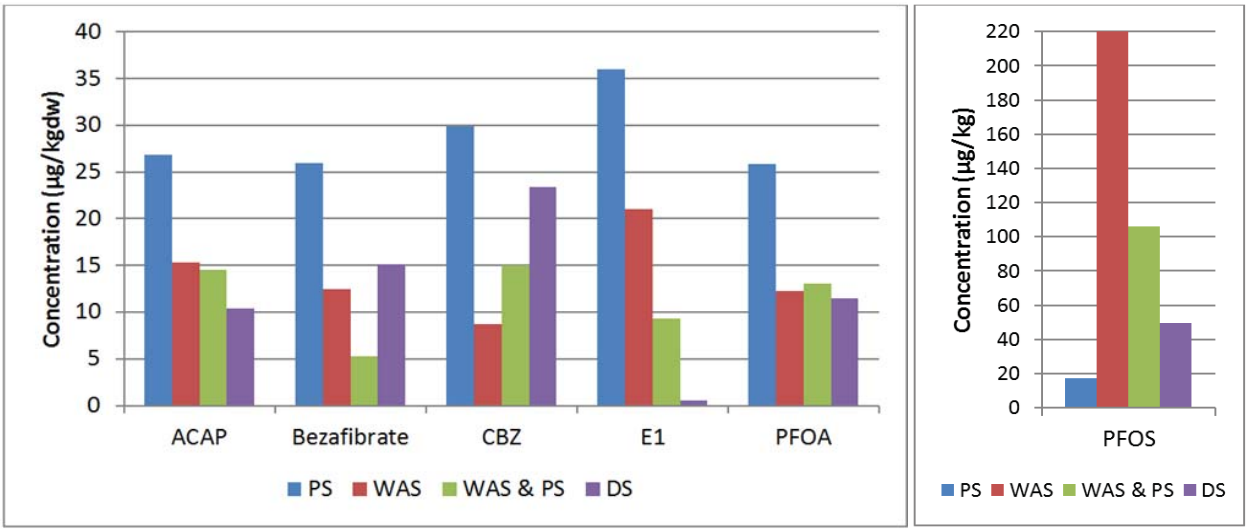


Figure 3-3: EDCs Concentrations Sludge Feedstock to the PCS Process

It should be noted that the sludge samples were collected on different days. However since the samples were composite it was accepted that the measured values represent average concentrations in the sludge. The following conclusions were drawn from the results.

Pharmaceuticals

PS had the highest concentration of all pharmaceuticals with carbamazepine slightly higher than acetaminophen and bezafibrate (15 and 10% higher). In WAS, acetaminophen had the highest concentration in followed by carbamazepine and then bezafibrate. Digested sludge from the full-scale conventional MAD had higher concentrations of bezafibrate and carbamazepine indicating that the concentration per dry weight of combined PS & WAS increased during anaerobic digestion. Coetzee et al. (2017) also found that acetaminophen had the highest concentration in WAS. However in PS,

bezafibrate had the highest concentration followed by acetaminophen while carbamazepine had the lowest concentration in all sludge types.

Oestrogens

Similar to pharmaceuticals, PS had the highest concentration of oestrone and WAS had the second highest concentration. The concentration was also 20-39% and 40-141% higher in than the concentration of pharmaceuticals in PS and WAS respectively. DS had a very low oestrone concentration indicating that anaerobic digestion reduced the concentration of oestrone in the combined PS & WAS feedstock.

PFAS

PFOS was the most prevalent PFAS in all sludge types with the highest concentration in WAS (~10 times that in PS). PHxA and PFDA were found to be below the limit of detection in all sludge types. Coetzee et al. (2017) also found that PFOS had a much higher concentration than PFDA in all sludge types. Other studies also found PFOS to be the most prevalent PFAS in sludge. DS from the full-scale MAD had lower concentration per dry weight of both PFOA and PFOS than the combined PS & WAS feedstock. Qualitative screening for other PFAS that were not selected for this study found that:

- PFUnA, PFDoA, PFTrDA and PFBS were not detected in any samples
- PFHpA, PFNA and PFTA were detected in all samples
- PFHxS was detected only in WAS and mixed PS & WAS samples

3.3.2 PCS Process EDCs Removal Efficiency

Calculation of EDCs Removal Efficiency

The removal efficiency of the PCS process was defined as the overall removal of EDCs from both the liquid supernatant and sludge. Since the process is a wet process with very little gas emitted and the compounds are thermodynamically stable and non-volatile, it was assumed that volatilization of the EDCs was negligible. Sorption onto the steel reactor walls was also assumed to be negligible. Thus any reduction in EDCs was attributed to degradation during the catalysed hydrothermal polymerisation process. Although details of the removal mechanisms of EDCs by the PCS process was beyond the scope of this project, previous studies on EDCs removal during conventional HTC at temperatures of 190-210°C concluded that degradation was the main mechanism for removal of trace organic compounds during HTC. It has therefore been assumed that the same mechanism occurs in the PCS process.

The removal efficiencies for each target compound were therefore calculated taking into account the mass in the influent feedstock (M_{inf}) and the mass in the effluent product (M_{eff}) as follows:

$$\frac{(M_{inf} - M_{eff}) * 100}{M_{inf}}$$

The masses of the EDCs in the solid and supernatant portions were calculated from the measured EDC concentrations and the total sample solid mass and liquid volume respectively.

EDCs Removal Efficiency Results

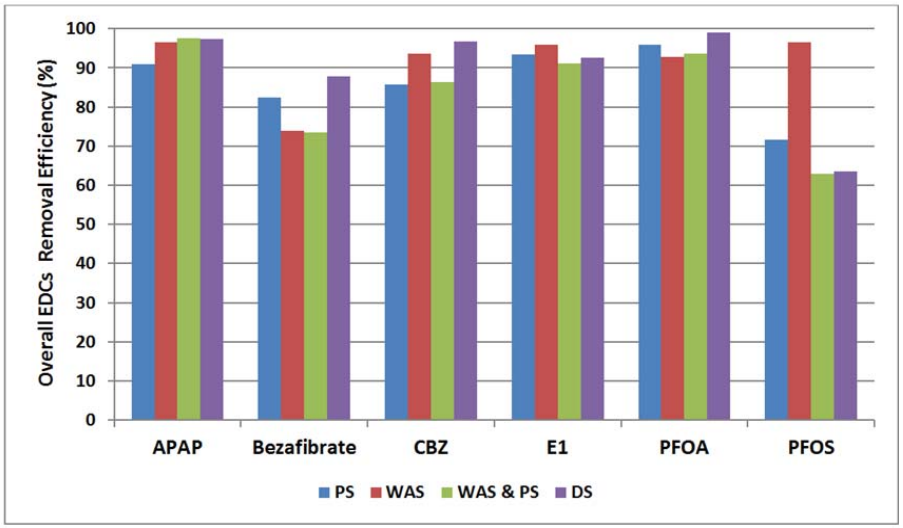
A summary of the EDC concentrations (feedstock and product) and the removal efficiencies are given in Table 3-2. The overall removal efficiency and the fractions removed in the liquid and solid portions of the sludge are illustrated graphically in Figure 3-4.

Table 3-2: Summary of EDCs Removal Efficiency in the Pilot Scale PCS Process

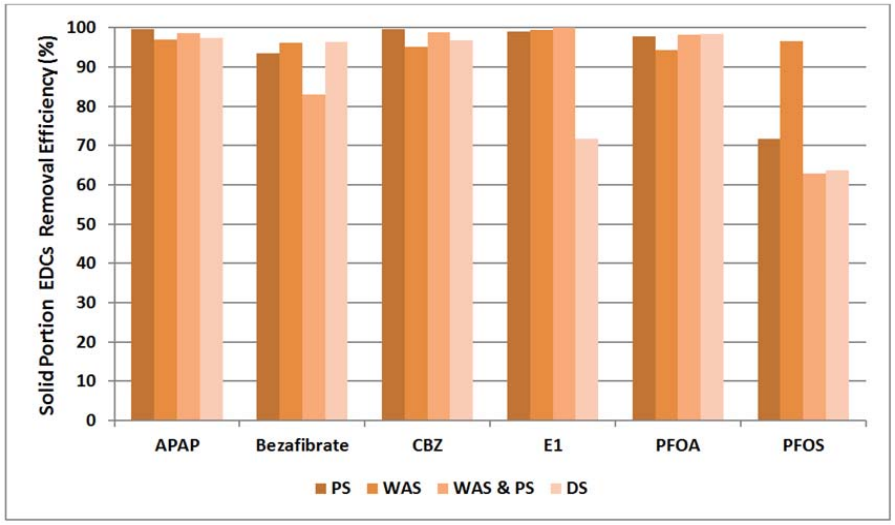
	Units	APAP	Bezafibrate	CBZ	E1	PFOA	PFOS[a]
PS							
Feedstock Sludge	µg/kgdw	26.9	25.9	29.9	36.0	25.9	17.4
Hydrochar	µg/kgdw	0.4	5.4	0.4	1.1	1.8	17.2
Feedstock Supernatant	µg/l	1.0	4.0	4.0	3.0	2.4	
Process Supernatant	µg/l	0.3	1.0	1.0	0.4	0.1	0.35
Overall Removal	%	91	82	86	93	96	72
Fraction Removed from Solid		0.72	0.35	0.41	0.52	0.49	
Fraction Removed from Liquid		0.19	0.47	0.45	0.41	0.46	
WAS							
Feedstock Sludge	µg/kgdw	15.4	12.4	8.7	21.0	15.4	220
Hydrochar	µg/kgdw	1.0	1.0	0.9	0.2	1.5	25.1
Feedstock Supernatant	µg/l	0.01	3.0	0.5	3.0	2.0	
Process Supernatant	µg/l	0.0	1.0	0.04	0.2	0.2	0.0
Overall Removal	%	97	74	94	96	93	97
Fraction Removed from Solid		0.96	0.47	0.61	0.39	0.34	
Fraction Removed from Liquid		0.01	0.28	0.32	0.56	0.59	
PS & WAS							
Feedstock Sludge	µg/kgdw	14.6	5.3	15.0	9.3	14.6	106
Hydrochar	µg/kgdw	0.6	2.6	0.5	0.0	0.7	97
Feedstock Supernatant	µg/l	0.5	3.5	2.2	2.2	1.5	
Process Supernatant	µg/l	0.03	1.0	0.5	0.3	0.2	0.17
Overall Removal	%	98	73	86	91	94	63
Fraction Removed from Solid		0.74	0.11	0.40	0.30	0.46	
Fraction Removed from Liquid		0.23	0.62	0.46	0.61	0.59	
DS							
Feedstock Sludge	µg/kgdw	10.4	15.2	23.4	0.6	11.5	49.3
Hydrochar	µg/kgdw	0.9	1.8	2.9	0.5	0.6	74.7
Feedstock Supernatant	µg/l	0.0	1.9	0.0	0.2	0.5	
Process Supernatant	µg/l	0.0	0.4	1.0	0.0	0.0	1.7
Overall Removal	%	97	88	97	93	99	64
Fraction Removed from Solid		0.97	0.44	0.97	0.19	0.69	
Fraction Removed from Liquid		0.00	0.44	0	0.74	0.30	

Notes:

a. The liquid portion of the sludge feedstock was not separately analysed. Only dry and wet sludge feedstock and dry hydrochar and process supernatant were analysed.



(a)



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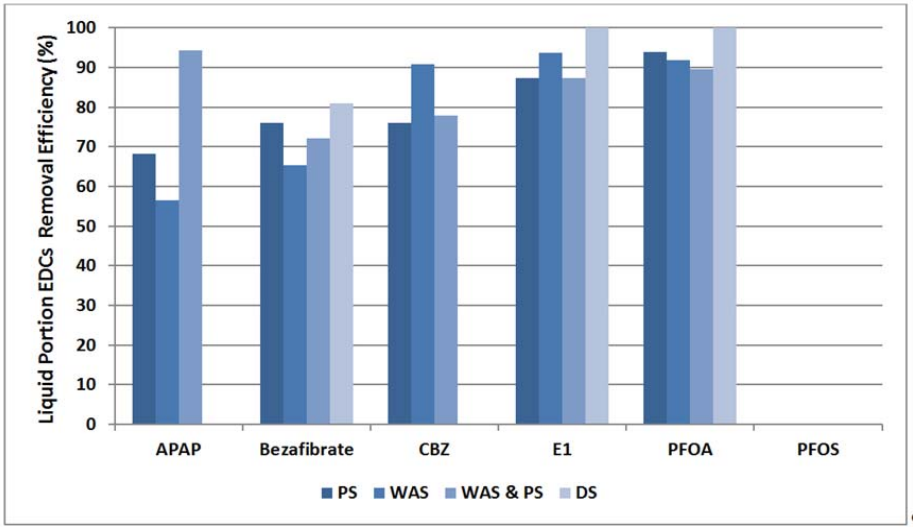

