UNIVERSITEIT VAN PRETORIA
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Assessment on the occurrence and removal of Triclosan and Triclocarban from a wastewater treatment plant and their potential ecological risks

Submitted in fulfilment of the requirements for the degree

Master of Engineering

Department of Chemical Engineering

in the

Faculty of Engineering, Built Environment, and Information Technology

at the

University of Pretoria

by

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April 2022

DECLARATION

I, Blessing Sanele Mazibuko, declare that this thesis, which I hereby submit for the degree of Master of Engineering in the Department of Chemical Engineering, Faculty of Engineering, Built Environment, and Information Technology, University of Pretoria, is my own original work with guidance from the supervisors. In addition, I acknowledged and referenced all the sources used.

Signature:

ACKNOWLEDGEMENTS

I would like to express my gratitude to the following people and institutions for their support in fulfilling this work:

- Prof. Ndeke Musee and Dr. Lakesh Maharaj for their supervision and guidance throughout this research. I am grateful for all the knowledge, values, guidance and principles instilled in me during this journey.
- The Water Research Commission (WRC) of South Africa is thanked for funding and supporting this project.
- The University of KwaZulu Natal, Department of Chemistry and Physics for allowing me the use of their state of the art equipment for the analysis of wastewater samples. I would like to thank Dr. Bhekumuzi Gumbi for method development, guidance and expertise in GC-MS analysis.
- Umgeni Water for allowing me unlimited access to the Darvill WWTP to take samples at various stages of the process.
- My friends and colleagues for their assistance during market surveys to collect and verify products for inventory development, and
- My family for all their love and support throughout this journey.

SUMMARY

Increasing use of triclosan (TCS) and triclocarban (TCC) from pharmaceutical and personal care products (PPCPs), personal care products (PCPs), and other industrial applications have resulted in their continuous release into the environment. This is due to their incomplete removal in treated wastewater, and from non–diffuse sources e.g., runoffs. In addition, industrial effluents also release other forms of pollutants into wastewater treatment plants (WWTPs) that are not readily biodegradable in conventional biological treatment plants. In this study, the occurrence and removal of TCS, TCC and other contaminants in the WWTP from domestic and industrial influent (Darvill WWTP, Pietermaritzburg, South Africa) were investigated. The target compounds TCS and TCC were quantitatively analysed using gas chromatography–mass spectrometry (GC–MS), and yielded the measured environmental concentrations (MECs). Conversely, other forms of pollutants were qualitatively assessed using GC–MS in selected ion monitoring (SIM) mode. Both target compounds were detected in the influent and effluent, and, at across different process units. Moreover, using the sales data for the major product sources of TCS and TCC feeding the Darvill WWTP, predicted environmental concentrations (PEC) of the target compounds were determined. Risk quotients (RQs) were calculated to predict the likely risks of both chemicals in the wastewater, freshwater, and soil environmental matrixes.

The MECs obtained for TCS were in the µg/L range, and the highest in the influent in the ranges of 1.02– 3.4 µg/L; whereas in the final effluent (after chlorination) detected values were <LOD–1.1 µg/L. Lower concentrations of TCC levels of two- to three-folds were measured as 0.45–1.1 µg/L and LOD–0.58 µg/L in the effluent (before chlorination) and final effluent (after chlorination), respectively. And, the concentrations showed variability across different treatment processes. The overall removal efficiency was 59% and 45% for TCS and TCC, respectively. Generally, TCS concentrations were higher than TCC concentrations from all treatment units assessed. Other pollutants detected in the influent and effluent were diisoprophylnaphthalenes (DIPNs), 2–Heptyl–4–phenyl–1,3–dioxolane, and polychlorinated biphenyls (PCBs) – hence providing evidence of industrial influent into the Darvill WWTP as these chemicals are mostly used in industrial processes.

Four transformation products (TPs) of TCS and TCC were detected, namely; methyl triclosan (MeTCS), 2,4–dichlorophenol (2,4–DCP), non–chloro carbanilide (NCC), and 4–

chloroanaline (4–CA). 2,4–DCP and NCC were detected in all samples analysed at concentration ranges of 0.26–0.4 µg/L and 1.13–2.02 µg/L, respectively. However, MeTCS and 4–CA were not detected above limit of detection in all samples analysed. The formation of TPs, however, was not exclusively due to the TCS and TCC biodegradation along the WWTP alone. This is because both 2,4–DCP and NCC were successfully detected in the influent stream.

The modelled PECs were in good agreement with MECs with average PEC/MEC ratios of 1 and 3 for TCS and TCC, respectively. Hence, indicative of reliability of using PECs as a practical approach to quantify the concentrations of contaminants from household products in the aquatic environment. TCS and TCC RQs for microorganisms were > 1 and < 1, respectively, suggesting possible negative impact of the former to the performance of biological wastewater treatment plants. Results of TCS and TCC showed potential risks to freshwater species irrespective of the tropic level of focus (algae, crustacean, and fish) with RQs obtained exceeding 1. RQ results in terrestrial system were all < 1, indicating low or no risks. All these results taken together, calls for the protection of the freshwater systems by banning incorporation of TCS in products as has been done in other jurisdictions including the USA, European Union, and Canada.

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LIST OF ABBREVIATIONS

ADWF	Average Dry Weather Flow
AOP	Advanced Oxidation Process
BNR	Biological Nutrient Removal
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DM	District Municipality
DO	Dissolved Oxygen
EC	Emerging Contaminant
EU	European Union
GAC	Granular Activated Carbon
GC – MS	Gas Chromatography –Mass Spectrometry
LC – MS	Liquid Chromatography –Mass Spectrometry
LM	Local Municipality
LOD	Limit of Detection
LOQ	Limit of Quantification
MEC	Measured Environmental Concentration
MFA	Material Flow Analysis
MLSS	Mixed Liquor Suspended Solids
PAC	Powdered Activated Carbon
PCP	Personal Care Product
PEC	Predicted Environmental Concentration
PPCP	Pharmaceutical and Personal Care Products
RQ	Risk Quotient
SA	South Africa
SPE	Solid Phase Extraction
TCC	Triclocarban
TCS	Triclosan
TP	Transformation Product
TSS	Total Suspended Solids
UF	Ultra Filtration
USA	United States of America

UV	Ultraviolet
WHO	World Health Organisation
WTP	Water Treatment Plant
WWTP	Wastewater Treatment Plant

CHAPTER 1:

INTRODUCTION

1.1. BACKGROUND

The 2030 Agenda for Sustainable Development (SDs) recognizes safe drinking water and sanitation as basic human right[s], and chiefly to ensure availability and sustainable management of water and sanitation for all by 2030 (UN, 2019). According to the World Economic Forum's Annual Global Risks Report (WEF, 2019), in the previous two years water crisis was ranked as fourth and fifth, respectively, with respect to highest likelihood to manifest and highest impact globally in the next decade. This means, tackling both water scarcity and water pollution can result to substantial increase in water availability to the broader society. For example, this is achievable by means of enhanced water use efficiencies across different sectors and improved wastewater treatment effectiveness, among other interventions.

South Africa, a country with economy in transition is severely vulnerable to systemic challenges of rapid increase in water demand owing to dramatically growing population among other key drivers (UN, 2019). Moreover, similar to other countries, water, energy, infrastructure as well as increasing environmental pollution are among constraints that impedes economic growth. As an example, efforts to improve the quality of life through innovation entailing the incorporation of variant chemicals have resulted to deleterious impacts to the environment (e.g., loss of biodiversity at different levels of organization and human health).

The total number of industrial chemicals globally were estimated to some 40 000 to 60 000 by year 2018, with an economic value of (USD) 5.68 trillion; thus, making it the second largest manufacturing industry in the world (UNEP, 2019). The World Health Organization (WHO) estimated some 1.6 million mortalities due to chemicals by 2016 (WHO, 2016); yet they are avoidable through sound chemicals management including their reduction in release into the environment.

Pharmaceutical and personal care products (PPCPs) are a class of products deemed to enhance the quality of life (e.g., pharmaceutical drugs, cosmetics, disinfectants, etc.). However, there is also evidence of PPCPs deleterious impacts to aquatic organisms after use and widespread pollution of water resources (Barbara et al., 2008; Larsson et al., 2007; Sim et al., 2011; Jin et al., 2014; Chen et al., 2021). Among key chemicals of great concern are the triclosan (TCS) (5 –chloro–2–(2,4–dichlorophenoxy) phenol) and triclocarban (TCC) (3,4,4 – trichlorocarbanilide). Both TCS and TCC have been in use since 1950s and 1960s, respectively, largely owing to their unique antimicrobial properties, however, they have also been defined by adverse effects to the environment (Levy, 2002; Yazdankhah et al., 2006; Oggioni et al., 2013; Carey and McNamara, 2015; Carey et al., 2016).

TCS and TCC are polychlorinated, binuclear, and aromatic antimicrobial agents commonly incorporated into personal care products (PCPs) like soaps, detergents, toothpastes, skin care creams, and shampoos (Halden and Paull, 2005; Halden, 2014; Musee, 2018). More than 2 000 PCPs, households, and medical products in the United States were reported to contain TCS and TCC (Young, 2013; Smith, 2013; Halden, 2014). Further, In a recent survey in South Africa for products in retail commerce 128 and 52 products (PCPs, kitchenware, pet care, first aid, and office accessories) were identified to contain TCS and TCC, respectively (Musee, 2018). TCS has a halogenated biphenyl ether chemical structure; hence, exhibits properties similar to those of polybrominated diphenyl ethers, bispenol A, and dioxins – chemicals known with potential to induce endocrine disruption (Dhillon et al., 2015). Conversely, TCC is an endocrine disruptor (Lozano et al., 2013), and bioaccumulates in fish and snails (Klein et al., 2010).

Recently, the use of TCS and TCC have already been limited in the US and EU by introducing a ban in certain product categories (Halden et al., 2017). The European Commission banned the use of TCS in biocidal products for skin, while the United States Food and Drug Administration banned the use of both TCS and TCC in consumer antiseptic washes (EU, 2016; US FDA, 2016). The Florence Statement on Triclosan and Triclocarban also called for a limit in production and use of these chemicals due to their detrimental impact to the environment and human health (Halden et al., 2017). This suggests that comprehensive data is still required to better manage human and ecological risks posed by TCS and TCC. It is in this context, the current study aims to further and make contribution to address knowledge gaps concerning the fate and risks of both chemicals in wastewater and surface waters.