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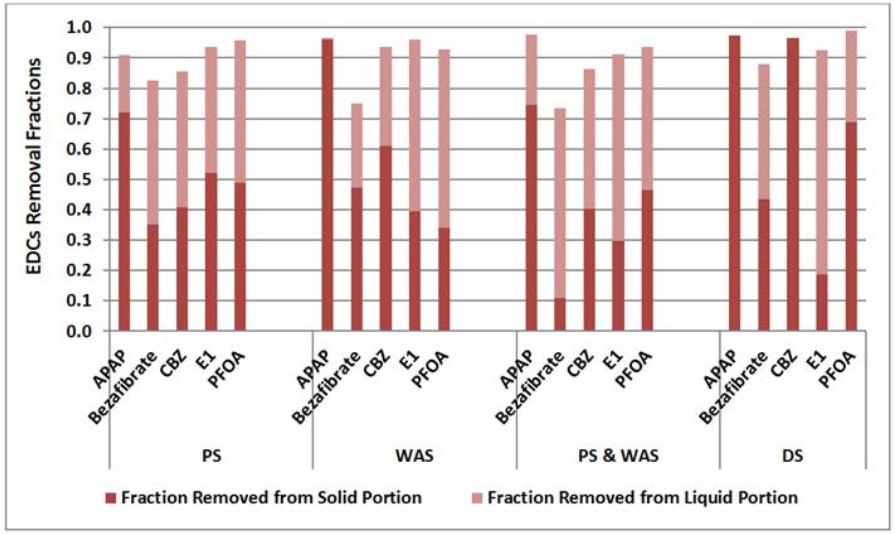


(d)

Figure 3-4: Graphical Illustration of (a) Overall EDCs % Removal in the PCS Process (b) Fraction Removed in the Solid and Liquid Portions of the Sludge (c) EDCs % Removal in Solid Portion (d) EDCs % Removal in Liquid Portion

Key findings from the results were as follows:

Pharmaceuticals

Acetaminophen removal was 91% for PS, 97% for WAS and 98% for PS & WAS. Bezafibrate removal was 82, 74, and 73% for PS, WAS and PS & WAS respectively and carbamazepine removal was 86, 94 and 86% for PS, WAS and PS & WAS respectively. Thus the average removal from untreated sludge was

- acetaminophen 95%
- bezafibrate 77% and
- carbamazepine 89%

The PCS process also removed 98, 88 and 93% of residual acetaminophen, bezafibrate and carbamazepine from DS. The highest removal for each EDC were

- acetaminophen from combined PS & WAS as well as DS at 97%
- bezafibrate from DS at 88% and
- carbamazepine from DS at 97%

Estrogens

Oestrone removal was 93, 96, 91% from PS, WAS and PS & WAS respectively averaging 93% removal from untreated sludge. Removal of residual oestrone from DS was 93%. The highest removal was from WAS.

PFAS

PFOA removal was 96, 93, and 94% for PS, WAS and WAS & PS respectively while PFOS removal of 72, 97 and 63% was achieved for PS, WAS and PS & WAS respectively. Thus the average removal from untreated sludge was

- PFOA 95% and
- PFOS 77%

Removal of residual PFOA and PFOS from DS was 99% and 64% respectively. The highest removal was from WAS for both PFOA and PFOS.

Residual EDCs in Hydrochar

The concentration (per kilogram dry weight) of residual EDCs in the hydrochar is graphically illustrated in Figure 3-5. The following is noted:

- acetaminophen concentration is 1 µg/kgdw or less in all sludge with the highest concentration of 1 µg/kgdw in hydrochar from processing WAS
- the highest concentration of bezafibrate is in hydrochar from processing PS (5.4 µg/kgdw) with concentrations in the other sludge less than 3 µg/kgdw
- the concentration of carbamazepine is highest in hydrochar from processing DS with the rest of the concentrations less than 1 µg/kgdw
- Oestrone concentration is highest in hydrochar from PS at 1.1 µg/kgdw. The other concentrations are 0.5 µg/kgdw or less
- PFOA concentrations are less than 2 µg/kgdw with the highest value of 1.8 µg/kgdw in hydrochar from processing PS
- PFOS has the highest residual concentrations with values ranging from 17 to 97 µg/kgdw. The highest concentration of 97 µg/kgdw is in hydrochar from processing combined PS & WAS

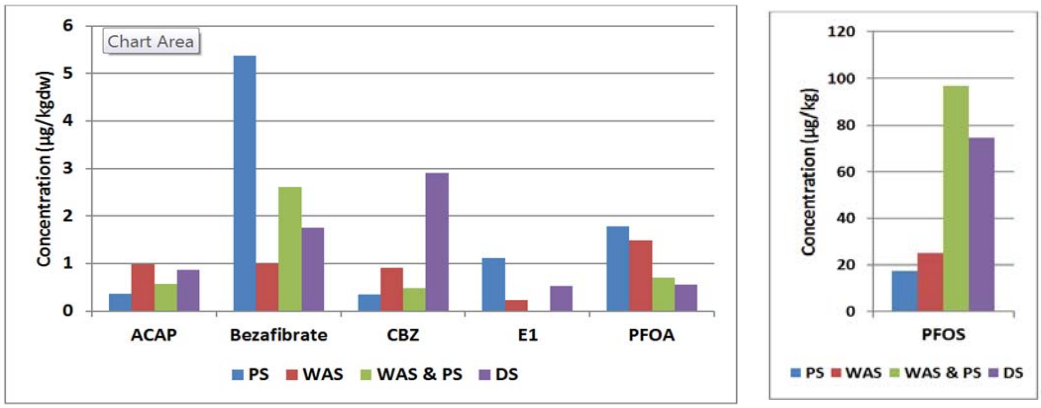


Figure 3-5: Concentration of Residual EDCs in Hydrochar from the PCS Process

There are no EDCs regulations in South Africa and regulations from elsewhere reviewed in Section 2.6 do not include the EDCs selected for this study. Therefore the impact of residual EDCs in the hydrochar on soils if the hydrochar were beneficially utilized for agriculture or disposed on land could not be evaluated.

3.3.3 Comparison of PCS Process and Conventional MAD EDCs Removal Efficiencies

Table 3-3 summarises the efficiencies for the PCS process from this project and the efficiency of a laboratory scale conventional MAD that processed similar sludge from Daspoort WWTP (Coetzee et al., 2017). Also included is the EDCs removal efficiency of the full-scale conventional MAD that process combined PS & WAS at Daspoort WWTP. A graphical comparison of the PCS process and laboratory scale conventional MAD efficiencies is shown in Figure 3-6.

Table 3-3: Comparison of EDCs Removal Efficiency for the Pilot Scale PCS Process and Laboratory Scale Conventional MAD

Removal Efficiency	APAP	Bezafibrate	CBZ	E1	PFOA	PFOS
PS						
% Removal PCS	91	82	86	93	96	69
% Removal Lab Scale MAD	27	61	16			55
WAS						
Overall Removal	97	74	94	96	93	97
% Removal Lab Scale MAD	43	33	33			91
PS & WAS						
% Removal PCS Process	98	73	86	91	94	63
% Removal Lab Scale MAD	34	66	20			89
% Removal Full Scale MAD	41	17	38	93	44	-17
DS						
% Removal PCS Process	98	88	93	93	99	64
Average Untreated Sludge (PS, WAS, PS & WAS)						
Average % Removal PCS	95	77	89	94	94	76
Average % Removal MAD (Lab & Full scale)	36	44	27	93	44	72

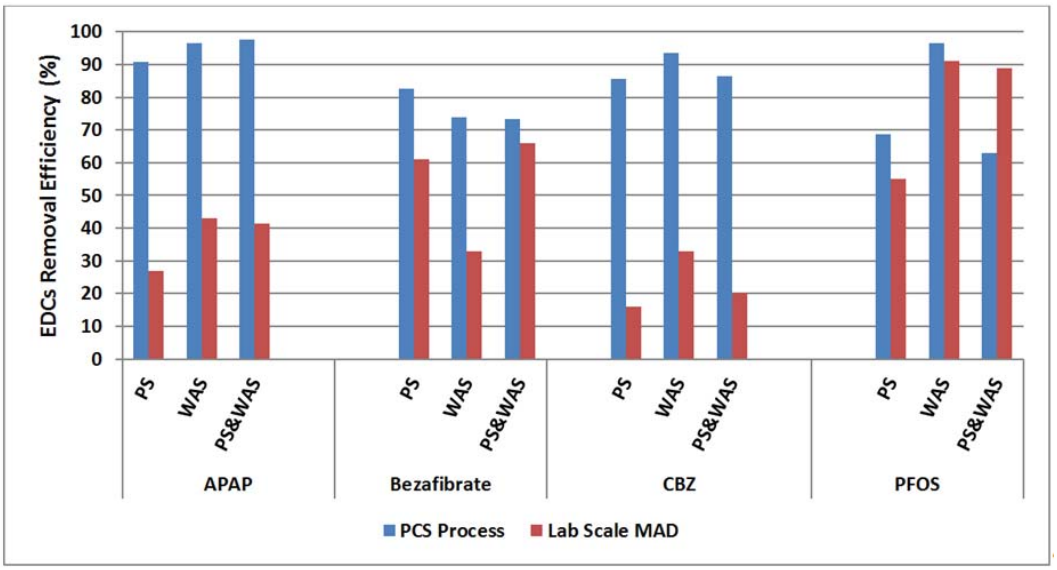


Figure 3-6: EDCs Removal Efficiency for Pilot Scale PCS Process & Laboratory Scale MAD

Oestrone and PFOA were not analysed in the laboratory scale MAD study by Coetzee et al. (2017).

The following is noted for the EDCs that were analysed for both processes:

- The average removal efficiency from untreated sludge (average of removal efficiencies for PS, WAS and combined PS & WAS) by the PCS process was 95%, 77% and 89% for acetaminophen, bezafibrate and carbamazepine respectively. The laboratory scale MAD average efficiency was much lower at 35%, 53% and 23% for acetaminophen, bezafibrate and carbamazepine respectively. Thus the average removal efficiency from untreated sludge in the PCS process was 174, 44, and 285% higher for acetaminophen, bezafibrate and carbamazepine respectively than the laboratory scale MAD efficiencies.
- The PCS process also had higher removal efficiency from combined PS & WAS (98, 73 and 86%) compared to the full-scale MAD (41, 17 and 38%) for acetaminophen, bezafibrate and carbamazepine respectively. The PCS process removal efficiency was therefore 136, 331 and 129% higher for acetaminophen, bezafibrate and carbamazepine respectively than the full-scale conventional MAD that processes combined PS & WAS MAD at Daspoort WWTP
- Oestrone removal efficiency from combined PS & WAS in the PCS process was 91%. The full-scale MAD had a slightly higher removal efficiency of 93%.
- The average removal efficiency of PFOS in the laboratory scale MAD was slightly higher (78%) than in the PCS process (76%). The removal of both PFOA and PFOS from combined PS & WAS by the PCS process were 94% and 65% respectively. The full-scale MAD achieved 45% removal for PFOA and there appeared to be a 17% increase in PFOS after full-scale MAD.

Discussion

Apart from oestrone and PFOS where the removal efficiency was closely similar, the PCS technology achieved significantly higher average EDCs removal efficiency from untreated sludge than conventional MAD. The technology also significantly reduces residual EDCs in previously anaerobically digested sludge. In South Africa conventional MAD is the most widely applied sludge treatment technology. The technology is applied to treat either PS on its own (usually at trickling filter plants with co-settling of PS and humus sludge) or combined PS & WAS (usually at ASPs that generate both

PS and WAS)[7]. The results from previous research and this project thus indicate that the PCS technology can be feasibly applied as a replacement sludge processing technology to anaerobic digestion and will not only meet current sludge regulations but also possible future regulations on EDCs. Comparison of the removal efficiency of the PCS process with other emerging technologies (e.g. advanced oxidation) could not be undertaken because of limited literature reported data on the performance of these technologies in removing EDCs targeted in this project.

It should be noted that evaluation of the mechanisms of EDCs removal in the PCS process and MAD were beyond the scope of this project. Therefore, the removal efficiencies calculated in this project did not evaluate degradation pathways and account for any potential transformation compounds formed during the process reactions. Formation of transformation compounds with MAD and other technologies has been reported in the literature for various EDCs particularly in the degradation of hormones and PFAS. Currently there are no regulations limiting the quantity of EDCs in sludge in South Africa. Most countries also do not have regulations apart from a few EU countries that have limits on some EDCs in sludge reused for agriculture. Should regulations be implemented in South Africa in future, detailed understanding of process mechanisms will be required in order to optimise designs for full-scale implementation of these technologies.

[7] MAD of PS only is also applied at extended aeration ASPs where the generated WAS is stable enough to be disposed of without further treatment. ASPs that treat raw wastewater and generate WAS only are usually extended aeration hence no further treatment is required and such plants generally do not have anaerobic digesters.

Chapter 4. Conclusions and Recommendations

4.1 PROJECT SUMMARY

This project evaluated at pilot scale, the efficiency of the emerging enhanced hydrothermal polymerisation PCS technology in removing targeted EDCs from various types of sludge generated at Daspoort WWTP. PS, WAS, combined PS & WAS and DS from the existing full-scale conventional MAD were batch processed in a 60 litre PCS reactor. The pilot scale setup reflected possible full-scale application of the PCS technology to treat not only untreated sludge but also post-treat previously anaerobically digested sludge. Both the sludge feedstock and the processed product (hydrochar and supernatant) from the PCS reactor were analysed for the following targeted EDCs:

- pharmaceuticals (acetaminophen, bezafibrate and carbamazepine)
- oestrogens (oestrone)
- PFAS (PFOA, PFDA, PFOS and PFHxA).

The removal efficiency for each EDC was calculated using a simple mass balance approach. The results from the pilot study were compared with removal efficiencies of conventional MAD operated at (i) laboratory scale (from a study by Coetzee et. al, 2018) and (ii) full scale at Daspoort WWTP treating combined PS & WAS. Evaluation and analysis of process removal mechanisms, degradation pathways and formation of any possible transformational compounds in both the PCS process and conventional MAD were beyond the scope of this investigation.

A literature review on technologies that remove EDCs from sludge as well as legislation and regulations governing EDCs in sludge disposed on land was also conducted as part of the project scope.

4.2 CONCLUSIONS

The following conclusions were drawn from the study:

- Apart from oestrone and PFOS where the average removal efficiencies were almost the same, the emerging PCS technology indicated significantly higher average removal efficiency (76-95%) for the targeted EDCs from untreated sludge (i.e. PS, WAS and combined PS & WAS) than conventional MAD (27-72%) that is commonly applied for sludge treatment at most South African WWTPs. The PCS process also significantly removed (64-99%) residual EDCs from DS generated from treatment of combined PS & WAS in the conventional MAD at Daspoort WWTP.
- Since South Africa does not have regulations on the amount of EDCs in wastewater sludge, no conclusions could be drawn on the impact of residual EDCs in the hydrochar if it were to be disposed on land or beneficially utilised for agriculture in line with the Department of Water and Sanitation “Guidelines for Utilisation and Disposal of Wastewater Sludge (WRC, 2006 & 2009)”. Although some EU countries have implemented regulations on certain EDCs, the EDCs targeted in this study are not regulated in any of these countries.

- Previous studies showed that the hydrochar produced from processing sludge in the PCS process is sterile and can be used for multiple purposes (e.g. as a biofuel, as a soil conditioner in agriculture, building material and adsorption media). Thus the ability of the PCS process to remove EDCs at significantly higher efficiencies than conventional processes demonstrates that it is a feasible technology for treating sludge to a higher quality and is better positioned to meet the requirements of future legislation on EDCs if implemented.

4.3 RECOMMENDATIONS

In order to continue building the body of knowledge on the removal of EDCs in wastewater sludge in South Africa, the following is recommended based on the findings from this project:

- Development of a unified approach to analytical methods for detection of EDCs in liquid wastewater and sludge with the objective of increasing laboratory capabilities in South Africa.
- Continued qualitative and quantitative monitoring of target EDCs that are considered at a national level to be of concern in sludge to build a comprehensive national database
- Investigation and mathematical modelling of the mechanisms for removal of target EDCs in conventional MAD, emerging technologies such as the PCS process as well as other sludge treatment technologies most likely to be implemented in South Africa. The research needs to also focus on those aspects that were not adequately addressed in this project, e.g.
    - detailed evaluation of degradation pathways as well as analysis of any possible transformational compounds formed during processing of sludge
    - detailed monitoring and quantitative analysis of PFAS since some compounds that were not targeted in this project were detected in the sludge samples
- Comprehensive research on the fate of EDCs in treated sludge applied to land both for non-agricultural and agricultural purposes to fully understand the potential risks to the environment and human health
- Investigation of application of hydrochar generated from processing sludge in the PCS process as adsorption media to remove EDCs from wastewater effluent, thus advancing the principles of converting WWTPs into resource recovery facilities within a circular economy

REFERENCES

Adams, C., Wang, Y., Loftin, K. and Meyer, M. (2002). Removal of antibiotics from surface and distilled water in conventional water treatment processes. Journal of Environmental Engineering, 128 (3), 253.

Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Thomaidis, N.S. and Xu, J. (2017). Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review. Journal of Hazardous Materials, vol. 323, pp 274-298.

Andersen, H.R., Siegrist, P., Halling-Sorensen, B., Ternes, T.A. (2003). Fate of estrogens in a municipal sewage treatment plant. Environ Science and Technology 18:4021-6.

Archer, E., Petrie, B., Kaspryzk-Hordern, B. and Wolfaardt, G.M. (2017). The fate of Pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites and illicit drugs in a WWTP and environmental waters.

AWWARF (2006). Endocrine Disrupters in Sewage Sludge: Analytical Method Development.

Barrett, J.R. (2005). Phthalates and baby boys: potential disruption of human genital development. Environmental health perspectives 113: A542.

B.C. Ministry of the Environment and Climate Change Strategy (2018). Organic Matter Recycling Regulation (OMRR). Policy Intentions Paper. Available at: https://www2.gov.bc.ca/assets/gov/environment/waste-management/organic-waste/reports-and-papers/2018_omrr_intentions_paper.pdf

B.C. Water and Waste Association (BCWWA) (2016). Land Application of Biosolids. Issue Analysis Paper and Position Statement.

Bedia, C., Dalmau, N., Jaumot, J. and Tauler, R. (2015). Phenotypic malignant changes and untargeted lipidomic analysis of long-term exposed prostate cancer cells to endocrine disruptors. Environmental research 140: 18-31.

Bernal-Martinez, A., Carrere, H., Patureau, D., Delgenes, J.P. (2007). Ozone pre-treatment as improver of PAH removal during anaerobic digestion of urban sludge. Chemosphere 68:1013-9

Bette, H. (2007). California bans phthalates in toys for children. Chemical and Engineering News 12.

Birkett, J.W. and Lester, J.N. (2003). Endocrine Disrupters in Wastewater and Sludge Treatment Processes. Lewis Publishers, London, England.

Brown, D.P. (1987). Mortality of workers exposed to polychlorinated biphenyls—an update. Archives of Environmental Health: An International Journal 42: 333-339.

Brown, N.W., Roberts, E.P.L., Garforth, A.A. and Dryfe, R.A.W. (2004). Electrochemical

Burger, A.E.C. (2010). Implementation of the Extended Research Plan on Endocrine Disruptor Chemicals in Water Resources. WRC Programme on Endocrine Disrupting Compounds (EDCS) 4.

Burnett, M.E. and Wang, S.Q. (2011). Current sunscreen controversies: a critical review. Photodermatology, photoimmunology & photomedicine 27: 58-67.

Caliman, F.A. and Gavrilescu, M. (2009). Pharmaceuticals, personal care products and endocrine disrupting agents in the environment – a review. CLEAN-Soil, Air, Water 37: 277-303.

Carballa, M., Omil, F., Alder, A.C. and Lema, J.M. (2006). Comparison between the conventional anaerobic digestion of sewage sludge and its combination with a chemical or thermal pre-treatment concerning the removal of pharmaceuticals and personal care products. Water Science and Technology 58 (8): 109 -117.

Carballa, M., Omil, F., Ternes, T., Lema, J. M. (2007). Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge. Water Research 41 (10), 2139-2150.

Carballa, M., Fink, G., Omil, F., Lema, J.M., Ternes, T. (2008). Determination of the solid-water distribution coefficient (Kd) for pharmaceuticals, estrogens and musk fragrances in digested sludge. Water Research 42 (1-2), 287-295.

Citulski, J. (2010). Fate of Endocrine – Active Compounds during Municipal Biosolids Treatment: A Review. Environmental Science and Technology.

Coetzee, M.A.A., Momba, M.N.B., Kibambe, G.M., Thobela, K.T., Kgositatu, T. and Mahlangu, P. (2017). The removal of endocrine disrupting compounds by wastewater treatment plants. Water Research Commission. Pretoria, South Africa.

Colborn, T. (1995). Statement from the work session on environmentally induced alterations in development: a focus on wildlife. Environmental Health Perspectives: 3-5.

Colborn, T. and Clement, C. (1992). Chemically-induced alterations in sexual and functional development: the wildlife/human connection: Princeton Scientific Pub. Co.

Colborn, T., Vom Saal, F.S. and Soto, A.M. (1993). Developmental effects of endocrine-disrupting chemicals in wildlife and humans. Environmental health perspectives 101: 378.

Costa, L.G. and Giordano, G. (2007). Developmental neurotoxicity of polybrominated diphenyl ether (PBDE) flame retardants. Neurotoxicology 28: 1047-1067.

Crisp, T.M., Clegg, E.D., Cooper, R.L., Wood, W.P. and Anderson, D.G. (1998). Environmental endocrine disruption: an effects assessment and analysis. Environmental health perspectives 106: 11.

Czajka, C.P. and Londry, K.L. (2006). Anaerobic biotransformation of estrogens. Science of the Total Environment 367 (2-3), 932-941.

Daly, G.L. and Wania, F. (2005). Organic contaminants in mountains. Environmental science & technology 39: 385-398.

Damstra, T., Barlow, S., Bergman, A., Kavlock, R. and Van Der Kraak, G. (2002). Global assessment of the state-of-the-science of endocrine disruptors. Geneva: World Health Organization.

Daso, A.P., Fatoki, O.S., Odendaal, J.P. and Olujimi, O.O. (2013). Polybrominated diphenyl ethers (PBDEs) and 2, 2′, 4, 4′, 5, 5′-hexabromobiphenyl (BB-153) in landfill leachate in Cape Town, South Africa. Environmental monitoring and assessment 185: 431-439.

Davis, K.S. (1971). The Deadly Dust: The Unhappy History of DDT: American Heritage Publishing Company, Incorporated.

De Leon-Condes, C., Barrera-Diaz, C., Barrios, J., Becerril, E. and Reyes-Perez, H. (2017). A coupled ozonation-electrooxidation treatment for removal of bisphenol A, nonylphenol and triclosan from wastewater sludge. International Journal of Environmental Science and Technology 14: 707-716.

Diamanti-Kandarakis, E., Bourguignon, J-P., Giudice, L.C., Hauser, R. and Prins, G.S. (2009). Endocrine-Disrupting Chemicals: An Endocrine Society Scientific Statement. Endocrine Reviews 30: 293-342.

Eriksson, P., Fischer, C. and Fredriksson, A. (2006). Polybrominated diphenyl ethers, a group of brominated flame retardants, can interact with polychlorinated biphenyls in enhancing developmental neurobehavioral defects. Toxicological Sciences 94: 302-309.

Ether, D. (2008). Toxicological Review of Decabromodiphenyl Ether (BDE-209).

EC (2010). Environmental, economic and social impacts of the use of sewage sludge on land, Final Report page 18. Available at: https://ec.europa.eu/environment/archives/waste/sludge/pdf/part_iii_report.pdf

EU (1986). Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Available at: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex:31986L0278

EU (2008). Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy. Available at: https://eur-lex.europa.eu/eli/dir/2008/105/oj

Falconer, I.R., Chapman, H.F., Moore, M.R. and Ranmuthugala, G. (2006). "Endocrine-Disrupting Compounds: A Review of Their Challenge to Sustainable and Safe Water Supply and Water Reuse", Research Report, University of Adelaide Medical School, Adelaide, South Australia.

Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (2017). Sewage Sludge Ordinance. Available at: https://www.bmu.de/en/law/sewage-sludge-ordinance/

Feigal, D. (2002). PVC Devices Containing the Plasticizer DEHP. FDA Public Health Notification (12 July 2002).

Fertilizer Act of 9 January 2009. Federal Law Gazette IS 54, 136

Fiorini, R., Pagliarani, A., Nesci, S., Pirini, M. and Tucci, E. et al. (2012). Structural and functional changes in gill mitochondrial membranes from the Mediterranean mussel Mytilus galloprovincialis exposed to tri-n-butyltin. Environmental Toxicology and Chemistry 31: 877-884.

Fisher, J.S. (2004). Environmental anti-androgens and male reproductive health: focus on phthalates and testicular dysgenesis syndrome. Reproduction 127: 305-315.

Flint, S., Markle, T., Thompson, S. and Wallace, E. (2012). Bisphenol A exposure, effects, and policy: A wildlife perspective. Journal of Environmental Management, 104:19-34.

Francis, E. (1994). Conspiracy of Silence: The story of how three corporate giants—Monsanto, GE, and Westinghouse—covered their toxic trail. Sierra Magazine.

French Minister of ecological and solidarity transition. Decree No. 97-1133 of 08/12/97 relating to the spreading of sludge from wastewater treatment. Available at: https://translate.google.com/translate?hl=en&sl=fr&u=https://aida.ineris.fr/consultation_document/3061&prev=search

Fürst, P. (2006). Dioxins, polychlorinated biphenyls and other organohalogen compounds in human milk. Levels, correlations, trends and exposure through breastfeeding. Molecular nutrition & food research 50: 922-933.

Furlong, E.T., Gray, J.L., Quanrud, D.M., Teske, S.S., Esposito, K., Marine, J., Ela, W.P., Stinson, B., Kolpin, D.W. and Phillips, P.J. (2010). Fate of estrogenic compounds during municipal sludge stabilization and dewatering. Water Environment Research Foundation. Biosolids: Final Report.

German Federal Ministry for the Environment, Nature Conservative and Nuclear Safety (2017). New Sewage Sludge Ordinance in force. Text of ordinance on Federal Gazette 2017-09-27. Available at: https://www.bmu.de/en/law/sewage-sludge-ordinance/

German Federal Environment Agency (2017). New German Sewage Sludge Ordinance. HELCOM Workshop on sewage sludge handling practices, Vilnius, 27.10.2017.
Available at: https://portal.helcom.fi/meetings/SEWAGE%20SLUDGE%20HANDLING%20WS%201-2017-495/Related%20Information/New%20German%20Sewage%20Sludge%20Ordinance_Roskosch.pdf

Gómez-Canela, C., Barth, J.A.C. and Lacorte, S. (2012). Occurrence and fate of perfluorinated compounds in sewage sludge from Spain and Germany. Environmental Science and Pollution Research 19(9):4109-19

Gore, A.C. (2010). Neuroendocrine targets of endocrine disruptors. Hormones (Athens, Greece) 9: 16.