Wastewater treatment plants (WWTPs) play a key role in the circular economy approach e.g., towards increased access to freshwater as a source for water reclamation (Neczaj and Grosser, 2018). However, this in itself also poses herculean challenges as the management of WWTPs, e.g., operated by municipalities in South Africa are deemed to be in a state of distress; thus necessitates considerable improvements and investments (Green Drop, 2014). This is to achieve the goal of meaningful water reclamation and treatment of influent to acceptable standard in compliance to variant legislations, e.g., South African National Standard (SANS) 241:2015. More so, this challenge is exacerbated by dramatic increase on presence of emerging contaminants (ECs) in wastewater including TCS and TCC (Bester, 2004; Corada –Fernández et al., 2015; Musee, 2018). This, in turn, exerts additional concerns to undesirable implications of wastewater effluent to the freshwater resources. Among the adverse impacts includes threat to source of direct potable water, and degradation of ecological habitants for millions of species with numerous benefits to human quality of life (Fraker and Smith, 2004; Orvos et al., 2002; Tatarazako et al., 2003; Yang et al., 2008).

1.2. PROBLEM STATEMENT AND JUSTIFICATION

Release of TCC and TCS to the environment occurs throughout their lifecycle from production to disposal phase. Both compounds are released into the environment through incomplete removal from wastewater treatment plants (WWTPs), run –offs, and wide usage of sludge for agricultural purposes or leachates from landfills (Armstrong et al., 2018; Musee, 2018). Measured environmental concentrations (MECs) of TCS and TCC have been widely reported in different environmental compartments e.g., soil, groundwater, freshwater and sediments (Ying and Kookana, 2007; Cha and Cupples, 2009; Gottschall et al., 2012; Lv et al., 2014; Chen et al., 2019a), and the data has been widely summarized in recent works (Luo et al., 2014; Montaseri and Forbes, 2016; Musee, 2018; Luo et al., 2019).

For example, Lv et al., (2014) detected both TCS and TCC in Jiulong River water in China with concentrations in the range of under method quantification limit to 64 ng/L, and from 0.05 to 14.1 ng/L, respectively. Moreover, TCS concentrations of up to 75 ng/L were detected in surface waters receiving effluent discharge from five WWTPs in Australia (Ying and Kookana, 2007). TCS and TCC have also been detected in soil in Michigan, USA, following land application with biosolids (Cha and Cupples, 2009). In South Africa, TCS and TCC have also been detected in wastewater at high concentration ranges of 197– 27,700 ng/L and 86 – 2840 ng/L in the influent and 30–22,900 ng/L and <LOD – 1890 ng/L in final effluent, respectively

(Madikizela, et al, 2014; Amdany et al, 2014; Lehutso et al, 2017). Further, occurrence of both compounds in groundwater from land application have been ascertained (Gottschall et al., 2012). However, although there is substantial occurrence data, it is not possible to assume the values are applicable to all regions globally both at local and national levels. The variance is closely linked to factors including effectiveness of local WWTPs and associated treatment technologies, sources (both industrial and domestic), nature of the product sources, degradation of parent compound based on influent physicochemical properties, just to mention a few.

However, there still remain information deficits concerning the environmental concentrations of both chemicals in Africa (Musee, 2018), and especially in the developing countries and countries with economies in transition (Ebele et al., 2017). To date, for example, there is lack of MECs for TCS and TCC in South Africa, hence in turn, raises a need to monitor and quantify them in pursuit to improve their management both in the technical (e.g., WWTPs, dams, etc.) and natural systems. Several studies using experimental and modelling approaches have quantified the concentrations of TCC and TCS in South Africa environments, and have demonstrated to be highest reported globally (Musee, 2018). However, these are too few to offer insights on their occurrence in any given region, or across South Africa. Therefore, data is necessary to support robust risk assessment studies in different environmental compartments for both TCS and TCC to support robust decision making, for example, with respect to the development of discharge limits to safeguard ecological health and human health.

Numerous studies have reported the formation of transformation products (TPs) in wastewater treatment (pilot scale) (Lee et al., 2012; Lozano et al., 2013; Tohidi and Cai, 2017; Armstrong et al., 2018). Among TPs identified includes methyltriclosan (MeTCS), 4 –chlorocatechol, 4,4′ –dichlorocarbanilide (DCC), 1–(3 –chlorophenyl)−3–phenylurea (MCC), and carbanilide (NCC), and 4 –Chloroaniline (4–CA), 2,4–Dichlorophenol (Lee et al., 2012; Lozano et al., 2013; Tohidi and Cai, 2017; Armstrong et al., 2018). Thus, existence of TPs also raises the need to monitor them to fully account for the potential risks of using TCC and TCS in the aquatic environments. This is because certain TPs are potentially more toxic and persistent than their parent compounds (Lozano et al., 2012). In a recent study, 2,4–Dichlorophenol was detected in rivers receiving wastewater effluent from WWTPs in South Africa (Yahaya, et al., 2019), although the TP's ecological implications remain poorly quantified, and therefore largely unknown. This, among many examples raise urgent necessity for the monitoring of both parent TCC and TCS compounds, and their TPs in WWTPs and the receiving waters.

At present, the removal of ECs from wastewater is rather incidental. This is because most treatment systems were designed as biological nutrient removal (BNR) systems with the organic load as key target (Metcalf and Eddy, 2003). Broadly, in South Africa the common wastewater treatment process employed is the conventional activated sludge that includes coagulation and flocculation, sedimentation, BNR reactor, filtration, and disinfection processes. Therefore, the extent to which ECs are removed is largely dependent on the combination of treatment processes in a given WWTPs, and EC in question. As an example, from variant studies the overall removal efficiency of ECs in WWTPs were observed to range from 58 to 98% dependent on the type of treatment process, and the EC investigated (Ying and Kookana, 2007; Bock et al. 2010; Lozano et al., 2013). The wastewater treatment processes therefore need to be examined in relation to the removal of TCS and TCC to safeguard ecological life and human health, e.g., in regions where water reuse is considered as an alternative in pursuit to alleviate water scarcity.

To address these knowledge gaps, in this study the overarching aim was to investigate and quantify the concentrations of TCC and TCS in Darvill WWTP in Pietermaritzburg, South Africa. Due to limited MECs in South Africa, both experimental and modelling approaches were employed in this study. The experimental analysis were carried out using gas chromatography–mass spectrometry (GC–MS) because of its proven application in the determination of TCS and TCC in aquatic systems (Montaseri and Forbes, 2016), and ease of access in South Africa. In addition, the PECs were estimated using material flow analysis (MFA) model as previously documented by Musee (2018). Lastly, the ecotoxicological risks posed by TCS and TCC on different environmental compartments were assessed by computing the risk quotient (RQ) of organisms at different levels of organization.

1.3. STUDY OBJECTIVES

The overall objective of this study is to assess the flows and distribution of TCS and TCC, and to evaluate their removal efficiencies from a wastewater treatment plant (biological activated sludge process) in Pietermaritzburg, South Africa (Darvill WWTP) using both experimental and modelling approaches.

The following are the study specific objectives:

1. Assess the distribution and quantification of TCS and TCC at selected stages of the wastewater treatment unit processes using experimental approach;

2. Evaluate the removal efficiency of TCS and TCC from the WWTP;
3. Determine the presence of TPs of TCS and TCC at different treatment units to elucidate probable transformation of TCC and TCS in WWTPs, and
4. Evaluate the ecological risks of TCS and TCC exposure using the modelling approach based these chemicals from variant products,

1.4. DISSERTATION OUTLINE

This section provides a brief summary of the subsequent chapters of the thesis.

Chapter 2 presents literature review chapter wherein the dynamics of the study case area of Msunduzi Local Municipality are discussed. This is followed by an introduction to PPCPs with discussions on general properties, applications, and environmental fate in different environmental compartments of target compounds, i.e., TCS and TCC. Quantification of TCS and TCC in the ecosystem using analytical and modelling techniques, and global occurrence are also discussed. The removal of TCS and TCC from variant treatment processes, ecotoxicity and risk assessment analysis in different environmental compartments close off this chapter.

Chapter 3 details the analytical and modelling approaches followed in this study. First, an introduction of the studied WWTP and population demographics of the local municipality is presented. Secondly, the analytical approach (solid phase extraction and gas chromatography – mass spectrometry) applied to measure the environmental concentrations of TCS and TCC is described. Lastly, the modelling approach is outlined that entailed inventory collection of household products (categories, concentrations of TCS and TCC per item, etc.), model calculations of predicted environmental concentrations (PECs) of TCS and TCC, and risk assessment by estimating the risk quotient (RQ).

Chapter 4 summarises the results, and an analysis, and discussion of the analytical and modelled findings. The initial assessment of possible emerging contaminants present in the study WWTP are provided. This is followed by the analysis of TCS and TCC results derived from analytical and modelling, and their likely implications to aquatic environments.

Chapter 5 presents conclusions and recommendations.

CHAPTER 2:

LITERATURE REVIEW

2.1. INTRODUCTION

The TCS and TCC are two antimicrobial compounds commonly incorporated in pharmaceutical and personal care products (PPCPs) (Perencevich et al., 2001; SCCP, 2009; QYResearch, 2015, Musee, 2018). These chemicals have been in existence since the 1950s and 1960s and their increase usage in PCPs over the years has resulted to presence in different environmental compartments including freshwater, soil, etc., (Lv et al., 2014; Chen et al., 2019a), and have already been banned in Europe and USA (EU, 2016; US FDA, 2016). The major pathways in which these chemicals enter the environment are through incomplete removal from wastewater, run off, sludge use for land for agricultural purposes, and leachates from landfills.

Herein, the review seeks to address the following aspects, viz.: (i) the applications of TCS and TCC, and their physicochemical properties relevant to wastewater removal and environmental persistence; (ii) their widespread occurrence/fate and impact in the environment (WWTP, freshwater, and terrestrial systems), and removal from wastewater; and (iii) introduce the concept of risk assessment to estimate TCS and TCC risks to aquatic, wastewater, and terrestrial organisms and ultimately their implications to the environment.

2.2. PHARMACEUTICAL AND PERSONAL CARE PRODUCTS

2.2.1. Introduction of PPCPs as ECs

The PPCPs broadly refer to any product with healthcare or medical purposes, and are classified broadly into two main groups, viz., pharmaceuticals (e.g., antibiotics, hormones, analgesics, anti –inflammatory drugs, blood lipid regulators, β–blockers, and cytostatic drugs), and personal care products (PCPs) (preservatives, bactericides/disinfectants, insect repellents, fragrances, and sunscreen ultraviolet (UV) filters) (Kosma et al., 2010; Liu and Wong, 2013). TCC and TCS – chemicals investigated in this study – are representative compounds mostly

incorporated into PCPs as bactericides and/or disinfectants (Perencevich et al., 2001; SCCP, 2009; QYResearch, 2015, Musee, 2018).