Government for Canada, Department of Health (2019). Water Talk – Perfluoroalkylated substances in drinking water. Available at: https://www.canada.ca/en/services/health/publications/healthy-living/water-talk-drinking-water-screening-values-perfluoroalkylated-substances.html

Grun, F. and Blumberg, B. (2006). Environmental obesogens: organotins and endocrine disruption via nuclear receptor signaling. Endocrinology 147: s50-s55.

Grun, F. and Blumberg, B. (2009). Minireview: the case for obesogens. Molecular Endocrinology 23: 1127-1134.

Grun, F., Watanabe, H., Zamanian, Z., Maeda, L. and Arima, K. et al. (2006). Endocrine-disrupting organotin compounds are potent inducers of adipogenesis in vertebrates. Molecular Endocrinology 20: 2141-2155.

Grunwald, M. (2002). Monsanto hid decades of pollution. Washington Post 1.

Guerra, P., Kim, M., Teslic, S. et al. (2015) Bisphenol-A removal in various wastewater treatment processes: Operational conditions, mass balance, and optimization. J Environ Manage 152:192-200.

Haiba, E. and Nei, L. (2017). Sewage Sludge Composting and Pharmaceuticals. European Scientific Journal. Special Edition.

Hallegue, D., Rhouma, K.B., Tebourbi, O. and Sakly, M. (2003). Impairment of testicular endocrine and exocrine functions after dieldrin exposure in adult rats. Polish Journal of Environmental Studies 12: 557-562.

Hamid, H. and Eskicioglu, C. (2012). Fate of estrogenic hormones in wastewater and sludge treatment: A review of properties and analytical detection techniques, Water Research, 46 (18), 5813-5833.

Hamid, H. and Eskicioglu, C. (2013). Effect of microwave hydrolysis on transformation of steroidal hormones during anaerobic digestion of municipal sludge cake. Water Research, 47, 4966-4977.

Harrison, P., Humfrey, C., Litchfield, M., Peakall, D. and Shuker, L. (1995). Environmental oestrogens: consequences to human health and wildlife: Institute for Environment and Health.

Herbert, M. (2007). Public acceptance and independent certification of biosolids in Canada. Water Practice and Technology 897-903.

Heath, R., Boyd, L., Malete, O. and Masoabi, D. (2013). Introduction to the management of EDCs – Volume I. Water Research Commission Report No. TT 560/13, Pretoria, South Africa.

Herbst, A.L., Ulfelder, H. and Poskanzer, D.C. (1971). Adenocarcinoma of the vagina: association of maternal stilbestrol therapy with tumor appearance in young women. New England journal of medicine 284: 878-881.

Holbrook, R.D., Novak, J.T., Grizzard, T.J. and Love, N.G. (2002). Estrogen Receptor Agonist Fate during Wastewater and Biosolids Treatment Processes: A Mass Balance Analysis. Environmental Science Technology: 36(21): 4533-4539.

Ifelebuegu, A.O. (2011). The fate and behaviour of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes. Int. J Environ. Sci. Tech 8 (2): 245-254.

Ifelebuegu, A.O. (2013). Removal of endocrine disrupting chemicals in wastewater treatment applications, PhD Thesis, Coventry University, Coventry, UK.

Ivashechkin, P., Corvini, P.F. and Dohmann, M. (2004). Behaviour of endocrine disrupting chemicals during the treatment of municipal sewage sludge. Water Science Technology 50 (5):133-40.

Institute of Environment and Health (IEH) (2012). A review of latest endocrine disrupting chemicals research implications for drinking water. Final Report DWI: 70/2/266.

Jensen, S. (1969). DDT and PCB in marine animals from Swedish waters. Nature 224: 247-250.

Johnson, A. and Sumpter, J. (2001). Removal of endocrine disrupting chemicals in activated sludge treatment works. Environmental Science and Technology, 35 (24).

Jones, S., Boisvert, A., Naghi, A., Hullin-Matsuda, F. and Greimel, P. (2016). Stimulatory effects of combined endocrine disruptors on MA-10 Leydig cell steroid production and lipid homeostasis. Toxicology 355: 21-30.

Kaiser, J. (2005). Panel finds no proof that phthalates harm infant reproductive systems. Science 310: 422-422.

Knobeloch, L., Turyk, M., Imm, P., Schrank, C. and Anderson, H. (2009). Temporal changes in PCB and DDE levels among a cohort of frequent and infrequent consumers of Great Lakes sportfish. Environmental research 109: 66-72.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. and Buxton, H.T. (2002). Pharmaceuticals, hormones and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environmental Science and Technology, 36:1202-1211

Kodavanti, P.R.S. (2005). Neurotoxicity of persistent organic pollutants: possible mode (s) of action and further considerations. Nonlinearity in Biology, Toxicology, Medicine 3: dose-response. 003.003. 002.

Land Resource Consulting Services (LRCS) (2016). A literature review of risks relevant to the use of biosolids and compost from biosolids with relevance to the Nicola Valley, BC.

Langston, W., Pope, N., Davey, M., Langston, K. and O'Hara, S. (2015). Recovery from TBT pollution in English Channel environments: A problem solved? Marine pollution bulletin 95: 551-564.

Lema, S.C., Dickey, J.T., Schultz, I.R. and Swanson, P. (2008). Dietary exposure to 2, 2', 4, 4'-tetrabromodiphenyl ether (PBDE-47) alters thyroid status and thyroid hormone-regulated gene transcription in the pituitary and brain. Environmental health perspectives 116: 1694.

Leon-Condes, C., Barrera-Dıaz, C., Barrios, J., Becerril, E. and Reyes-Pe´rezInt, H. (2017). A coupled ozonation-electrooxidation treatment for removal of bisphenol A, nonylphenol and triclosan from wastewater sludge. Environ. Sci. Technol. 14:707-716.

Liu, Z., Kanjo, Y. and Mizutani, S. (2009). "Removal Mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment – physical means, biodegradation, and chemical advanced oxidation: A review" Science of the total environment, 407 (2009), 731-748.

Loomis, D., Browning, S.R., Schenck, A.P., Gregory E and Savitz D.A. (1997) Cancer mortality among electric utility workers exposed to polychlorinated biphenyls. Occupational and Environmental Medicine 54: 720-728.

Lundholm, C. (1997). DDE-induced eggshell thinning in birds: effects of p, p'-DDE on the calcium and prostaglandin metabolism of the eggshell gland. Comparative Biochemistry and Physiology Part C: Pharmacology, Toxicology and Endocrinology 118: 113-128.

Marques-Pinto, A., Carvalho, D. (2013). Human infertility: are endocrine disruptors to blame? Endocrine Connect 2(3):15-29

Martín, J., Santos, J.L., Aparicio, I. and Alonso, E. (2015). Pharmaceutically active compounds in sludge stabilization treatments: Anaerobic and aerobic digestion, wastewater stabilization ponds and composting. Sci. Total Environ. 503-504: 97-104.

Matthiessen, P. and Gibbs, E.P. (1998). Critical appraisal of the evidence for tributyltin-mediated endocrine disruption in mollusks. DOI 10:1002

McNamara, P.J., Weirich, C.A., Miller, T.R., Zitomer, D. and Ross, J.J. Emerging Investigators Series: Pyrolysis Removes Common Microconstituents Triclocarban, Triclosan, and Nonylphenol from Biosolids. Environmental Science: Water Research and Technology 2: 282-289.

Mills, L. and Chichester, C. (2005). Review of Evidence: Are Endocrine-Disrupting Chemicals in the Aquatic Environment Impacting Fish Populations? Science of the Total Environment 343 (1-3):1-34

Miltner, R.J., Baker, D.B., Speth, T.F. and Fronk, C.A. (1989). Treatment of seasonal pesticides in surface waters: Journal American Water Works Association, 81 (1), 43-52.

Ministry of Environmental and Food of Denmark. Available at: https://eng.mst.dk/trade/industry/industrial-air-pollution/statutory-orders-and-guidelines/

Muller, M., Combalbert, S., Delgenès, N. and Bergheaud, V. (2010). Occurrence of Estrogens in Sewage Sludge and Their Fate during Plant-Scale Anaerobic Digestion. Chemosphere 81(1):65-71.

Mullerova, D., Kopecky, J., Matejkova, D., Muller, L. and Rosmus, J. (2008). Negative association between plasma levels of adiponectin and polychlorinated biphenyl 153 in obese women under non-energy-restrictive regime. International Journal of Obesity 32: 1875-1878.

Musvoto, E.V., Mgwenya, N., Mangashena, H. and Mackintosh, A. (2018). Energy recovery from wastewater sludge – A review of appropriate emerging and established Technologies for the South African Industry. Water Research Commission TT752/18.

Okoro, H.K., Fatoki, O.S., Adekola, F.A., Ximba, B.J. and Snyman, R.G. (2011a). Sources, environmental levels and toxicity of organotin in marine environment-a review. Asian Journal of Chemistry 23: 473.

Okoro, H.K., Fatoki, O.S., Adekola, F.A., Ximba, B.J., Snyman, R.G. and Opeolu, B. (2011b). Human exposure, biomarkers, and fate of organotins in the environment. Reviews of Environmental Contamination and Toxicology Volume 213: Springer. pp. 27-54.

Olujini, O.O., Fatoki, O.S., Daso, A.P., Akinsoji, O.S., Oputu, O.U., Oluwafemi, O.S. and Songca, S.P. (2013). Levels of Nonylphenol and Bisphenol A in Wastewater Treatment Plant Effluent, Sewage Sludge and Leachates around Cape Town, South Africa. Handbook of Wastewater Treatment.

Organization WH (1976). Environmental Health Criteria 2. Poly chlorinated biphenyls and terphenyls: United Nations Environment Programme/WHO, Geneva, Switzerland.

Organization WH (1997). Flame retardants: a general introduction. Environmental Health Criteria.

Organization WH (2013). Effects of human exposure to hormone-disrupting chemicals examined in landmark United Nations report. ScienceDaily.

Petrie, B., Barden, R. and Kasprzyk-Hordern, B. (2017). A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. Water Research, 72, 3-27.

Pham, M.H., Zita, S., Tu, B.M., Pham, H.V., Fabrice, G.R. (2011). Pesticide pollution in agricultural areas of Northern Vietnam: Case study in Hoang Liet and Minh Dai communes. Environmental Pollution 159 (12):3344-50.

Qiang, Z., Nie, Y., Ben, W., Qu, J. and Zhang, H. (2013). Degradation of endocrine-disrupting chemicals during activated sludge reduction by ozone. Chemosphere 91: 366-373.

Ried, A. and Mielcke, J. (2003). Municipal wastewater treatment for reuse: Combining ozone and UV techniques for advanced wastewater treatment. Disinfection and degradation of endocrine substances. IUVA News, 5 (1), 17-21.

Ried, A., Mielcke, J., Kampmann, M., Ternes, T.A. and Teiser, B. (2004). Ozone and UV

Ritter, L., Solomon, K.R. Forget, J., Stemeroff, M. and O'Leary, C. (1995). Persistent Organic Pollutants. An assessment report on: DDT-Aldrin-Dieldrin-Endrin-Chlordane Heptachlor-Hexachlorobenzene Mirex-Toxaphene Polychlorinated Biphenyls Dioxins and Furans. The International Programme on Chemical Safety (IPCS) within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC)

Rolland, R., Gilbertson, M. and Peterson, R.E. (1997). Chemically induced alterations in functional development and reproduction of fishes. SETAC Press.

Sarkar, S. (2013). Fate of Estrogens in Anaerobic Digestion and their removal in Advanced Oxidation. Electronic Thesis and Dissertation Repository. 1415.

Salihoglu, N.K., Karaca, G., Salihoglu, G. & Tasdemir, Y. (2012): Removal of polycyclic aromatic hydrocarbons from municipal sludge using UV light, Desalination and Water Treatment, 44:1-3, 324-333

Sawyer, C.N., McCarty, P. and Parkin, G. (1994). Chemistry for Environmental Engineering, 4th Edition. McGraw Hill.

Selcen, A.K. (2012). Treatment of xenobiotics during anaerobic digestion and its enhancement upon post-ozonation of the anaerobically treated sludge. A Thesis submitted to the Graduate School of Natural and Applied Sciences of Middle East Technical University.

Semblante, G.U., Hai, FI, Huang X, Ball AS and Price WE (2015). Trace organic contaminants in biosolids: impact of conventional wastewater and sludge processing technologies and emerging alternatives. Journal of Hazardous Materials, 300: 1-17.

Schug, T.T., Janesick, A., Blumberg, B. and Heindel, J.J. (2011). Endocrine disrupting chemicals and disease susceptibility. The Journal of Steroid Biochemistry and Molecular Biology, 127:204-215.

Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F. and Field, J.A. (2006). Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility. Eviron Sci Technol 40 (23): 7350-7357

Scruggs, C., Hunter, G., Snyder, E. and Long, B. (2004). "EDCs in Wastewater: What's the next step? Report to the Water Environment Federation, Kansas City.

Scruggs, C., Hunter, G., Snyder, E., Bruce Long, B. and Snyder, S. (2004). EDCS in wastewater: what's the next step? WEFTEC.

Short, P. (1999). Statement from the work session on health effects of contemporary-use pesticides: the wildlife/human connection. Toxicology and Industrial Health 15: 1-5.

Sinks, T., Steele, G., Smith, A.B., Watkins, K. and Shults, R.A. (1992). Mortality among workers exposed to polychlorinated biphenyls. American journal of epidemiology 136: 389-398.

Smith, S. (2009). Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling.

Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., Lester, J.N. (2008). Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. Environment International 34(7):1033-49.

Stoner, H. (1953). Effect of 2, 2-bis (Parachlorophenyl)-l, l-Dichloroethane (DDD) on the Adrenal Cortex of the Rat. Nature 172: 1044-1045.

Stockholm Convention (2017). National implementation plan for Stockholm convention on persistent organic pollutants.

Swan, S., Liu, F., Hines, M., Kruse, R. and Wang, C. (2010). Prenatal phthalate exposure and reduced masculine play in boys. International journal of andrology 33: 259-269.

Szlinder-Richert, J., Barska, I., Mazerski, J. and Usydus, Z. (2008). Organochlorine pesticides in fish from the southern Baltic Sea: levels, bioaccumulation features and temporal trends during the 1995-2006 period. Marine Pollution Bulletin 56: 927-940.

Tang, N-J., Liu, J., Coenraads, P., Dong, L. and Zhao. L-J. (2008). Expression of AhR, CYP1A1, GSTA1, c-fos and TGF-α in skin lesions from dioxin-exposed humans with chloracne. Toxicology letters 177: 182-187.

Tauber, O.E. and Hughes, A.B. (1950). Effect of DDT Ingestion on Total Cholesterol Content of Ovaries of White Rat.∗. Proceedings of the Society for Experimental Biology and Medicine 75: 420-422.

Tetreault, G. et al (2011). Intersex and Reproductive impairment of two species wild fish exposed to multiple municipal wastewater discharges in Canada. Aquatic Toxicology 104: 278-290.

The European Commission (EU) (2013). DIRECTIVE 2013/39/EU of the European parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Available at: http://www.legislation.gov.uk/eudr/2013/39/annex/i

The European Commission (EU) (2015). Commission Implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. Official Journal of the European Union.

The European Commission (EU) (2015). Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32018D0840

Tiemann, U. (2008). In vivo and in vitro effects of the organochlorine pesticides DDT, TCPM, methoxychlor, and lindane on the female reproductive tract of mammals: a review. Reproductive Toxicology 25: 316-326.

Tijani, J.O. (2013). A Review of Pharmaceuticals and Endocrine-Disrupting Compounds: Sources, Effects, Removal, and Detections. Water, Air, & Soil Pollution 224:1770

Tumburu, L., Shepard, E.F., Strand, A.E. and Browdy, C.L. (2012). Effects of endosulfan exposure and Taura Syndrome Virus infection on the survival and molting of the marine penaeid shrimp, Litopenaeus vannamei. Chemosphere 86: 912-918.

Uemura, H., Arisawa, K., Hiyoshi, M., Satoh, H. and Sumiyoshi, Y. (2008). Associations of environmental exposure to dioxins with prevalent diabetes among general inhabitants in Japan. Environmental research 108: 63-68.

U.S. EPA (2000). Environmental Regulations and Technology Control of Pathogens and Vector Attraction in Sewage Sludge.

U.S. EPA (2019). EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan. EPA Report 823R18004. Available at: www.epa.gov/pfas

U.S. EPA (2019). Biosolids Biennial Review Reporting Period 2016-2017. Available at: https://www.epa.gov/sites/production/files/2019-06/documents/2016-2017-biosolids-biennial-review.pdf

Venkatesan, A.K. and Halden, R. (2016). Modeling the pH-mediated extraction of ionizable organic contaminants to improve the quality of municipal sewage sludge destined for land application. Science of the Total Environment 550: 736-741.

Verhulst, S.L., Nelen, V., Den Hond, E., Koppen, G. and Beunckens, C. (2009). Intrauterine exposure to environmental pollutants and body mass index during the first 3 years of life. Environmental health perspectives 117: 122.

Visser, M.J. (2007). Cold, clear, and deadly: Michigan State University Press.

Von Eyser, C., Schmidt, T.C. and Tuerk, J. (2016). Fate and behaviour of diclofenac during hydrothermal carbonization. Chemosphere 153: 280-286.

Vranitzky, R. and Lahnsteiner, J. (2009). Ozone treatment of organic micro-pollutants in sewage sludge. Paper presented at the 12th IWA Sludge Conference – Sustainable Management of Water and Wastewater Sludges Harbin, P.R. China, August 2009

Wee, S.Y. and Aris, A.Z. (2019). Occurrence and public-perceived risk of endocrine disrupting compounds in drinking water. Nature Partner Journals: Clean water 2:4.

White, C. (1999). Handbook of Chlorination and Alternative Disinfectants. New York: John Wiley & Sons, Inc.

World Health Organization (WHO) (2013). State of the Science of Endocrine Disrupting Chemicals.

Wintgens, T., Lyko, S., Melin, T., Schäfer, A.I., Khan, S., Sherman, P. and Ried, A. (2004). Removal of estrogenic trace contaminants from wastewater and landfill leachate with advanced treatment processes. Proc. IWA Leading Edge Technologies Conf.

WRC (2003). "Endocrine Disrupting Compounds – Workshop on Knowledge Gaps and Research Needs of EDC in Water Systems", a report following the workshop held in Pretoria in 2002.

Wu, X., Dodgen, K.L., Conkle, J.I. and Gan, J. (2015). Plant uptake of pharmaceutical and personal care products from recycled water and biosolids: a review. Science of the Total Environment 536: 655-666.

Yoon, Y., Westerhoff, P., Snyder, S., Song, R. and Levine, B. (2002). A Review on removal of endocrine-disrupting compounds and pharmaceuticals by drinking water treatment

Zhang, A. and Li, Y. (2014). Removal of phenolic endocrine disrupting compounds from waste activated sludge using UV, H202 and UV/H2O2 oxidation processes Effects of reaction conditions and sludge matrix. Science of the Total Environment 493: 307-323.

Zheng, J., Kennedy, K.J. and Eskicioglu, C. (2009). Effect of low temperature microwave pretreatment on characteristics and mesophilic digestion of primary sludge. Environmental Technology 30 (4), 319-327.

Zhou, H., Zhou, J., Wang, M., Wang, X., Zhang, Q., Zhang, Q. and Zhan, Y. (2015). Removal of typical pharmaceutically active compounds in sewage sludge using mesophilic and thermophilic anaerobic digestion processes. International Journal of Environmental Science Technology 12: 2169-2178.

APPENDIX A:

LITERATURE REVIEW: PROCESSES & TECHNOLOGIES THAT REMOVE EDCS FROM LIQUID WASTEWATER

A1 Overview of EDCs Removal from Wastewater

Municipal wastewater treatment plants are not specifically designed to handle the trace levels of EDCs found in wastewater and many EDCs pass through conventional treatment systems without being degraded. Furthermore, EDC compounds belong to different classes of organic compounds and have a variety of functional groups which can make them less amenable to removal by established treatment techniques used in municipal WWTPs (sedimentation, biology, filtration, flocculation/precipitation, etc.) The fate of EDCs in wastewater is determined by the physicochemical properties of the different organic compounds (Birkett and Lester, 2003, Sawyer et al., 1994) and based on the properties removed EDCs can be achieved via the following mechanisms (Birkett and Lester, 2003):

- Adsorption onto suspended solids, fats and oils
- Biological degradation
- Chemical transformations: hydrolyses, photolysis, and oxidation and reduction reactions
- Volatilization

The most important properties are the octanol/water partition coefficient (K_{OW}), Henry's law constant (H), the organic carbon to water partition coefficient (K_{OC}), and the solubility of the organic compound in water (Caliman and Gavirlescu, 2009; Coetzee et al., 2017). Possible removal mechanism can be predicted by using the coefficients and constants of a specific organic compound.

A2 EDCs Removal in Established Conventional Wastewater Treatment Plants

EDC removal in conventional WWTP through biological processes, combined with absorption and adsorption mechanisms can achieve up to 99% removal of EDCs. Within the treatment process, primary sedimentation that removes EDCs through adsorption onto primary sludge and FOGs has been shown to remove the lowest quantity of EDCs. Removal is dependent on the physico-chemical properties of the compound, characteristics of the wastewater as well as retention time (Hamid and Eskicioglu, 2012; Kohl et al., 2008). Data observed on PSTs indicates a wide variation in removal rates (0-46%) depending on EDC type (Coetzee et al., 2017). The bulk of EDCs is removed through biological treatment, and the following key factors have been observed (Caliman and Gavrilescu, 2009; Ifelebuegu, 2010; Coetzee et al., 2017):

- Compounds with high pseudo first order biodegradation constants (k_{biol}) and low sludge water distribution coefficients (K_{OC}) such as ibuprofen are efficiently transformed independently of sludge retention time (SRT) or hydraulic retention time (HRT)
- Compounds with low k_{biol} and high K_{OC} values, such as musks, are retained in the aeration tank by sorption and significantly transformed at sufficient SRT

- Compounds with low k_{biol} and medium K_{OC} values, such as oestrone and 17 ß-estradiol, are moderately transformed independently of HRT and slightly dependent of hydraulic retention
- Compounds with low k_{biol} and K_{OC} values, such as carbamazepine, are neither removed nor bio-transformed no matter which STR and HRT is used.

Among all conventional wastewater treatment processes, the activated sludge process has been found to be the most efficient in EDCs removal. Since the proportion of removal by adsorption in primary setting, chemical precipitation, aeration volatilization and WAS absorption is small, the majority of EDCs in wastewater is removed by biodegradation. Factors that have a significant impact on removal efficiency are the type of activated sludge process (aerobic, nitrification, denitrification (P removal) and sludge age. Long sludge ages increase the removal efficiency of most EDCs.

Activated sludge plant configured for biological nutrient removal generally showed better removal of the endocrine disrupting chemicals compared to conventional activated sludge plant effluents. A comparison of removal technologies by (Ifelebuegu, 2010) indicated that the removal efficiency of the treatment processes were in the order activated sludge > oxidation ditch > biofilter > rotating biological contactors. Coetzee et al. (2017) carried out the most extensive study on EDC removal in South Africa. The study compared the removal efficiency of a range of Oestrogens, PFAS and Pharmaceuticals at three full scale WWTPs (Daspoort, Zeekoegat and Phola). The removal efficiencies in each EDC group varied from, 'not removed' to >99% removal. Removal efficiencies also varied with the different treatment technologies. The Integrated Ponds system at Phola achieved better removals of the oestrogens and PFCs, with PFOS as the exception. Comparison of the two activated sludge plants indicated that for most of the EDCs the removals were better in the Zeekoegat plant than at Daspoort. Factors that could have contributed to the improved removals at Zeekoegat were the longer SRT, higher MLSS content and the improved oxygen transfer

Table A1: Comparison of removal efficiencies of a biological filter and an activated sludge plant (Kasprzyk-Hordern et al. (2009)

Compound	% Removal	
	Biological filter	Activated sludge plant
Antibacterial drug		
Trimethoprim	47	70
Erythromycin-H2O	14	72
Metronidazole	59	38
Anti-inflammatory/analgesics		
Paracetamol	94	99
Ibuprofen	84	94
Diclofenac	0	31
Ketoprofen		
Naproxen	56	86
Aspirin	96	99
Salicylic acid	97	99
Mefenamic acid		
Codeine	49	61
Tramadol	0	42
Antiepleptic		
Carbamazepine	0	13
Gabapentin	0	86
Beta-adrenoceptor blocking drug		
Propranolol	52	57
Metoprolol	8	56
Atenolol	78	85
Lipid regulating agent		
Bezafibrate	45	71
H2-receptor antagonists		
Ranitidine		92
Cimetidine	26	79
Sulfasalazine	0	0
Sulfapyridine	70	91
5-Aminosalicylic acid	0	94
Diuretics		
Furosemide	21	77
Calcium channel blockers		
Diltiazem	65	77
Antidepressants		
Amitriptyline	84	96

Table A2 shows the removal efficiency of different EDCs though various wastewater treatment processes.

Table A2: Treatment Types and Removal Efficiencies for Selected EDCs from WWTPs

Compound	Process Type	Removal Efficiency
PCB (polychlorinated biphenyls)	Biofiltration	90%
	Activated sludge	96%
	Biofiltration/activated sludge	99%
NP (nonylphenol)	High loading/non-nitrifying	37%
	Low loading/nitrifying	77%
NP_1EO**	High loading/non-nitrifying	-3% produced as degradation product
	Low loading/nitrifying	31%
NP_2EO**	High loading/non-nitrifying	-5% produced as degradation product
	Low loading/nitrifying	91%
NP_6EO**	High loading/non-nitrifying	78%
	Low loading/nitrifying	98%
17β-estradiol/17α-ethinylestradiol	Filtration – Sand/microfiltration	70%
	Advanced treatment - Reverse osmosis	95%
Organotins	Primary effluent	73%
	Secondary effluent	90%
	Tertiary effluent	98%
Triazines	Conventional two-stage	<40%

*Taken from Birkett and Lester (2003).
**NP_nEO = Nonylphenol ethoxylate, where n = specific number of EO groups

A3: Advanced and Emerging Treatment Technologies

Findings reported in the literature indicate that removal efficiency through conventional biological wastewater treatment varies considerably depending on the type of compound and removal process. Also some non-biodegradable organic EDCs cannot be sufficiently removed using biological treatment processes. Thus advanced physical and chemical treatment technologies are being widely researched with a view for full-scale application. A review of some of these technologies with the potential for full-scale implementation is given below.