Population growth, emergence of new diseases, increased awareness on essence of hygiene, and dramatic demand for beauty products has resulted to increased development and production of PPCPs in pursuit to improve human health, and quality of life. By 2011, in excess of 50 000 PPCPs products totalling to approximately 30 000 tonnes were consumed worldwide (Yu, 2011). Pharmaceutical drugs consumed by humans and animals, as a result of incomplete uptake, are excreted from the body and discharged to the environment (Montforts, 1999; Kim et al., 2011). Conversely, PCPs are discharged to the environment through body washing and other recreational activities (Brausch and Rand, 2011). Existence of PPCPs in the aquatic environment is from variant sources and pathways including WWTPs, water treatment plants (WTPs), hospital discharges, disposal of unused drugs, diffuse sources (including runoffs from populations with no sewage systems), and from manufacturing facilities (Leung et al., 2012; Liu and Wong, 2013). Notably, the WWTPs are the predominant pathway of PPCPs into the environment (Benotti and Brownawell, 2007; Focazio et al., 2008; Padhye et al., 2014; Gaw et al., 2014; Luo et al., 2014), chiefly due to their incomplete removal at variant influent treatment processes.

At present, myriad studies have documented the occurrence of PPCPs in technical (e.g., WWTP, WTP, etc.) and natural (e.g., groundwater, surface water, etc.) systems at concentrations ranging from ng/L to µg/L (Scheurer et al., 2009; Bu et al., 2013; Liu et al., 2013; Tewari et al., 2013; Carmona et al., 2014; Sun et al., 2015; Kuzmanović et al., 2015; Thomaidi et al., 2015; Ebele et al., 2017; Balakrishna et al., 2017;). The occurrence of these chemicals and their residuals in the environment is of great concern owing to their deleterious effects to ecological and human health. For example, numerous PPCPs still remain biologically active even after reaching the environment. This, in turn, can induce deleterious effects on aquatic organisms e.g., endocrine disruption, genotoxicity, carcinogenicity, fetal development deficiencies (Jin et al., 2014). Among PCPs of concern includes TCC and TCS, and both chemicals constitutes the focus of this work.

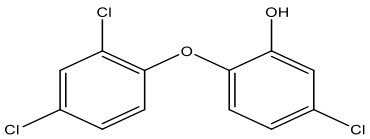
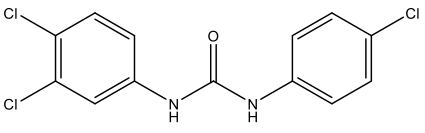
2.2.2. Triclosan and Triclocarban

Triclosan (TCS, 5–chloro–2–(2,4–dichlorophenoxy) phenol) and triclocarban (TCC, 3,4,4–trichlorocarbanilide), are antimicrobial agents commonly incorporated into PCPs like soaps,

toothpastes, deodorants, skin creams and plastics (McAvoy et al., 2002; Halden and Paull, 2005; Halden, 2014). They are halogenated aromatic hydrocarbon compounds with phenolic, diphenyl ether and polychlorinated biphenyl (PCB) substructures. The global production of these chemicals is estimated at 15 000 tonnes and 10 000 tonnes (Singer et al., 2002; TCC Consortium, 2002; TSCA, 2003; Miller et al., 2008), and with 128 and 52 products containing TCS and TCC, respectively, were identified in the South African market (Musee, 2018).

TCC and TCS are persistent in different environmental compartments (Halden and Paull, 2005) as per data set out in Table 2.11. For instance, Halden and Paull (2005) predicted the half – lives of both TCC and TCS in air, water, soil, and sediment to be 0.75 d, 60 d, 120 d, and 540 d, respectively. A summary of the general properties of TCS and TCC are summarized in Table 2.1. These chemicals have high octanol–water partitioning coefficients ($10^{4.8}$ and $10^{4.9}$ for TCS and TCC, respectively) indicating high hydrophobicity, persistent, and particle sorption potential (Halden and Paull, 2005; Dhillon et al, 2015). Further, both have low solubility in water (2000–4000 and 650–1550 $\mu g \cdot L^{-1}$ at 25 °C for TCS and TCC, respectively), and relatively non –volatile (vapour pressure of 5.2×10^{-6} and 3.6×10^{-9} mm Hg for TCS and TCC, respectively) (Halden and Paull, 2005; Dhillon et al, 2015). These physicochemical characteristics among others are important as they play a key role on their removal from wastewater treatment processes through settling with biosolids.

Table 2.1: Summary of general properties of TCS and TCC.

Property	**Triclosan**	**Triclocarban**	**Reference**
CAS No.	3380 –34 –5	101 –20 –2	
Structure	 Triclosan	 Triclocarban	
Molecular Formula	$C_{12}H_7Cl_3O_2$	$C_{13}H_9Cl_3N_2O$	
Molecular Weight (g/mol)	289.54	315.58	
Chlorine content (% w/w)	33.7	36.7	3
Density (g/cm^3)	1.49	1.53	1
Dissociation constant (pK_A) (20 °C)	7.8	12.7	4

Henry constant (H_c) (atm $mol^{-1} \cdot m^{-3}$)	1.5 x 10^{-7} (25 °C)	4.5 x 10^{-11} (25 °C)	2; 5
Octanol – water Partition coefficient (log K_{ow})	4.8 (25 °C)	4.9	3; 5
Melting Point	180 °C	140 °C	3
Water Solubility ($\mu g \cdot L^{-1}$)	2000 – 4000 (25 °C)	650 – 1550 (25 °C)	3
Vapor pressure (mm Hg)	5.2×10^{-6} (25 °C)	3.6×10^{-9} (25 °C)	5
Half –life (days)	60 (water); 120 (soil)	60 (water); 180 (soil)	3; 6

References: 1: TCC Consortium, 2002; 2: EPA, 2003; 3: Halden and Paull, 2005; 4: Miller et al, 2008; 5: Dhillon et al, 2015; 6: Clarke et al., 2016

2.2.3. Applications of TCS and TCC

TCS and TCC are widely used as antimicrobial and antifungal agents in PCPs, health, sport and other household products (Halden and Paull, 2005; Young, 2013; Smith, 2013; Halden, 2014). They are incorporated into these products at concentration ranges of 0.1 to 0.3% (w/w) (Sabaliunas et al., 2003) and 0.02 to 1.5% (Musee, 2018) for TCS and TCC, respectively. The range of products in which these chemicals are used includes hand soaps, detergents, shampoo, hair conditioners, skin creams, toothpaste, mouth washes, deodorants, antiperspirants, softeners, acne treatment products, fabrics, bedding, trash bags, paints, and plastic cutting boards. Other product types are kitchen utensils, dish washing products, carpet cushions, hot tubs, plastic lawn furniture, impregnated sponges, pesticides, computer equipment, polymers, textiles, coatings, ceramics, paper and adhesives, first aid, antiseptic products, surgical hand scrubs, antimicrobial agent, surgical gloves, preservatives, implantable medical devices, shoes, and toys (McAvoy et al., 2003; Bester, 2003; Halden and Paull, 2005;Young, 2013; Smith, 2013; Halden, 2014; Musee, 2018). These chemicals are predominantly incorporated into PCPs with previous studies estimating 68% to 85% of TCS global usage (SCCP, 2009; QYResearch, 2015). Recently in an inventory developed for South Africa, PCPs were estimated to account for 86.9% and 100% usage of TCS and TCC, respectively (Musee, 2018).

2.3. ENVIRONMENTAL FATE

WWTPs are the major pathway through which TCS and TCC enter the environment. This is because PPCPs are washed down the drain into the sewer network from households, commercial and manufacturing sources, and eventually find their way to WWTPs. Incomplete removal of TCS and TCC from the WWTPs and agricultural land application of biosolids introduce these chemicals to aquatic and terrestrial environments. The lifecycle phases of TCS and TCC includes production (chemical production, and consequent incorporation into products e.g., PCPs), to human consumption, and eventual release into different environmental compartments including soil, freshwater, sediments, and air. This study does not account for chemical manufacturing due to limited manufacturing data of TCS and TCC in South Africa. The release pathways to the environment considered herein include WWTPs (effluent and sludge disposal), direct runoffs, and solid waste. Release to the air is also not considered because incineration of sludge is limited, or to large extent nonexistence in South Africa largely to the legislative framework. Hence, the dominant sludge disposal practices in South Africa are landfill and agricultural application.

2.3.1. Global occurrence of TCS and TCC

The global occurrence data for TCS and TCC in different compartments are summarized in Table S1 and Table S2, respectively. However, the environmental concentrations data for TCC and TCS are limited in Africa as only four studies, to date, have reported MECs (Madikizela, et al 2014; Amdany et al, 2014; Sorensen et al., 2015; Lehutso et al, 2017), and a single study that estimated their environmental concentrations using modelling approaches (Musee, 2018). In addition, the MECs detected in South Africa were among the highest in the world. This is for two-fold reasons. First, this was attributed to high TCS and TCC concentrations incorporated in PCPs compared to other countries, for example up to 1.5% per article relative to 0.3% elsewhere (Musee 2018). Secondly, the removal efficiency of chemicals from the WWTPs are low due to aging infrastructure relatively to other regions globally (Musee, 2011). Further, many studies were conducted in China and USA for TCS and TCC. Occurrence data for TCC is scarce especially in Europe and Africa although is likely to be an alternative for the TCS as the former has been banned.

Summary on the global occurrence of TCS and TCC in wastewater is shown in Figure 2. 1 with detailed concentrations presented in the supplementary information (Table S1 and Table S2).

Results showed that measured concentrations in wastewater influent ranged from 33 to 127 770 ng/L, and 97 to 10,000 ng/L for TCS and TCC, respectively. Moreover, concentrations detected in the effluent from WWTPs are in the ranges of 10 to 22 900 ng/L and 48 to 1 890 ng/L for TCS and TCC, respectively. In freshwater systems, TCS and TCC concentrations are in the range of 0.02 to 8 720, and 2.2 to 1 119 ng/L, respectively. And, the observed concentrations in sediments ranges from 0.004 to 7 060, and 0.003 to 9 280 µg/kg for TCS and TCC, respectively.

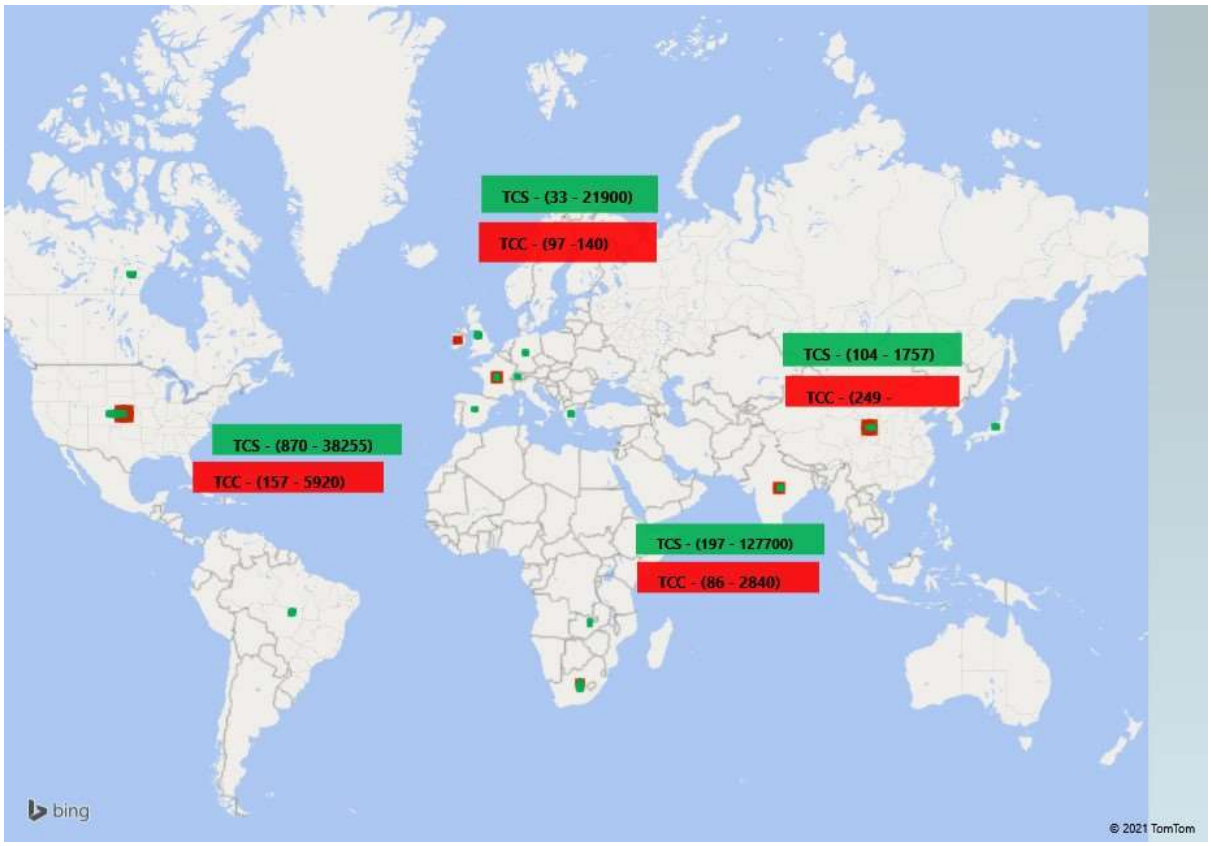


Figure 2. 1: Summarized global occurrence data ranges for TCS and TCC in wastewater treatment systems (ng/L) based on data retrieved from literature, and set out in Table S1 and Table S2.

2.3.2. Transformation processes and formation of transformation products

Formation of TPs of TCS and TCC in different environmental compartments (e.g., wastewater, freshwater, etc.) is of an issue of global great concern. This for the reason that most TPs are carcinogenic, persistent, and in certain cases more toxic relative to parent compounds (Lores

et al., 2005; Aranami and Readman, 2007; Anger et al., 2013). For example, TPs of TCS, namely; 2–chlorophenol, 2,4–DCP, 2,4,6–TCP, and pentachlorophenol are among the priority chemicals listed by the EPA and European Commission (Decision No 2455/2001/EC, 2001) owing to their elevated risk to aquatic lifeforms. Hence, this raises the urgent need for improved management of TPs. The TPs are formed as by-products during the degradation of TCS and TCC under various environmental conditions. Photodegradation and chlorination/de-chlorination are the common reaction pathways, and in turn, results to the formation of intermediates and transformation by-products (Li et al., 2018).

Several studies have assessed the degradation of TCS and TCC in wastewater, and the formation of TPs (Lindström et al., 2002; Chen et al., 2011; Lee et al., 2012; Armstrong et al., 2018). For example, Lee et al. (2012) conducted a pilot study on the degradation of TCS by a wastewater microorganism (Sphingopyxis strain KCY1). A complete dechlorination of TCS was observed after 72 h with 2,4–DCP as the final degradation product. Four intermediate products, namely; monohydroxy–triclosan, 6–chloro–3–(2,4–dichlorophenoxy)–4–hydroxycyclohexa–3,5–diene–1,2–dione,3–chloro–4–(5,7–dichloro–3–oxo–2,3 dihydrobenzo[1,4]dioxin–2–yl)–2–oxobut–3–enal and 3,5–dichloro–4,6 –dihydroxycyclohexa –3,5–diene–1,2–dione were formed during the first 8 hours of the experiments.

Armstrong et al. (2018) studied the degradation of TCS and TCC from aerobically run benchtop wastewater reactors under variant hydraulic retention times (HRT), sludge retention times (SRT), and temperature conditions. Results indicated the degradation of TCS increased at higher temperatures (21–30℃), and dependent on the retention times i.e., HRT (8 h) and SRT (55 h). Degradation of TCC, however, were slower relative to that of TCS and required a higher HRT of 96 h at lower temperature of 21℃. The researchers also detected the formation of MeTCS, 2,4–DCP and 4–CA as TPs. MeTCS has been shown to occur as result of biological degradation of TCS under aerobic conditions, and largely adsorb to the sludge (Lindström et al., 2002; Chen et al., 2011). The formation of TCC and TCS TPs in wastewater through chlorination occur during the final effluent disinfection. Notably, chlorine based disinfectants including chlorine gas, sodium hypochlorite, and calcium hypochlorite are commonly used in South Africa for the destruction of pathogens in the final effluent before discharge to the environment. This, in turn, raises the possibility on the formation of TPs from the TCC and TCS widely incorporated into products widely commercialized in South Africa.

In freshwater, several TPs are formed including 2,4–DCP, 2,4,6–DCP, 2,7–DCDD, 2,8 DCDD, tetraclosan and pentaclosan. 2,4,6–DCP, tetraclosan and pentaclosan through the chlorination of the phenolic ring during the disinfection of wastewater in the presence of TCS by chlorine dioxide. Also, formation of 2,7–DCDD and 2, 8 DCDD has been observed under dark conditions, thus an indication of TCS transformation to dioxins via intramolecular chemical substitution (Li et al., 2018). Similarly, in complex media (nutrient broth and mineral salts), formation of monohydroxy –TCS, dihydroxy-TCS, dechlorinated dihydroxy –TCS, 2,4 –dichlorophenol, 3,5–dichlorocatechol, 4–chlorocatecho, and 2–methoxy–3,5–dichlorophenol have been observed following the biodegradation of TCS by *Sphingomonas sp*. PH –07 (Kim et al., 2011).

In soils and sediments, presence of DCC, MCC and NCC were attributed to TCC dechlorination under anoxic conditions in deep sediments (Miller et al. 2008). Chen et al. (2019a) also observed and indicated the formation of these TPs to TCC dechlorination in WWTP sludge across China. Global summary of TPs (commonly determined qualitatively) from the degradation of TCS and TCC in different environmental media are summarised in Table 2.2.

Table 2.2: Summary of TCS and TCC transformation products detected in different media across the globe using qualitative techniques.

Country	Transformation Product	Exposure Media	Reference
	Triclosan		
USA	Monohydroxy-triclosan 6-chloro-3- (2,4-dichlorophenoxy)-4-hydroxycyclohexa-3,5-diene-1,2-dione 3-chloro-4-(5,7-dichloro-3-oxo-2,3-dihydrobenzo[1,4]dioxin-2-yl)-2-oxobut-3-enal 3,5-dichloro-4,6-dihydroxycyclohexa-3,5- diene-1,2-dione 2,4-dichlorophenol	Wastewater - Sphingopyxis strain KCY1 degradation – Pilot study	Lee et al., (2012)
-	Monohydroxy-TCS		

	Dihydroxy-TCS Dechlorinated dihydroxy-TCS 2,4-Dichlorophenol 3,5-Dichlorocatechol 4-Chlorocatecho 2-Methoxy-3,5-dichlorophenol	Complex media, nutrient broth and mineral salts	Kim et al., 2011
Denmark	Methyltriclosan	Wastewater	Chen et at., 2011
	2,4-Dichlorophenol Methyltriclosan	Wastewater	Armstrong et al., 2018
USA	Methyltriclosan	Wastewater	Lozano et al., 2013
China	Methyltriclosan 2,4 - Dichlorophenol 2,8-dichlorodibenzoparadioxin (2,8-DCDD)	Wastewater	Tohidi and Cai., 2017
South Africa	2,4-dichlorophenol	River – following wastewater treatment	Yahaya et al., 2019
Hong Kong	5-chloro-2-(2,4,5-trichlorophenoxy)phenol 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol 4,5-dichloro-2-(2,4,5-trichlorophenoxy)phenol 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol 2,8-DCDD 2,3,7-TrCDD	Seawater	Wu et al., 2019

	1,2,8-TrCDD 2,3,7,8-TeCDD 1,2,3,8-TeCDD		
China	2,7-DCDD 2,8-DCDD 2,4-DCP 2,4,6-TCP tetraclosan pentaclosan	Water treatment – bench scale experiments	Li et al., 2018
Denmark	4-Chlorocatechol 2,4-Dichlorophenol Triclosan-methyl monohydroxy-Triclosan dihydroxy-Triclosan Triclosan-*O*-Sulfate	Wastewater	Chan et al., 2015
	Triclocarban		
USA	DCC, MCC, NCC	Sediments – near wastewater treatment plant	Miller et al, 2008;
USA	DCC, MCC	Sediments	Venkatesan et al., 2012
China	DCC, MCC, NCC, tetra-chlorinated carbanilide	WWTP Sludge	Chen et al., 2019a
USA	4-Chloroaniline	Wastewater	Armstrong et al., 2018

2.4. QUANTIFICATION OF TCC AND TCS IN THE ECOSYSTEMS

2.4.1. Analytical approaches

Numerous analytical techniques have been developed to detect and quantify TCSand TCC in different environmental matrixes. In certain cases, the methods are used to simultaneous determine other PPCPs. In this respect, chromatography–based methods constitutes among the most widely used. Until now, environmental concentrations of TCS and TCC using different techniques and analytical methods in different aquatic systems have been reported in literature globally, and illustrative examples are listed in Table S3. The four broad common classes of analytical techniques widely applied to determine TCS and TCC are chromatography–mass spectrometry, electrochemical, electrophoresis, and optical methods, and a summary of merits and demerits of each technique are set out in Table 2.3. In this section, only a brief overview of each of these techniques' are outlined, and therefore, not construed to be comprehensive.

Table 2.3: Merits and demerits of the different analytical techniques for the determination of TCS and TCC in the environmental matrixes.