A3.1 Activated Carbon Adsorption

Activated carbon adsorption has been widely used in both water and wastewater treatment to remove heavy metals and other micro-pollutants. In recent years a number of studies have applied these technologies to EDCs removal at WWTPs. The two types of activated carbon that are frequently used are powdered and granulated activated carbon (PAC and GAC). Investigations conducted in a full scale WWTP in Switzerland where 19 micro contaminants were monitored before and after adding PAC in a WWTP showed that at least 80% of each micro contaminant was removed by the PAC at a dose of 15 g PAC/m^3. Dissolved organic carbon (DOC) was also reduced by about 45%. It was also proved that the performance of PAC in eliminating micro-contaminants depended on the PAC dose, contact time,

the molecular structure and behaviour of the targeted compound as well as the water/wastewater composition (Boehler et al., 2012).

Grover et al. (2011) studied the effect of installing a GAC unit at the effluent stream of a WWTP in Swindon (UK) where three representative EDCs and five detected pharmaceutically active compounds (PhACs) were monitored. Two EDCs were below detection limit after the GAC unit and 64% of the third one was removed. Concentrations of PhACs were also substantially reduced in post-GAC effluents. On average, the additional removal of PhACs by GAC was between 17% for propranolol and >98% for indomethacin.

A3.2 Ozonation

Ozone is a powerful but selective oxidant. During ozonation molecular ozone and hydroxyl radicals to some extent may transform EDCs and PPCPs (Yoon et al., 2002). The effects of ozonation after biological treatment for micro contaminant removal have been widely studied. The removal efficiency for 220 micro pollutants was studied at a full-the scale WWTP upgraded with post-ozonation in Switzerland. The results revealed that of the 55 micro contaminants identified after the secondary clarifier, only 11 were detected after ozonation using a moderate dose of 0.62 gO_3/gDOC (Hollender et al., 2009). Other investigators at different WWTPs demonstrated that the number of micro contaminants with a concentration above 100 ng/l was reduced from 52 compounds in the effluent of the biologically treated wastewater to 30 compounds after the ozonation with an average ozone dose (Margot et al., 2 Investigations conducted in a WWTP in Tokyo monitored 24 PhAcs and found that the combination of ozonation and sand filtration with activated sludge treatment led to an efficient removal (>80%) of most of the target compounds mainly due to the ozonation step.

One of the main problems with ozonation is the generation of undesired by-products. Hollender et al. (2009) studied the generation of bromate when bromide-containing wastewater was ozonated using the highest dose of ozone tested (1.4 gO_3/gDOC). Due to the formation of reactive transformation products during the process, it was recommended to install a stage with biological activity (e.g. sand filter) after ozonation of the wastewater so that the by-products could be fully biodegraded. Biological sand filtration proved to be an economically affordable complement to ozonation that removed both biologically degradable by-products and suspended solids (Hollender et al., 2009; Margot et al., 2013).

A3.3 Membrane Technologies

Membrane filtration technologies such as ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO) are an alternative treatment method for removal of EDCs from wastewater (Yoon et al., 2006). Where RO was implemented as a treatment method complete removal of EDCs was achieved. However the higher energy consumption is an important drawback to be considered.

Khan et al. (2004) investigated the effectiveness of MF in the removal of some commonly prescribed PhACs as well as natural and synthetic hormones found in municipal wastewater using an advanced water recycling demonstration plant. The study found that the partial reduction in concentration for

all target compounds could have been attributable to adsorption on the membrane rather than removal by size exclusion. The great concern from the study was that the adsorption capacity of the membrane for a particular compound would reach saturation and therefore the compounds would be desorbed from the membrane when the concentration in the influent becomes lower. Other studies reported that the incorporation of UF after a conventional activated sludge process increased the removal of antibiotics (including sulfamethoxazole) by up to 30% probably due to the activity of the biofilm formed on the membrane surface that incidentally makes the bio-membrane a tighter physical and chemical barrier. Despite all that, EDCs are generally inadequately removed during treatment by MF and UF because the membrane pore sizes are much larger than the molecular sizes of micro contaminants (Sahar et al., 2011).

Some studies have shown that membrane bioreactors (MBRs) could remove more than 80% of organic potential EDCs from wastewater (Wintgens et al., 2002).

A3.4 Advanced Oxidation Processes (AOPs)

Combinations such as UV plus hydrogen peroxide (H_2O_2), ozone plus H_2O_2 and UV plus ozone are powerful oxidation processes that effectively oxidize contaminants. These combinations are designed specifically to increase the concentration of hydroxyl radicals formed since hydroxyl radicals have less selectivity as oxidants. Substances that are difficult to biodegrade and not removed are oxidized and the oxidized by-products may be more amenable to biodegradation. Depending on the situation AOPs can be followed by a biological process to further degrade the by-products or natural purification processes may be relied upon for treatment (Ried and Mielcke, 2003). A number of pilot studies have been conducted where WWTP secondary effluent was treated using UV /H_2O_2. The findings showed that 90% removal efficiency was achieved for 39 of the 42 PhACs found in the secondary effluent. The UV dose (254 nm) was 923 mJ/cm^2 and the contact time and H_2O_2 concentration were 5 min and 7.8 mg/l respectively (Kim et al., 2009). A study of degradation of steroids, PhACs, pesticides and industrial chemicals by ozonation at pilot scale concluded that the addition of H_2O_2 caused little benefit and in some cases even decreased the efficiency of O_3. The main disadvantages of AOPs are their high chemical requirement and energy consumption which translate into high operating costs. The use of H_2O_2 also has significant limitations, for example the additional costs and complexities associated with chemical storage, handling, and injection.

A3.5 Hybrid Systems

Hybrid wastewater treatment methods are efficient in removing EDCs from wastewater. However, these processes are part of emerging technologies and are not commonly applied for conventional wastewater treatment in many countries. However, the increased focus on limiting EDCs discharged into the environment from WWTPs will also increase interest in incorporating hybrid technologies into

conventional WWTPs in future. Studies have shown that EDCs removal efficiency in hybrid systems follows the following trend:

- hybrid MBR with reverse osmosis or nanofiltration or ultrafiltration > flocculation-activated sludge-ultrafiltration > constructed wetland (Ahmed et al., 2017).

EDCs removal efficiencies achieved by some hybrid processes from various studies are given in Table A3.

Table A3: EDCs Removal Efficiency achieved by Hybrid Systems (Ahmed et al., 2017)

Category	ECs	Treatment process	ECs source	Influent ($\mu g\,L^{-1}$)	Removal (%)
EDCs	E1	MBR + UF	Synthetic WW	5	99.4
		MBR + RO	Synthetic WW	5	99.6
		Flocculants + AS + UF	WW	0.025	96.0
		MBR + NF	Synthetic WW	5	99.3
	E2	MBR + UF	Synthetic WW	5	99.5
		MBR + RO	Synthetic WW	5	99.4
		Flocculants + AS + UF	WW	0.014	96.5
		MBR + NF	Synthetic WW	5	99.6
	EE2	MBR + UF	Synthetic WW	5	95.5
		MBR + NF	Synthetic WW	5	94.0
		MBR + RO	Synthetic WW	5	93.61
		Flocculants + AS + UF	WW	0.041	95.0
	E3	MBR + NF	Synthetic WW	5	97.7
		MBR + RO	Synthetic WW	5	96.1
		MBR + UF	Synthetic WW	5	98.3
	17β-estradiol-17-acetate	MBR + UF	Synthetic WW	5	99.0
		MBR + NF	Synthetic WW	5	99.3
		MBR + RO	Synthetic WW	5	100
	Bisphenol A	Flocculants + AS + UF	WW	0.857	95.0
		MBR + UF	Synthetic WW	5	98.6
		MBR + NF	Synthetic WW	5	89.3
		MBR + RO	Synthetic WW	5	90.5
		VFCWs + HFCWs + FWCWs	Urban WW	4.06	99.0
	4-*n*-nonylphenol	MBR + UF	Synthetic WW	5	96.9
		MBR + NF	Synthetic WW	5	96.6
		MBR + RO	Synthetic WW	5	100
		Flocculants + AS + UF	WW	14.635	97.0
	4-*tert*-butylphenol	MBR + UF	Synthetic WW	5	95.5
		MBR + UF	Synthetic WW	5	98.2
		MBR + NF	Synthetic WW	5	91.0
		MBR + NF	Synthetic WW	5	95.7
		MBR + RO	Synthetic WW	5	83.5
		MBR + RO	Synthetic WW	5	93.8
		Flocculants + AS + UF	WW	4.385	98.0

A4 Practical Performance of Technologies used for the Removal EDCs in Liquid Wastewater

A4.1 Ozone Oxidation and Ultrafiltration

As discussed above a lot of research has explored several treatment methods for removing EDCs from wastewaters. Among these technologies UF and ozonation exhibited advantages in practical reclaimed water projects for EDC removal (Si et al., 2018). However the EDC removal rate in UF on its own is limited by the large membrane pore size in relation to EDCs (Jin et al., 2013). Ozone can rapidly reduce EDC concentrations but might generate harmful brominated by-products which are harmful to the human body and ecological environment (Hollender et al. 2009). The combined process is a promising method for EDC removal. UF can retain EDCs to reduce ozone dosage and cost and also reject hazardous brominated by-products to ensure the biological safety of reclaimed water. Si et al. (2018) investigated the removal efficiency of EDCs from WWTP secondary effluent using the combined

ozonation and UF process. The 5 selected EDCs for the study were E1, E2, E3, EE2 and BPA. Concentrations for the different EDCs from the secondary effluent are given in Table A4.

Table A4: EDC Concentrations from the Secondary Effluent (Si et al., 2018)

Sample Name	Unit	Amount
TOC	mg/L	6.47
Conductivity	µs/cm	1001
pH	mg/L	7.8
E1	ng/L	42.04
E2	ng/L	157.73
E3	ng/L	2.67
EE2	ng/L	138.34
BPA	ng/L	34.85

An O_3/UF process configuration shown in Figure A1 was utilised to investigate the removal efficiency of EDCs. The secondary effluent reacted with O_3 inside the reaction tank. After the reaction was completed the effluent was placed inside the feed tank then filtered into the UF cup by a peristaltic pump.

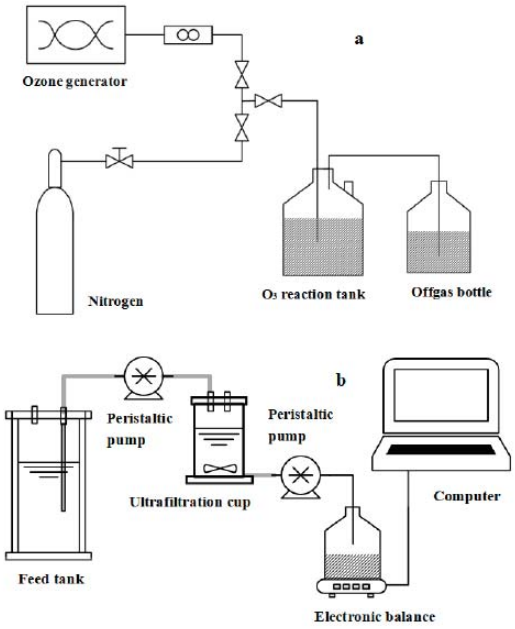


Figure A1: Schematic diagram of (a) ozone and (b) ultrafiltration unit (Adapted from Sil et al., 2018)

The EDCs removal efficiency, estrogenicity and acute eco-toxicity were greater than that of the O_3 or UF alone. When EDCs were treated by the combination of O_3 and UF about 100% EDC removal efficiency was achieved. Moreover, O_3 oxidation alleviated UF membrane fouling. Overall, the combined application of O_3 and UF offers an effective approach to control the concentration and eco-toxicity of EDCs in secondary effluent.

A4.2 Membrane Bioreactor/Reverse Osmosis/Nanofiltration

Removal of EDCs from a WWTP designed for possible agricultural, recreational and potable water reuse of wastewater effluents was evaluated using a plant consisting of several pilot-scale treatment processes (Wintgens et al., 2002). The pilot plants had a flow capacity of 1 m^3/day and included a MBR followed by RO and NF. The MBR system consisted of an activated sludge tank followed by plate and frame type membrane modules and a hollow-fiber membrane module. RO and NF were evaluated using spiral-wound membranes. Samples were collected before and after each unit process, extracted using solid phase extraction and analyzed by LC-MS/MS.

Table A5 gives the concentrations of EDCs found in the influent prior to treatment and from the different treatment units after treatment. The MBR system was efficient in removing hormones (estriol, testosterone, androstenedione) and certain pharmaceuticals (acetaminophen, ibuprofen, and caffeine) with approximately 99% removal. Between the two MBR modules used in this study (plate and frame versus hollow-fiber), no difference in target compound removal was found. RO and NF membrane processes showed excellent removal rates (95%) for all compounds.

Table A5: Removal of different EDCs in Wastewater using MBR, NF and RO Membrane Technologies (Wintgens et al., 2002)

Compound	Class	Influent (ng/L)	MBR (P) (ng/L)	MBR (K) (ng/L)	NF (ng/L)	RO (ng/L)
Androstenedione	Hormone	140	<10	<10	<1	<1
Estriol	Hormone	318	<10	<10	<5	<5
Testosterone	Hormone	60	<10	<10	<1	<1
Acetaminophen	Pharmaceutical	11500	<11	21	<1	<1
Trimethoprim	Pharmaceutical	21	31	28	<1	<1
Naproxen	Pharmaceutical	262	168	154	<1	<1
Ibuprofen	Pharmaceutical	5320	52	90	<1	<1
Diclofenac	Pharmaceutical	10	25	22	<1	<1
Carbamazepine	Pharmaceutical	42	46	44	<1	<1
Caffeine	Pharmaceutical	9680	<100	104	<10	<10
Erythromycin	Pharmaceutical	44	40	42	<1	<1
Sulfamethoxazole	Pharmaceutical	194	70	58	<1	<1

A4.3 Ozonation and Activated Carbon Adsorption

Margot et al. (2013) conducted a study at a municipal WWTP in Switzerland that treats domestic wastewater as well as effluent from a major hospital and several clinics. The treatment process consists of primary clarifiers, biological activated sludge without nitrification and a moving bed biofilm bioreactor (MBBR) with partial to complete nitrification. Two pilot scale advanced treatment technologies namely (i) oxidation by ozonation followed by sand filtration (SF) and (ii) PAC adsorption followed by UF membranes were tested in parallel. The pilot plant for ozonation was designed to treat a maximum flow of 100 l/s and consisted of a plug flow reactor separated into four chambers (nine compartments) in series to ensure optimal hydraulic conditions and a minimal reaction time of 20 minutes (Figure A2). Ozone-containing gas was fed with pure oxygen. 60% of the gas was injected counter currently into the 1st or 2nd chamber depending on the water flow rate and 40% in the 3rd

chamber. The reaction time in the reactor ranged between 20 and 60 minutes. The ozone dosage was automatically adjusted to the water quality by varying the gas flow to maintain a constant residual concentration of dissolved ozone (around 0.1 mgO_3/l). The transfer efficiency of ozone into the dissolved phase was from 70 to over 90% depending on the gas flow. The effluent from the ozone reactor was then filtered through a rapid sand filter with biological activity to remove reactive oxidation products.

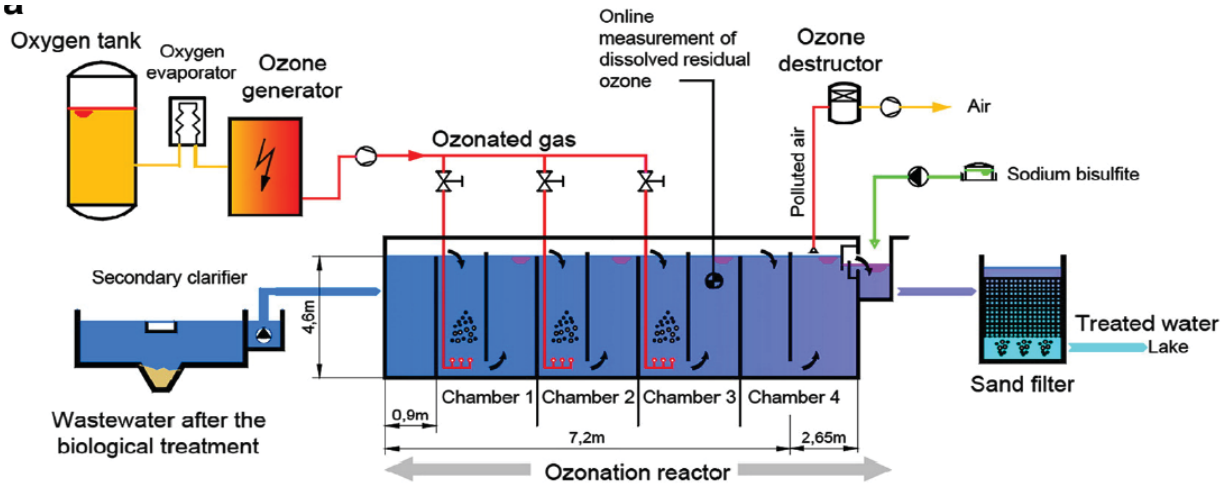


Figure A2: Ozonation followed by Sand Filtration Pilot Plant (Margot and Magnet, 2013)

The PAC pilot plant was designed to treat WWTP effluent at a flow of 10-15 l/s. Two PACs brands were selected for the pilot study investigations and used separately during the first and second half of the study followed by UF. The installation was composed of a well-mixed contact reactor (volume 30 m^3) where PAC slurry was added continuously in proportion to the wastewater flow to reach a final dosage of 10 to 20 mg PAC/l. A $FeCl_3$ coagulant was added to improve the subsequent separation of the PAC from the liquid. Treated water was then filtrated through the UF membranes to remove the PAC.

Figure A3 shows the PAC installation with UF separation.

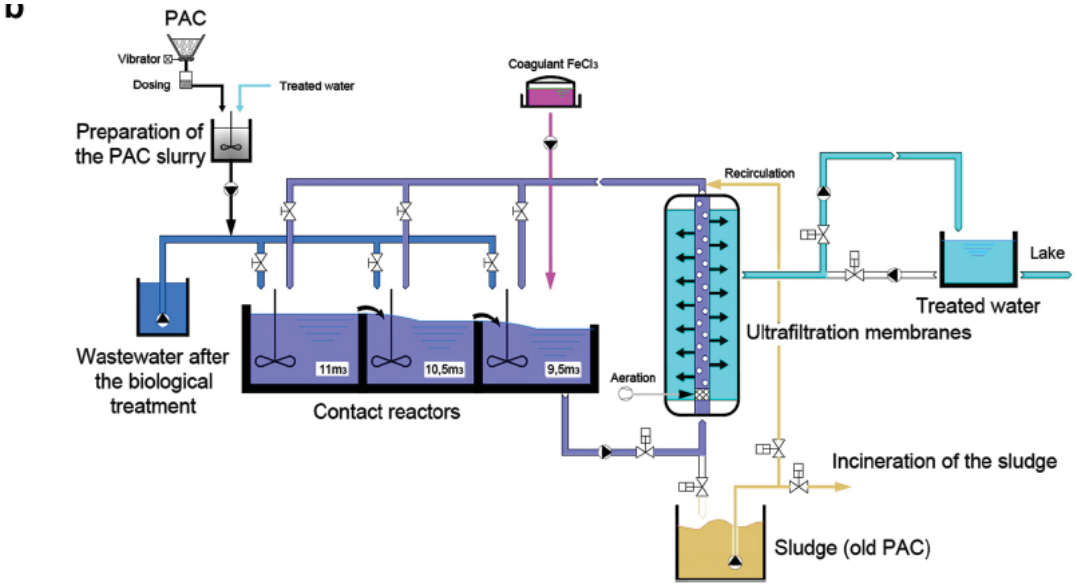


Figure A3: PAC with Ultrafiltration Pilot Plant (Margot and Magnet, 2013)

The findings of the study conducted by Margot et al. (2013) showed that from the 70 dissolved organic micro pollutants detected in untreated wastewater, 50 of them had on average removal rates less than 50% in conventional treatment. Addition of a nitrification step significantly improved the removal of 24 substances. Both advanced treatments (ozonation-SF and PAC-UF) reduced the concentration of the remaining compounds by an average of more than 70% at an average ozone dose of 5.65 mg O_3/l or an average PAC dose of 13 mg/l. Ozone was more effective and almost completely removed certain compounds. PAC acted better on a broad spectrum of micro-pollutants. Both advanced treatment technologies significantly reduced the toxicity of WWTP effluent with PAC-UF performing slightly better overall. Both treatments proved to be feasible at large scale and for long term operation in real WWTP conditions.

A summary of the results from the pilot study is given in Table A6.

Table A6: Concentrations of 70 micro-pollutants in wastewater influent, final effluent and removal efficiencies from Conventional WWTP, Ozonation and Powdered Activated Carbon-Ultrafiltration Systems (Adapted from Margot et al., 2013)

Compound	Compound class	LOD ($ng\ l^{-1}$)	Analytical method	Number of analysis (n)	Influent concentration ($ng\ l^{-1}$)	(n)	Effluent concentration ($ng\ l^{-1}$)	(n)	WWTP removal (%)	(n)	Ozone removal (%)	(n)	PAC-UF removal (%)
Pharmaceuticals													
Atenolol	Beta blocker	1.2	A	37	1274 (±436)	37	682 (±267)	37	42 (±27)	28	85 (±14)[a]	21	88 (±9)[e]
Azithromycin	Antibiotic	75.6	A	19	2272 (±1472)	19	935 (±333)	19	44 (±26)	12	74 (±10)[d]	8	76 (±8)[c]
Bezafibrate	Lipid regulator	1.5	A	37	953 (±262)	37	595 (±314)	37	38 (±26)	27	81 (±8)[a]	21	79 (±12)[e]
Carbamazepine	Anticonvulsant	0.1	A	37	482 (±586)	37	461 (±292)	37	7.6 (±18)	28	97 (±4)[a]	21	90 (±9)[e]
Ciprofloxacin	Antibiotic	36.5	A	19	2291 (±600)	19	779 (±372)	19	63 (±18)	12	53 (±29)[b8]	8	63 (±32)[f]
Clarithromycin	Antibiotic	0.4	A	37	709 (±418)	37	440 (±302)	37	37 (±26)	28	93 (±4)[a]	21	92 (±5)[e]
Clindamycin	Antibiotic	0.2	A	19	65 (±33)	19	115 (±69)	19	0 (±0)	12	99 (±1)[a]	8	82 (±13)[c]
Diatrizoic and iothalamic acid	Iodinated contrast medium	32.8	A	17	597 (±628)	19	370 (±366)	17	28 (±25)	12	16 (±16)[b2]	8	15 (±13)[e]
Diclofenac	Analgesic/anti-inflammatory	1.2	A	37	1197 (±497)	37	1187 (±389)	37	9 (±14)	28	94 (±3)[a]	21	69 (±19)[e]
Eprosartan	Antihypertensive	20	B	2	1055 (±488)	1	880	1	37	1	98[c]	1	65[c]
Fluconazole	Antifungal	20	B	2	120 (±14)	1	110	1	15	1	27[d]	1	>64[c]
Gabapentin	Anticonvulsant	1.8	A	37	3867 (±1339)	37	3692 (±1456)	37	9.2 (±12)	28	38 (±16)[b5]	21	11.8 (±11)[f]
Gemfibrozil	Lipid regulator	2.9	A	19	411 (±128)	19	265 (±159)	19	36 (±32)	12	94 (±5)[b11]	8	76 (±16)[d]
Ibuprofen	Analgesic/anti-inflammatory	13.4	A	19	4101 (±2465)	19	952 (±759)	19	57 (±46)	11	63 (±12)[b11]	6	83 (±7)[e]
Iohexol	Iodinated contrast medium	2177.3	A	35	21,275 (±6975)	34	15,191 (±7294)	32	31 (±27)	26	38 (±16)[a]	19	57 (±25)[e]
Iomeprol	Iodinated contrast medium	306.9	A	35	14,467 (±9657)	35	10,534 (±6338)	35	25 (±24)	28	43 (±12)[b2]	20	54 (±21)[c]
Iopamidol	Iodinated contrast medium	145.4	A	30	3360 (±2574)	30	2535 (±1587)	30	21 (±20)	24	42 (±13)[a]	16	49 (±21)[e]
Iopromide	Iodinated contrast medium	2044.6	A	22	6408 (±2663)	23	4141 (±2086)	21	29 (±27)	15	34 (±19)[a]	11	47 (±30)[c]
Irbesartan	Antihypertensive	20	B	2	4700 (±4808)	1	1700	1	79	1	51[b7]	1	98[c]
Ketoprofen	Analgesic/anti-inflammatory	6.0	A	19	1119 (±1328)	19	669 (±757)	19	32 (±21)	12	63 (±16)[a]	8	81 (±9)[c]
Levetiracetam	Anticonvulsant	10	B	2	2100 (±566)	1	330	1	87	1	18[a]	1	>97[c]
Losartan	Antihypertensive	20	B	2	2405 (±2256)	1	510	1	87	1	>96b7	1	80[c]
Mefenamic acid	Analgesic/anti-inflammatory	2.6	A	19	946 (±455)	19	581 (±299)	19	33 (±29)	12	98 (±2)[a]	8	93 (±2)[e]
Metformin	Antidiabetic	<1000	B	2	>10,000	1	>4000	1	–	0	–	1	>55[c]
Metoprolol	Beta blocker	4.4	A	19	561 (±299)	19	653 (±400)	19	4.6 (±13)	12	88 (±8)[a]	8	95 (±4)[f]
Metronidazole	Antibiotic	21.0	A	19	1168 (±866)	19	567 (±497)	19	45 (±34)	12	64 (±12)[b6]	5	79 (±17)[c]
Morphine	Analgesic/anti-inflammatory	20	B	1	270	1	190	1	30	1	>90[c]	1	>90[c]
Naproxen	Analgesic/anti-inflammatory	9.4	A	37	697 (±249)	37	380 (±110)	37	41 (±23)	28	90 (±8)[a]	21	81 (±12)[e]
Norfloxacin	Antibiotic	1.9	A	19	334 (±167)	19	59 (±35)	19	76 (±19)	12	75 (±29)[b9]	8	82 (±21)[c]
Ofloxacin	Antibiotic	0.4	A	19	234 (±60)	19	84 (±36)	19	61 (±17)	12	85 (±20)[c]	8	83 (±24)[c]
Oxazepam	Anxiolytic	20	B	2	305 (±134)	1	350	1	13	1	9[d]	1	69[c]
Paracetamol	Analgesic/anti-inflammatory	7.9	A	18	51,438 (±31,884)	18	<7.9	19	100 (±0)	1	>85[b11]	0	–
Primidone	Anticonvulsant	0.7	A	37	114 (±39)	37	97 (±21)	37	16 (±15)	28	57 (±11)[a]	21	51 (±19)[f]
Propranolol	Beta blocker	0.3	A	19	127 (±37)	19	114 (±17)	19	13 (±17)	12	99 (±1)[a]	8	99 (±1)[c]
Ritonavir	Antiretroviral	20	B	2	110 (±14)	1	90	1	25	1	>78[c]	1	>56[c]
Simvastatin	Lipid regulator	29.7	A	14	736 (±503)	14	98 (±96) 14	14	77 (±23)	8	>70[c]	4	>65[c]
Sotalol	Beta blocker	0.5	A	37	337 (±175)	37	247 (±63)	37	23 (±20)	28	99 (±1)[a]	21	81 (±15)[c]
Sulfamethoxazole	Antibiotic	0.2	A	37	340 (±261)	37	171 (±127)	37	38 (±30)	25	93 (±7)[a]	20	64 (±25)[e]
Trimethoprim	Antibiotic	0.2	A	37	235 (±52)	37	158 (±73)	37	35 (±23)	28	99 (±2)[a]	21	94 (±4)[f]
Valsartan	Antihypertensive	5	B	2	2250 (±354)	1	2100	1	16	1	61[b7]	1	65[c]
Venlafaxine	Antidepressant	10	B	2	235 (±21)	1	150	1	40	1	75[d]	1	46[d]

APPENDIX B: DIURNAL VARIATION OF EDCS CONCENTRATION IN THE LIQUID TREATMENT PROCESS AT DASPOORT WWTP

Hourly and composite samples were collected on the influent and effluent of Module 1 (trickling filters) and Module 2 (BNR ASP) The EDC analysis results for the hourly samples are given in Table B1 and the composite sample analysis results are given in Table B3. Graphical representations of the hourly variation of the influent and effluent samples are given in Figures B1 and B2.