Techniques	Merits	Demerits	References
Chromatography-mass spectrometry	Analyse many different pollutants in a single run	Waste production, use of toxic reagents	4;6; 9
	Low sample volume, rapid, selective, sensitive	Poor repeatability, laborious sample preparation	6; 9
	Low detection limits, high accuracy	High costs (capital and operation), require skilled labour	2; 3
Electrochemical	Simple to operate, rapid	Waste production, use of toxic reagents	1
	Low costs (capital and operation), pre –treatment not required	Poor sensitivity and selectivity, high limits of detection	5;10
Electrophoresis	Analyse many different pollutants in a single run	Waste production (lower than LC), use of toxic reagents	7; 8
	Low sample volume, rapid	Poor repeatability	7; 8
Optical	Cheap, rapid	Poor sensitivity	11

References: 1: Amiri et al.,2007; 2: Gibson et al., 2007; 3: Yu et al., 2007; 4: Guo et al., 2009; 5: Lui et al., 2009; 6: Zheng et al., 2011; 7: Gibbon et al., 2011; 8: Wang et al., 2013; 9: Kim et al., 2013; 10: Yu et al., 2015; 11: Montaseri and Forbes, 2016

2.4.1.1. Chromatography–Mass Spectrometry

Chromatography is an analytical technique that entails the separation of sample into its components; whereas mass spectrometry measures and quantifies the separated compounds. The separation principle of chromatography is based on the type of the mobile or carrier phase utilized. Three types of mobile phases are used, viz., inert gas, liquid, and superficial fluid. The inert gas and liquid phases are commonly used, and generically regarded as gas chromatography (GC) and liquid chromatography (LC), respectively. Helium and nitrogen are typically used inert gasses as mobile phase in GC to convey the sample through a column containing a stationary phase – typically a microscopic layer of liquid or polymer on an inert solid support. Separation occurs as the sample passes through the column due to differences in components travel speeds (Hussain and Maqbool, 2014).

For TCS and TCC as target analytes, sample preparation is an important step as their environmental concentrations are very low in the ng/L to µg/L range. Five pre–treatment methods have been widely used in the analysis of TCS and TCC, namely: solid–phase extraction (SPE), solid –phase microextraction (SPME), hollow fibre assisted liquid–phase microextraction (HF –LPME), dispersive liquid–liquid microextraction (DLLME), and stir–bar sorptive extraction (SBSE). Notably, the DLLME method offer distinctive advantages including low cost, simplicity, rapidity, recovery and shorter preparation time relative to other methods (Guo et al., 2009). The method entails preparation of a cloudy mixture of extraction and dispersive solvents followed by centrifugation at low speeds before transfer to GC or LC for analysis.

2.4.1.2. Electrochemical Methods

Electrochemical methods entail an electrochemical cell setup containing the analyte to be measured. Three common measuring techniques employed includes potentiometry, coulometry, and voltammetry. Previously, the use of electromechanical methods to detect and quantify TCS have been reported with cyclic voltammetry and screen–printed carbon electrodes (SPCEs) as the first method developed (Pemberton and Hart, 1999). Mercury based electrodes and other chemically modified electrodes e.g., composite nanozinc oxide–multiwalled carbon nanotube modified glassy carbon electrode have been used to accelerate electron transfer for electrooxidation of TCS (Vidal et al., 2008; Moyo et al., 2015). The

working principle is to enhance the electrochemical oxidation of the analyte by the active electrode. Overall, the limits of detection are in the range of 43.4 to 5 x 10^3 ngL^{-1} for water and wastewater samples using different electrode types (Fotouhi et al., 2010; Yola et al., 2015; Moyo et al., 2015).

2.4.1.3. Capillary Electrophoresis Methods

Capillary electrophoresis (CE) methods employ voltage to separate ions based on their electrophoretic mobility (Gibbon et al., 2011). The overall setup of the CE method is similar to chromatography–based methods, since the method also requires sample preparation, separation, and quantification. The common setup comprise of SPE followed by CE with UV detectors. Gibbons et al. (2011) developed the first CE–UV method to determine TCS and other PPCPs in wastewater using SPE as pre–treatment phase. The study analysed eight PPCPs compounds including TCS, and the detected concentrations were in the range of 1 600 to 68 700 ngL^{-1}. Results generated were comparable to those of LC–MS/MS derived. Similar to chromatography methods, CE also has capabilities to analyse different pollutants in a single run with higher resolution, shorter analysis time, and low waste generation (Koel and Kaljurand, 2006; Zhang et al., 2014).

2.4.2. Modelling approaches

Owing to dearth of measured environmental concentrations (MECs) of PPCPs in developing countries to assess their impacts to the environment (Ebele et al., 2017), model based approaches are used as alternative approaches. This is to generate likely predicted environmental concentrations (PEC). These approaches are usually based on the lifecycle of the products containing the target analyte(s) of interest, in this case TCS and TCC. The PEC values are estimated based on numerous and heterogeneous input model data including both product, population and WWTP factors. These factors includes market sales data, consumption rates, population data, excretion rate, waste generation per capita, and WWTP removal efficiencies. Various models based on material flow analysis (MFA) and substance flow analysis (SFA) have been developed to quantify micropollutants flows into the natural and technical systems including TCS and TCC (Ort et al., 2009; Huang et al., 2014; Musee, 2018). For example, Ort et al (2009) developed a model using graph theory to predict loads of 12 micropollutants in WWTP effluent across Switzerland into complex river systems. The PEC

results derived from the models were found to be in good agreement with MECs. Also in SA, TCS and TCC concentrations were predicted in WWTPs in Gauteng Province with the model results within the MEC ranges especially at the lower and moderate ranges (Musee, 2018). The model performance was refined against MECs data to ensure results derived from the models can be used with confidence. Previously, studies have used the PEC/MEC ratio criteria to evaluate the model performance, and their results are summarized in Table S12. Overall, the criteria proposed were observed to be dependent on the factors considered by the researchers in a given study.

2.5. TREATMENT OF TCS AND TCS IN WASTEWATER TREATMENT

Primarily, the design and construction of WWTPs is to treat domestic sewage, and occasionally industrial influent. The treatment typically involves physical, biological and chemical separation of nutrients, i.e., phosphorous, ammonia, and reduction of chemical oxygen demand (COD). Examples of physical processes includes screening and settling where separation is dependent on differences in size and weight, respectively. Biological systems work with the accumulation of biomass from bacterial growth in a biological reactor for the removal of organic matter (Metcalf and Eddy, 2003). Chemical reactions are often employed to precipitate out nutrients e.g., phosphorous and sulphur. Configuration of these treatment processes include suspended growth (e.g., conventional activated sludge), attached growth (e.g., trickling filters and rotating biological contact tanks), and membrane systems (e.g., membrane bioreactor) (Alvarino et al., 2018; Sheng et al., 2016).

The treatment train usually consist of primary treatment, secondary treatment, and tertiary treatment. The design for the primary treatment is to aid removal of grit, sticks, oil and grease, and a portion of suspended solids and organic matter (Metcalf and Eddy, 2003). The main treatment processes are screens (mechanical or bar), grit channels, and sedimentation. During the secondary treatment, biological removal of organic matter, suspended solids and nutrients occurs. And, the tertiary treatment step mainly focuses on final polishing of effluent (removal of residual suspended solids), and disinfection. In the following sections, a brief discussion is presented to outline the main unit processes with specific reference to the removal of TCS and TCC.

2.5.1. Sedimentation

Sedimentation process is used both during the primary and secondary treatment phases of wastewater. This is to remove suspended solids, and reduce organic load in the primary treatment. Up to 70% of suspended solids, and 40% of biological oxygen demand (BOD) can be removed during primary sedimentation phase (Metcalf and Eddy, 2003). In the secondary treatment, sedimentation aids to separate the final effluent and biosolids from the mixed liquor. The underpinning principle of operation is that the feed stream is separated into overflow and underflow streams by means of differences in particle weight. Particle settling velocity and aggregation therefore play critical roles in the removal efficiency of the sedimentation tanks. The sedimentation processes therefore play a key role in the removal of TCS and TCC in a WWTP due to their moderately high octanol-water coefficient values for TCS and TCC (Table 2.1). Results of Heidler and Halden (2007) demonstrated that 36–100% of TCS in the raw sewage was attached to the particulate fraction of wastewater.

Further, Lozano et al. (2013) observed removal efficiencies of 80.2% and 75.4% for TCC and TCS, respectively, during the primary treatment of a WWTP in the USA. Efficient operation of both primary and secondary settling processes offer significant removals of TCS and TCC. However, the downstream process of sludge treatment need due consideration to ensure safe biosolids disposal to avoid pollution to soils, and eventually water resources.

2.5.2. Biological reactor

The biological reactor is the heart of any conventional wastewater treatment process. In the reactor, COD reduction and nutrients decomposition is facilitated by use of active microorganisms (Metcalf and Eddy, 2003). The biological reactor can be configured in different forms with three main decomposition modes, viz.: aerobic, anoxic, and anaerobic (Metcalf and Eddy, 2003; Mackenzie, 2010). In the aerobic zones, air is utilized to facilitate the decomposition of waste through oxidation. The anoxic zone facilitates the reduction of ammonia intermediate products (nitrate) to nitrogen; whereas the anaerobic process facilitates the fermentation of organics.

Several studies have highlighted the removal of TCS and TCC in biological reactors (Miller et al., 2010; Lee et al., 2012; Armstrong et al., 2018). For example, Lee et al. (2012) observed complete degradation of TCS using a wastewater isolate (Sphingopyxis strain KCY1). In a recent investigation, Armstrong et al. (2018) reported the removal of both TCS and TCC from

benchtop reactors operated under aerobic conditions. Broadly, as a function of different reactor configurations and variability of operating conditions (e.g., temperatures, pH, and hydraulic retention time), therefore yields a different removal efficiencies of these pollutants from wastewater. Notably, however most of the reported studies were conducted in lab scale equipment, thus further studies are recommended for full-scale application. This is important given the detected presence of TCS and TCC in river systems post-treatment through WWTPs.

2.5.3. Advanced Oxidation Processes

The removal of recalcitrant trace organic chemicals and certain inorganic pollutants have proven to be ineffective in conventional water and wastewater treatment systems (Carballa et al., 2004). As a result, advanced oxidation processes (AOPs) technologies have been developed as they offer a wider range of reduction and deactivation of organic chemicals (Ruan et al., 2019). Over years, different AOP technologies have been developed, and these includes ozonation, UV irradiation, electrochemical, plasma, electron beam, ultrasound or microwave based AOPs, just to mention a few (Ali et al., 2011; Oturan and Aaron, 2014; Ruan et al., 2019). Herein, the study will focus on two widely used systems; the ozone– and UV–based AOP technologies.

The working principle of AOPs is based on the *in situ* generation of strong oxidants for the oxidation of organic and inorganic compounds. This includes processes based on the formation of hydroxyl radicals (OH·), sulphate radicals ($SO4^{\cdot-}$), and chlorine radicals (Miklos at al., 2018). The powerful oxidants are responsible to destruct the pollutants, and transform them into less but also non-toxic products (Deng and Zhao, 2015). Various studies have been conducted for the removal of TCC and TCS using photolysis- and ozone-based technologies in water and wastewater (Ali et al., 2011; Gerrity et al., 2011; Niu et al., 2015). For example, Niu et al. (2015) reported 75% TCS removal from wastewater using photolysis within 20 minutes. In another study, 99% removal of TCS was observed from the application of O_3/H_2O_2 during water reclamation (Gerrity et al., 2011). Elsewhere, 99% degradation in 10 minutes of TCC was observed using the UV photolysis (Ali et al., 2011). In general, the advanced oxidation processes have yielded relatively high removal efficiencies of TCS and TCC. However, their downside is that they are expensive to operate and produce additional toxic by-products. UV based processes are also complex to implement in a WWTP due to high turbidity of wastewater.