Table B1: Daspoort WWTP Diurnal Influent and Effluent EDCs Concentration

Time	Module 1 (µg/l)		Module 2 (µg/l)	
	Raw Influent	Trickling Filter Effluent	Raw Influent	BNR Effluent
Acetaminophen				
6:00	5.85	6.77	10.15	16.16
7:00	34.71	0.00	0.00	6.26
8:00	3.49	32.78	7.32	0.00
9:00	5.11	4.18	0.00	0.00
10:00	0.00	0.00	36.01	30.00
11:00	13.55	0.00	1.19	1.33
12:00	0.00	7.74	4.88	9.98
13:00	44.73	12.72	1.25	0.27
14:00	0.00	5.17	0.00	6.27
15:00	0.00	20.61	0.00	0.46
16:00	5.05	41.10	0.00	2.01
17:00	38.97	2.81		35.95
18:00	25.28	0.00		
Bezafibrate				
6:00	0.00	3.80	17.78	26.31
7:00	0.00	0.00	nd	0.77
8:00	0.00	0.00	9.89	20.24
9:00	0.00	0.00	35.34	22.19
10:00	0.94	0.00	nd	nd
11:00	0.00	0.00	4.00	8.19
12:00	0.00	1.15	30.07	30.17
13:00	0.00	0.00	0.71	16.61
14:00	0.00	0.00	nd	0.63
15:00	1.15	0.00	nd	nd
16:00	0.00	0.00	28.89	0.85
17:00	3.90	0.00	nd	9.23
18:00	0.00	6.90		0.05
Carbamazepine				
6:00	164.08	1.27	0.35	8.23
7:00	159.70	8.79	0.00	3.37
8:00	153.81	12.48	21.04	23.38
9:00	165.59	6.83	0.59	4.04
10:00	200.55	30.40	0.00	10.35
11:00	155.71	0.86	4.78	0.00
12:00	132.41	27.60	0.00	7.05
13:00	170.29	36.28	1.25	0.34
14:00	183.51	37.00	13.43	2.94
15:00	188.17	16.40	0.05	10.90
16:00	170.63	15.95	0.59	6.12
17:00	206.87	34.72	22.18	0.00
18:00	169.60	2.56		3.91
Oestrone				
6:00	26.89	0.00	0.99	nd
7:00	4.18	0.00	31.19	0.431
8:00	24.35	0.00	0.33	15.966
9:00	6.42	0.00	0.01	37.891

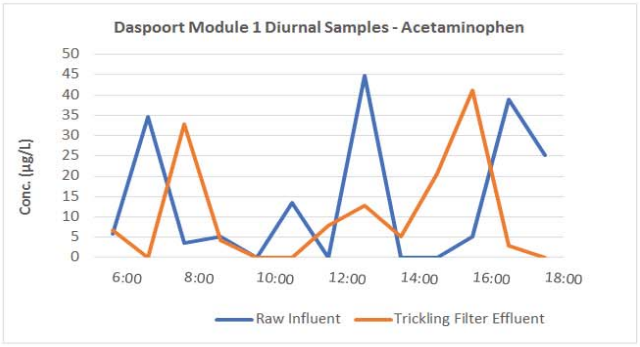
Time	Module 1 (µg/l)		Module 2 (µg/l)	
	Raw Influent	Trickling Filter Effluent	Raw Influent	BNR Effluent
10:00	36.45	3.33	33.04	8.86
11:00	4.08	6.56	9.92	41.0755
12:00	9.73	9.65	nd	1.009
13:00	28.50	31.22	27.87	0.203
14:00	0.57	3.92	3.44	38.9065
15:00	32.68	32.78	30.00	0.447
16:00	17.94	36.97	0.00	30.105
17:00	44.29	1.40	nd	5.5235
18:00	17.43	7.36		1.9495
PFOA				
6:00	115.71	24.50	56.14	7.7655
7:00	112.36	7.89	26.85	1.536
8:00	108.53	12.94	111.21	21.533
9:00	211.13	19.50	38.55	1.746
10:00	127.75	22.94	10.83	10.2935
11:00	208.87	29.94	10.12	29.4615
12:00	44.05	39.15	28.43	5.3565
13:00	35.06	24.40	5.01	21.9815
14:00	21.24	34.65	32.13	0.389
15:00	20.44	55.32	26.10	18.5515
16:00	14.65	25.48	102.81	34.3865
17:00	24.29	13.21	38.85	2.9235
18:00	16.58	29.01	47.94	6.355

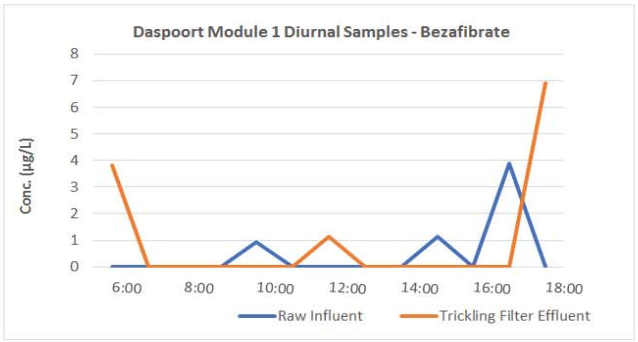
Table B-2: Raw Influent and Effluent EDC Concentrations for Daspoort WWTP

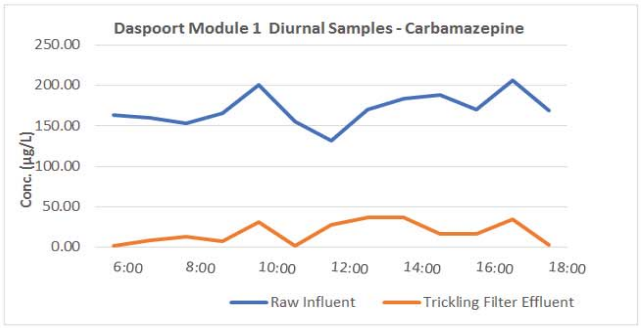
EDC	Module 1 (Trickling Filter) (µg/l)			Module 2 (BNR ASP) (µg/l)		
	Raw Influent	Effluent	% Reduction	Raw Influent	Effluent	% Reduction
Acetaminophen	13.59	10.30	24	5.07	8.36	-65
Bezafibrate	0.46	0.91	-98	18.10	12.30	32
Carbamazepine	170.84	17.78	90	5.36	6.20	-16
E1	19.50	10.24	47	13.68	15.20	-11
PFOA	81.59	26.07	68	41.15	12.48	70

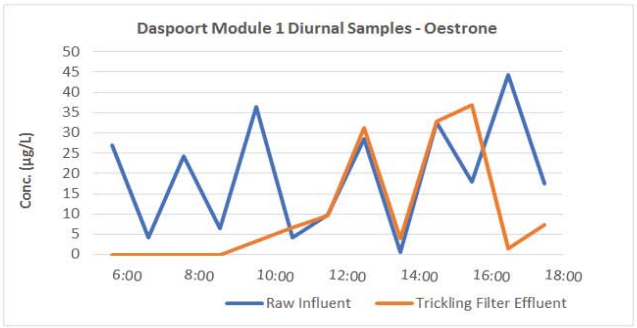
The following is noted from both the hourly and composite sample analysis results:

- Module 1 (trickling filters) reduces all EDC by 24-90% apart from bezafibrate. Removal of carbamazepine is highest at 90%
- Module 2 (BNR activated sludge) reduces only bezafibrate and PFOA by 32% and 70% respectively
- The hourly variation indicates peak influent concentrations between 7-8 am, 10-12 pm and 2-4 pm for some EDCs (e.g. acetaminophen, carbamazepine and PFOA). No clear peak concentrations are indicated for bezafibrate and E1.









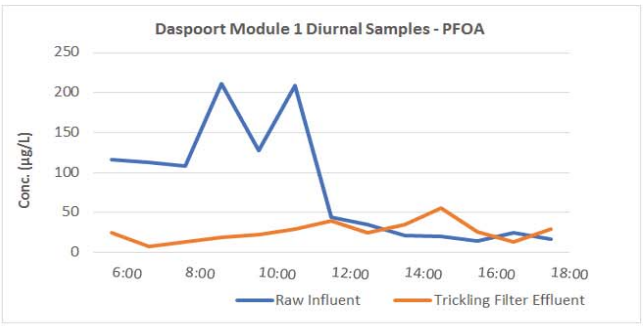
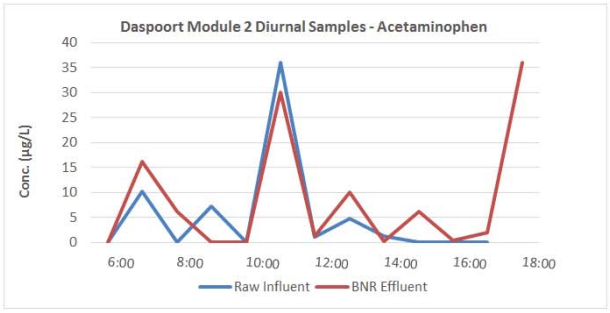
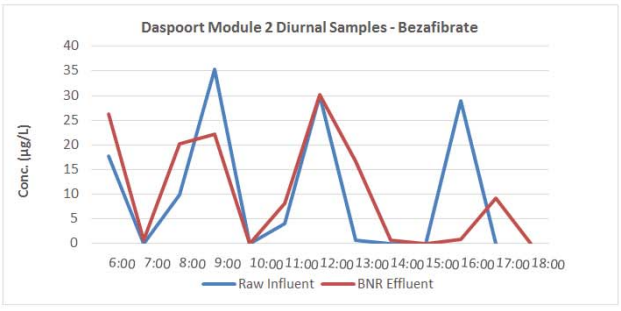
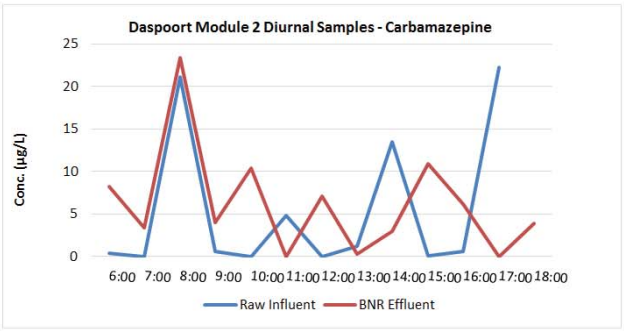
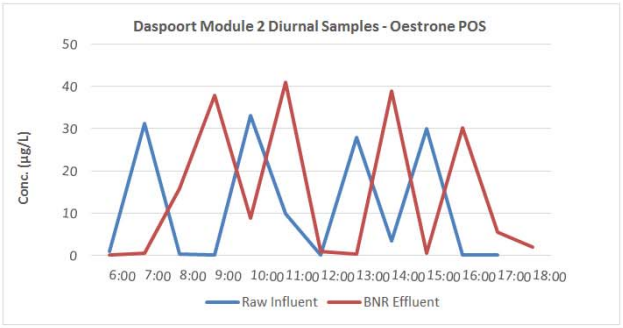


Figure B1: Daspoort WWTP Raw Influent and Trickling Filter Effluent Hourly EDC Concentration









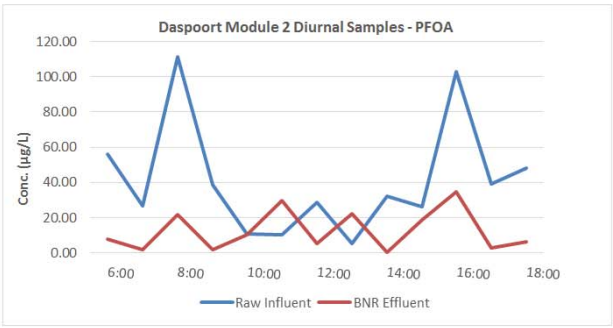


Figure B2: Daspoort WWTP Raw Influent and BNR Activated Sludge Effluent Hourly EDC Concentration