2.5.4. Granular Activated Carbon Filters

Granular activated carbon (GAC) is used in water and wastewater treatment to remove dissolved organic matter through the adsorption process. Organic molecules with affinity for carbon detach from solution, and in turn, bind with carbon. Adsorption processes (both powdered and granular activated carbon) to remove micropollutants are well documented in the literature, and characterised by variant removal efficiencies (Grover et al., 2011; Hernandez – Leal et al., 2011; Yang et al., 2011; Kovalova et al., 2013; Rostvall et al., 2018). For example, Rostvall et al. (2018) studied the removal of pharmaceuticals and other MPs from wastewater using different media filtration (in column tests) including GAC. Results indicated that GAC achieved 97% removal efficiencies for the investigated MPs. In another investigation, 95% removal of TCS was achieved using GAC treated wastewater among other MPs investigated (Hernández–Leal et al., 2011).

Nam et al. (2014) investigated the sorption characteristics of nine selected MPs including TCC in distilled water using bench scale experiments. The results indicated TCC had the highest removal efficiency of 96% at 1 mg/L of activated carbon dosage, and 30 min contact time. In water treatment, adsorption of TCS by activated carbon was investigated and found to achieve 75% removal efficiency (Fang et al., 2009). Taken together with other published data, TCS and TCC can be effectively removed using adsorption with activated carbon both in water and wastewater. And, the main process variables that exert influence on removal efficiency includes contact time, activated carbon dosage, pH, NOM, and temperature. Among the key advantages of activated carbon processes is they are easy to operate and can be retrofitted to existing WWTPs.

2.6. ECOTOXICITY OF TCS, TCC AND TPS

To date, a myriad of ecotoxicity data (acute and chronic) for TCS and TCC have been reported, but severely limited for their TPs (Orvos et al., 2002; Schultz et al., 2002; Ishibashi et al., 2004; Villeneuve et al., 2017). For example, exposure to TCS have been found to inhibit growth and mortality of blue-green algae, crustacean, bacteria, and fish (Orvos et al., 2002; Oliveira et al., 2009). Conversely, TCC was demonstrated to induce deleterious affects on reproduction and inhibit thyroid hormone function in zebrafish (Villeneuve et al., 2017; Dong et al., 2018). In this study, the review on TCS and TCC toxicity is limited to three aquatic organisms (*Daphnia*

magna, algae, and fish), bacteria in wastewater, and terrestrial (earthworms, bacteria, etc.) organisms. For the purpose of this work, toxicity data used were for variant species with specific reference to epic endpoints including reproduction, morphology, growth, and development.

A comprehensive summary of TCS and TCC toxicity data is set out in the supplementary information for the aquatic and terrestrial organisms (Table S4). For fish, the acute toxicity values [lethal and effect concentrations (LC_{50}/EC_{50})] ranges from 0.21 to 840 µg/L, and 184 to 36 200 µg/L for TCC and TCS, respectively. Further, the no observed effect concentration (NOEC) values are in the range of 0.06 to 18 000 µg/L, and 0.54 to 18 000 µg/L for TCC and TCS, respectively. Studies on algae showed lower acute toxicity relative to fish (from 17 to 29 µg/L (TCC) and 0.67 to 620 µg/L (TCS)), and chronic toxicity values of between 5.5 to 32 µg/L and 0.015 to 937 µg/L for TCC and TCS, respectively. Crustacean toxicity values ranged from 0.5 to 400 µg/L and 18 to 390 µg/L for TCC and TCS, respectively. From the retrieved data, the most sensitive group of aquatic organisms to TCS was algae (*Chlamydomonas sp.*); whilst fish (*Mysidopsis bahia*) was the most sensitive to TCC. Overall, published data on TCC and TCS to aquatic organisms indicate to range from toxic to highly toxic dependent on the organism and pollutant in focus. In the terrestrial systems, the toxicity values ranged from 40 to 1177 mg/kg and 300 to 1000 mg/kg for TCC and TCS, respectively.

2.7. ENVIRONMENTAL RISK ASSESSMENT

Quantification of risks of pollutants in the environment based on solely detected data derived using analytical tools, or using modelling approaches is insufficient. This is because of the inherent limitations of each approach. Therefore, to quantify risks of a pollutant to the environment, a comprehensive risk assessment analysis needs to be performed. For a contaminant to pose a risk, the requisite entails exposure to the chemical pollutant, and inherent hazard (ECB, 2003). Exposure to a chemical pollutant is dependent on its environmental concentration(s) level in a matrix of interest (and expressed as MEC or PEC). Acute toxicity endpoint data (EC_{50}) and chronic reference dosage concentrations, e.g., NOEC are used as data needed to estimate hazard. The risk assessment methodology applied in this study was based on the procedures prescribed in the Technical Guidance Document (ECB, 2003). Determination for the risk quotient (RQ) is based on the ratio of MEC and/or PEC to the

predicted no effect concentration (PNEC) to quantify risk threat of a chemical to the ecosystem and human health.

The risk assessment methodology has been applied in numerous problems in different regions globally to assess the impacts of TCS and TCC to the ecosystem and human health (Brausch and Rand, 2011; Tamura et al., 2013; Thomaidi et al. 2017; Musee, 2018; Mohan and Balakrishnan, 2019). For example, a study conducted in two WWTPs in India utilised MECs in the risk assessment calculations, and algae were observed as most vulnerable species to TCS (Mohan and Balakrishnan, 2019). In SA, the likely risks (RQs > 1) of TCS and TCC in freshwater were observed in a study conducted in Gauteng Province, with TCS also found to pose potential risks to wastewater bacteria (Musee, 2018). In China Yu et al. (2019a) conducted a risk assessment study of TCC and TCS from sewage sludge after composting process by computing the PECs in China. Results indicated that composting significantly reduced their ecological risks to soil organisms (with RQ < 0.1 for both TCC and TCS); where composted sludge was used as fertiliser at an application rate of 20 tons per hectare.

2.8. CONCLUDING REMARKS

Different studies across the globe have detected the presence of antimicrobials (TCS and TCC) at varying concentrations in different environmental matrixes. The antimicrobials persistent and poor removal from WWTPs is of great concern as this exposes aquatic and terrestrial organisms to potential adverse risks. The concentration levels reaching the aquatic system have shown to induce adverse effects to sensitive species e.g., algae and fish as evidenced by numerous ecotoxicological risk assessment reports. Also, the lack of environmental concentrations in many regions globally and especially in Africa is of concern. This is because although products containing TCS have been banned in certain jurisdictions (e.g., EU or USA), such products are expected to continue to be marketed in Africa, but dearth of exposure limits impedes the ability to assess their potential impacts to the environment and human health. This study, therefore, aims to address the data and knowledge gaps in this domain through use of both analytical and modelling approaches to understand the fate and removal of TCS and TCC in a South African WWTP, and neighbouring surface water resources.

CHAPTER 3:

MATERIALS AND METHOD

3.1. CASE STUDY AREA

3.1.1. Sewage treatment works – Darvill WWTP

The Darvill WWTPs is one of two WWTPs that services the Msunduzi Local Municipality (LM) residents both industrial and domestic with treatment capacities of 65 Ml/d and 0.2 Ml/d, respectively. Here, the Darvill WWTP located in the City of Pietermaritzburg in the Msunduzi LM, KwaZulu Natal Province, South Africa (–29.602118, 30.430884) was used as study case facility. The plant has an existing average dry weather flow (ADWF) design capacity of 65 Ml/d, and at present is under upgrading to a maximum capacity of 120 Ml/d. By 2018, the Msunduzi LM had a population of 618 536 people residing in 180 469 households of which only 51.6% (93 122) was connected to the sewer system (Stats SA, 2018).

At Darvill WWTP, the domestic sewage and industrial effluent account for 80 and 20% influent flow, respectively. This, in turn, raises likelihood of PPCPs constituent chemicals e.g., TCS and TCC presence in the influent stream. This is because of the widespread use of both compounds in household goods e.g., soaps, deodorants, etc. (Musee, 2018). Darvill WWTP is a conventional biological nutrient removal plant and consists of treatment stages including inlet works, screening, de-gritting, primary treatment followed by anaerobic digestion of thickened sludge, activated sludge treatment of the settled sewage, secondary settling, chlorine disinfection, and contact treatment in a maturation river. After treatment, the effluent are released into the Msunduzi River, and the treated sludge is some 480 tonnes annually. The sludge are pumped to adjacent 57 Ha for irrigational purposes. A summary of the operating parameters and population served at Darvill WWTP are set out in Table 3.1.

Table 3.1: Information on the population connected to, and operating parameters of the Darvill WWTP for various parameters and regulatory limits.

Parameter	Units	Quantity
Population	–	618,536
Households total/connected	–	180 469 /93 122
Wastewater influent – design	Ml/d	65
Wastewater per capita	l/d	90
Influent COD – design	mg/L	600
Effluent COD – limit	mg/L	75
Influent TSS – design	mg/L	300
Effluent TSS – limit	mg/L	25

3.1.2. Catchment area

The Msunduzi LM is among seven local municipalities, and the largest within the uMgungundlovu District Municipality (DM). The LM has a high population density of 976 persons/km^2, and an average economic growth rate of 2% between 2011 and 2016 (Stats SA, 2016). Approximately 49.2% households are connected to the sewer system, and 27.6% use pit latrines where the sewage influent is delivered to the Darvill WWTP use tankers.

In Msunduzi LM, the household income distribution (shown in Table S5) is as follows: 60% of the total population earn less than R38 200, 37% earn between R38 200–and R614 400, and 3% have an income of R614 400–R2 457 601 per annum (Stats SA, 2016). This suggests a likelihood of at least 40% of the population having the purchasing power for the PCPs including those that incorporates TCS and TCC. The catchment area of the Darvill WWTP also includes industrial influent from 54 different industries. Among the industries includes textiles, wash bays, metal finishers, tissue making, metal sheets making, cooking oil, and soap making companies. Notably, the contribution of the industrial effluent to TCS and TCC pollution in Darvill WWTP is likely minimal as the industries do not manufacture PCPs.

3.2. QUANTIFICATION OF TCS AND TCC USING AN ANALYTICAL APPROACH

3.2.1. Sample collection and preservation

Detection and quantification of environmental pollutants require consideration of complex and multifactorial influencing factors including time, rainfall (dilution factor), variability on the usage of products as sources of pollutants based on country and region of focus, and historical data for technical systems (e.g., WWTPs). Herein, the historical averages of monthly flows into the Darvill WWTP and rainfall in the catchment area of Pietermaritzburg were analysed for a five-year period (January 2015 to December 2019) (Figure 3.1). The analysis was aimed to inform the sampling strategy for the purposes of systemic detection and quantification of antimicrobials (TCS and TCC), and other organic pollutants at different stages of the Darvill WWTP.

Results in Figure 3.1 demonstrates that the dry season for the uMgungundlovu District Municipality region where the Darvill WWTP is situated is from April to August. Further, July is the driest month, and thus characterized by poor or no rainfall. Most monthly flows were observed to be below average dry weather flow (ADWF) of 65 Ml/d in the winter months for the years 2017 and 2018. The wet season runs from November to February, with December, January and February as the wettest months. The highest rainfall (700 mm) during the period of assessment was recorded in February 2017, and highest plant inflow of 102 Ml/d was documented in March 2018. Based on these data, the concentrations of target pollutants are plausibly high during the dry period, and low over the wet period as a result of minimal and maximum dilution effects, respectively.

Wastewater samples were collected in 1 L amber bottles from the Darvill WWTP, at different treatment units, and preserved at 4 ºC prior to analysis. Different sampling points entailed the influent, feed to reactor, primary settling tank (PST) underflow, return activated sludge (RAS), waste activated sludge (WAS), mixed liquor, secondary settling tanks (SST) overflow, and the final effluent. The sampling times were based on the hydraulic retention times (HRT) for each process unit, and all samples were collected in triplicates at each sampling point. The three samples were combined into one composite sample before analysis. All glassware, including

amber bottles used for sampling were soaked in acid, and then heated at 60 ºC for 12 h (except the sampling bottles) to prevent emulsion. TCS and TCC were analysed using the GC–MS.

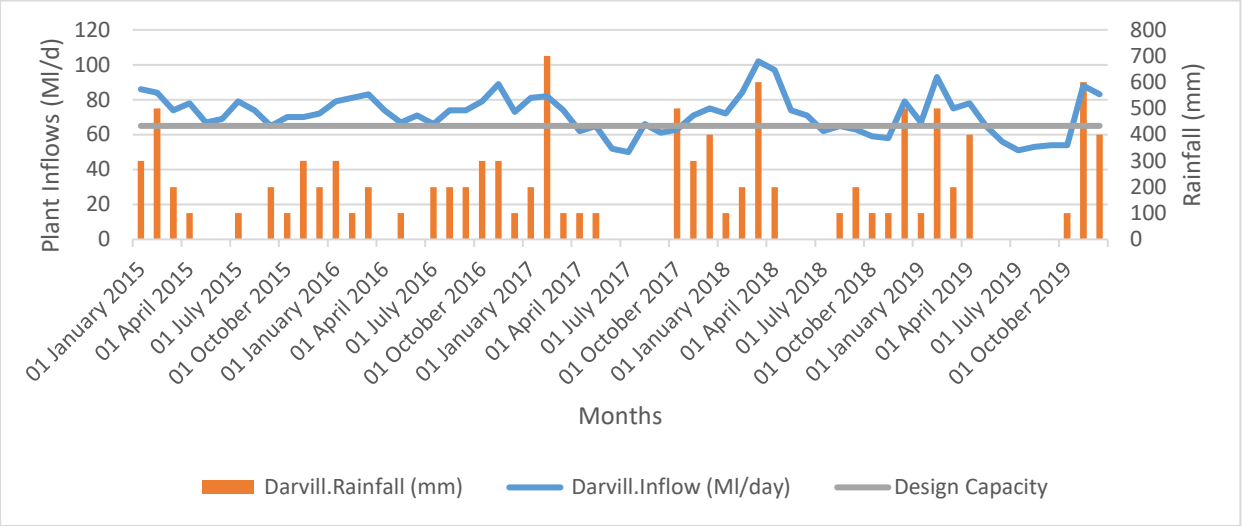


Figure 3.1: Darvill WWTP average monthly inflows and rainfall from January 2015 to December 2019.

3.2.2. Chemicals and reagents

All analytical standards for the 4 –chloroanilline, 2,4-dichlorophenol, triclocarban, triclosan, methyl–triclosan and carbanillide were sourced from Sigma –Aldrich, Schnelldorf, Germany. Derivatizing agent N,O–Bis(trimethylsilyl) trifluoroacetamide (BSTFA), and trimethylsilyl chloride (TMSC) were purchased from Sigma –Aldrich (Johannesburg, South Africa). Analytical grade hydrochloric acid used in the extraction process was bought from Merck (Johannesburg, South Africa). Dichloromethane, acetonitrile, ethyl acetate and methanol were chromasolv grade (99%) purchased from Sigma –Aldrich (Johannesburg, South Africa). Double distilled water was obtained using an aquation Biby A4000D water purification system (Biby Sterlin LTD, UK).

In addition, all carrier gases and the glass fibre filters were purchased from Afrox (Durban, South Africa), and Pall Corporation (Midrand, South Africa), respectively. All chemicals were used without further purification. Small volumes of chemical reagents were transferred using a micro-pipette with sizes ranging from 0.5 to 5000 µL, sourced from the Dragon Lab (Beijing, China). Extraction manifold and sorbents used for Oasis HLB cc (200 mg) were purchased via Microsep from Waters (Milford, USA).

3.2.3. Instruments

The GC–MS (QP2010SE Shimadzu) with a crossbond 5% diphenyl/95% dimethyl polysiloxane capillary column (intercap SMS/Sil 0.25 mmL. D x 30 M df = 0.25 µm) were used for the separation of the sample components. Auto injectors (AOC–20i and AOC–20s) were used to inject samples into the column.

3.2.4. Standard solutions preparation

Twenty–mg of each standard were dissolved in acetonitrile, and then transferred into 20 mL volumetric flask. The final stock solution concentration was 1000 µg/L. A working stock solution of multi-compounds standard of all target analytes was made with a concentration of 100 µg/L. The stock solution was used to make a series of standards with concentrations ranging from 0.5 to 30 µg/L. All standard solutions including the samples were evaporated to dryness under a gentle stream of nitrogen, and subjected to derivatization.

3.2.5. Preparation of wastewater for analysis

Collected wastewater samples were filtered to remove biosolid materials. 200 mL of the aliquot were transferred into a 250 mL bottle, and then acidified to pH 2 using HCl. Samples were extracted using 200 mg oasis HLB cartridges. Cartridges were first conditioned with 6 mL methanol at flow rate of 4–5 mL/min. Thereafter, methanol used for conditioning was then washed with 10 mL of acidified Millipore water at flow rate of 3–8 mL/min.

Target analytes were eluted with 6 mL of acetone/ethyl acetate in a ratio of 1:1 into a 10 mL vial. Moreover, solutions of acetonitrile, methanol, and dichloromethane of each 1 mL at a flow rate between 1 and 2 mL min^{-1} were added. Samples were then pre concentrated under a gentle stream of nitrogen to dryness. For the dried residues, 20 µL derivatizing agent and 10 µL TMSC were added before the vials were placed in an oven at 70 ºC for 30 min. The derivatized extracts were diluted using acetonitrile to 1 mL before they were transferred into gas chromatography vials.

3.2.6. Separation of TCC and TCS using GC–MS

Samples were analysed using a GC–MS (QP2010SE Shimadzu) system, and the separation was performed on a capillary column. The initial column oven temperature was 70 ºC with injection

port temperature kept at 250 ^{o}C, and 1 mL wastewater samples were auto-injected in splitless mode. Helium was used as a carrier gas at a constant flow rate of 8.0 mL/min, and 61.5 KPa. Oven temperature was programmed as follows: start at 70 ^{o}C held for 1 min, ramp to 190 ^{o}C at 30 ^{o}C/min (held for 1 min), ramp to 230 ^{o}C at 15 ^{o}C/min (held for 3 min), and then further ramp to 270 ^{o}C at 30 ^{o}C/min held for 1 min. For the MS detection, electron impact (EI) ionization was adopted, and the electron impact energy was 70 eV. Both the transfer line and ion source temperatures were set at 200 ^{o}C.

In this analysis, the ion trap detector (ITD) settings were as follows: mass range 50–850 m/z (full scan only) with start time of 4 min, and end time of 14 min. To quantify the analytes (TCC and TCS, and their TPs), ITD was operated in the selected ion monitoring (SIM) mode with mass range of 66–252 *m/z* to enhance their detectability in wastewater. For the retention times, main fragment ions that were detected, and the two *m/z* peaks (one for quantification, and another for qualitative information) selected for ion monitoring of the analytes are set out in Table S6 (Appendix).

3.2.7. Quality protocols

To determine validity and fitness of the analytical method used to analyse the targeted contaminants in WWTP, independent solutions were prepared in triplicate. This was achieved by spiking 200 mL of wastewater with the targeted analytes. The final concentrations used ranged from 0.0025 to 10 µg/L. These solutions were extracted using SPE method, and quantified following the method described in Section 3.2.6. And, the sample extracts were derivatized and detected by GC–MS using a set of parameters described in Table S6. Wastewater samples blanks were also quantified following the same procedure as target analytes; and their peak areas were subtracted from the spiked standard in order to obtain absolute recoveries as shown in Equation 3. Retention times and fragmentation patterns listed in Table S6 were used to identify the analytes in wastewater and, peak areas were used for quantification. The analytical method was validated based on limits of detection (LOD), limits of quantification (LOQ), linear regression, and linearity results summa in Table S7. Values of LOD and LOQ were estimated using Equations 1 and 2, respectively. Quality check was done following harmonized guideline of validated single laboratory method, and e (Thompson et al., 2002, and Gonzalez and Angeles Herrador, 2007). Thus the expressions were:

$$LOD = \frac{3\,\sigma}{s} \quad (1)$$

$$LOQ = \frac{10\,\sigma}{s} \quad (2)$$

$$R = \frac{spiked\ (area) - blank\ (area)}{standard\ (area)} \quad (3)$$

where 'σ' is standard deviation of spiked wastewater samples, R is the recoveries, and 's' is the slope of the calibration curve of each targeted analyte, LOD and LOQ are the limit of detection, and limit of quantification, respectively.

3.3. QUANTIFICATION OF TCS AND TCC USING A MODELLING APPROACH

3.3.1. Products inventory development

Herein, the MFA modelling approach was employed to quantify the environmental concentrations of TCS and TCC from variant product categories used within the Msunduzi LM region served by the Darvill WWTP. The estimated quantities of these chemicals entailed those that flow through the Darvill WWTP, and finally into the respective environmental compartments (e.g., recipient river and grounds where sludge is used for agricultural purposes), and via the run–off from areas with no sanitation services. To achieve this objective, the first step entailed the development of an inventory of PCPs containing TCS and TCC. As such, products containing TCS and TCC identified in the commercial centres in Msunduzi LM included soaps, deodorants, toothpastes, etc.

Herein, the approach described by Musee (2018) to identify products containing TCS and TCC was adopted. In brief, two approaches were followed, namely; using online searches, and visit to shops to ascertain the products in commerce in the Msunduzi LM. For the products identified online, they were verified to be, or absent in commerce through retail store visits in Msunduzi LM. Hence, products not found in the retail stores based on online searches within Msunduzi LM were excluded from the inventory. The actual TCS and TCC concentration was sourced from the ingredients list, and published technical and scientific literature. Where information was not available the maximum allowable concentrations (0.3% and 1.5% for TCS and TCC, respectively) specified by the South African Foodstuffs, Cosmetics, and Disinfectants Act

FCDA) of 1972 (Act No. 54 of 1972; Amendment Act, No. 39 of 2007) were used. Among the information incorporated into the inventory includes product category, quantity (mass and/volume), TCS/TCC content, and individual brands. The retrieved data for the developed inventory is listed in Table S14 and Table S15 for TCS and TCC, respectively.

3.3.2. Inventory data synthesis and analysis

To determine the daily usage rates of TCS and TCC from products described in Section 3.3.1 in the context of incomes in Msunduzi LM, daily usage rates published in Europe and USA (ECB, 2003; USEPA, 2011) were used. This was due to lack of data on daily usage of PCPs in SA, but they were adjusted using a set of correction factors. The first world countries values were adjusted to account for differences in income between SA (specifically Msunduzi LM), and the developed countries. Thus, the daily usage for different income groups in Msunduzi LM was calculated using the expression:

$$DQ_{Adjusted(i,j,k)} = DQ_{(i,j)} \times \frac{IP_k}{IP_H} \times \left(\frac{HI_{KZN}}{HI_{SA}}\right) \quad (4)$$

where $DQ_{Adjusted(i,j,k)}$ is the adjusted daily usage of PCPs (where *i* and *j* represent TCS and TCC, respectively) for the Msunduzi LM in g/c/d for a specific income group *k* (where *k* = 1, 2, 3 represents lower, middle and higher income groups, respectively), IP_k is the household income for a specific population group *k*, IP_H is household income for population group with highest income per capita in Msunduzi LM, and $\left(\frac{HI_{KZN}}{HI_{SA}}\right)$ is the ratio of household income of KwaZulu Natal (KZN) to South Africa (SA).

Next, the mass flows of TCS and TCC ($M_{(i,j,k)}$) [g/d] for each income group were estimated using the concentrations of TCS and TCC in each article ($C_{(i,j)}$) [expressed as % (w/w)], adjusted daily usage [g/c/d], and income group population as shown in equation 5.

$$M_{(i,j,k)} = C_{(i,j)} \times DQ_{Adjusted(i,j,k)} \times P_k \quad (5)$$

The calculated quantities represented the potential total mass flows of TCS and TCC released into the Msunduzi LM environment including from run-offs. To accurately account for probable usage, hence the market share for each article was calculated using the expression

previously proposed by Musee (2018) to take into account the local conditions in South African context using the equation:

$$MS_{(i,j)} = \left(\frac{N_{PB}}{N_{BC}}\right) \times \left(\frac{1}{N_P}\right) \times cf \quad (6)$$

where $MS_{(i,j)}$ is the market share for each product containing TCS or TCC, N_{PB} is the number of products in a given brand, N_{BC} is the number of brands in a given category of products, N_P number of specific products determined using the equation $\frac{\sum x_{number\ of\ articles\ sold\ from\ product\ type}}{N_b}$, N_b as the number of brands containing TCS or TCC. $cf = \frac{P_k}{P_T}$ is the ratio of the individual income group population to the total population of Msunduzi LM.

Finally, to obtain the total mass flows of TCS and TCC released to the environment were calculated using the following equation:

$$F_{(i,j)} = \sum M_{(i,j,k)} \times MS_{(i,j)} \times \left(\frac{365}{1000}\right) \quad (7)$$

where $F_{(i,j)}$ is the total quantity of TCS or TCC from all products released into Msunduzi LM region in kg/a.

3.3.3. TCC and TCS flows

TCS and TCC flows released into the Darvill WWTP were estimated based on the number of households (51.6%) connected to the sewer network in Msunduzi LM (Table S8) as shown in equation (8).

$$F_{(i,j)-Darvill} = F_{(i,j)} \times 51.6\% \quad (8)$$

TCS and TCC from industries and sewer tankers into the Darvill WWTP were not taken into account in this model. This is due to lack of data, and owing to likely none companies using these chemicals in the region. Flows into the aquatic system were calculated as the sum of quantities in the final effluent, and the run-offs. Next, quantities of each chemical in the final effluent and sludge were calculated using the estimated removal efficiencies of TCS and TCC. Quantities of TCS and TCC in the final effluent were calculated as follows:

$$F_{eff(i,j)} = F_{WWTP(i,j)} \times (1 - x_{removal}) \quad (9)$$

where $F_{eff(i,j)}$ is the mass flow of TCS or TCC in the final effluent, $x_{removal}$ is the removal efficiency of TCS or TCC from WWTP, and $F_{WWTP(i,j)}$ is the quantity of TCS or TCC in the influent stream at Darvill WWTP. Similarly, the quantities in the sludge were calculated based on removal rates from settling processes using the expression:

$$F_{sludge(i,j)} = F_{WWTP(i,j)} \times x_{sludge} \quad (10)$$

where, x_{sludge} is the fraction of sludge removed by the settling processes of WWTP.

3.3.4. Predicted environmental concentrations

The estimated quantities of TCS and TCC entering the WWTP divided by the plant inflow to estimate the PECs. The PECs in surface water were determined on the assumption that the final effluent and run-off were thoroughly mixed in the Msunduzi River following discharge. The PECs (ng/l) of TCS and TCC in the effluent were calculated using the equation:

$$PEC_{effluent} = \frac{F_{eff(i,j)} \times 10^6}{F_{WWTP\,(Total)} \times 365} \quad (11)$$

where $F_{eff(i,j)}$ is the residual flow of TCS and TCC present in the final effluent (in kg/year) calculated using equation 9, and $F_{WWTP\,(Total)}$ is the total wastewater flow rate in Ml/d. Predicted environmental concentrations in surface water were then calculated using the equation:

$$PEC_{freshwater} = \frac{PEC_{(effluent)}}{DF} \quad (12)$$

where $PEC_{freshwater}$ is the predicted environmental concentration in surface water, $PEC_{(effluent)}$ as the predicted environmental concentration in the final effluent, and DF is the dilution factor. Three different dilution factors (1, 3, and 10) were used to account for seasonal variation. The proposed dilution factors for SA range from 10 to 40 (Keller et al., 2014), however, lower values were selected for this study to account for low or no precipitation during

winter months based on the data listed in Table S16. Finally, the PECs in the sludge were calculated from the estimated quantities in sludge (using Equation 9), allowable maximum sludge application rate in South Africa (App_{sludge} = 1.0 kg/m^2.year (Synman and Herselman, 2006)), bulk density (RHO_{soil} = 1 700 kg/m^3), and agricultural mixing depth (D_{soil} = 0.2 m) (EEC, 1986; ECB, 2003) using the expression:

$$PEC_{soil} = \frac{C_{sludge(i,j)} \times App_{sludge}}{RHO_{soil} \times D_{soil}} \quad (13)$$

where, $C_{sludge(i,j)}$ is the concentration of TCS and TCC in the sludge calculated as the ration of chemical quantity in the sludge to the total sludge production as follows:

$$C_{sludge(i,j)} = \frac{F_{sludge(i,j)}}{F_{sludge(Total)}} \quad (14)$$

3.4. ENVIRONMENTAL RISK ESTIMATION

3.4.1. Predicted no concentration effect

Procedures prescribed in the Technical Guidance Document (ECB, 2003) and collected dose – response ecotoxicological data from literature were used to calculate predicted no effect concentrations (PNEC). PNEC is a ratio of the acute half maximum life concentration (EC_{50}) or half lethal concentration (LC_{50}) or no –observed –effect –concentration (NOEC) to the assessment factor (AF) (estimated from Table S9) expressed as:

$$PNEC = \frac{EC_{50}\ or\ LC_{50}\ or\ NOEC}{AF} \ . \quad (15)$$

The ecotoxicological data used in this study were for the taxa: fish, *Daphnia magna*, and algae (for freshwater), microorganisms (for wastewater), and soil plants, microorganisms, and earthworm (for terrestrial).

3.4.2. Ecological risk assessment

The risk characterization for TCS and TCC in different environmental compartments were estimated by the risk quotient (RQ) methodology. RQ is a ratio of PEC to PNEC, and expressed as:

$$RQ = \frac{PEC}{PNEC} \quad (16)$$

Risk characterization as proposed by ECB (2003) suggest likely risks if RQ > 1, and conversely unlikely for RQ <1.

CHAPTER 4:

RESULTS AND DISCUSSION

4.1. QUALITATIVE ANALYSIS

4.1.1. Analysis of TCC, TCS and their TPs in Darvill WWTP

A qualitative analysis was conducted to determine likely micropollutants of emerging concern present at Darvill WWTP. The assessment was aimed to generate initial data on the potential micro–contaminants present in the wastewater, and plausible impact to the WWTP functioning, and potential effects to aquatic life after eventual release into the ecological systems. In this work, analytes of interest were TCS, TCC, and their consequent TPs formed in wastewater.

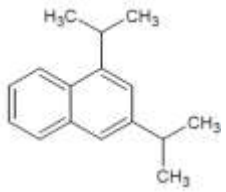
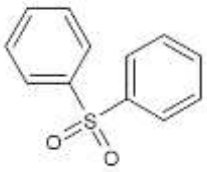
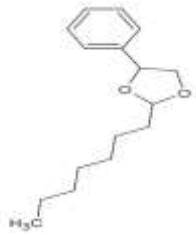
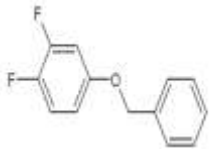
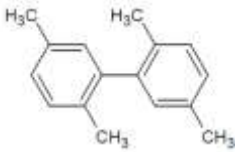
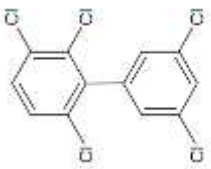
Analysis was done on the influent samples taken before the primary sedimentation stage. Results of the qualitative analysis indicated the presence of polycyclic aromatic compounds including diisoprophylnaphthalenes (DIPN) (namely 1,3–DIPN, 1,4–DPIN, 1,7–DPIN, and 2,6–DIPN), and diphenyl sulfone. DIPNs are synthetic compounds used in carbonless copying and thermal papers, paper wrappings, ink for inkjet printers, plant growth regulators, potato skin, heat-transfer media, and solvents for pesticides (Todd, 1988; Lewis et al., 1997; Terasaki et al., 2008; Suzuki et al., 2012). In addition, they are also used as substitutes for polychlorinated biphenyls (PCBs) in the manufacturing of printed paper (Terasaki et al., 2008), and food packaging materials (Nerín and Asensio, 2007).

Notably, DIPNs are highly persistent in the environment, and reports indicate they can bioaccumulate in green mussel, fishes and shrimp, and previously detected as contaminant in food (from wrapping with recycled paper) at non-toxic levels (Suzuki et al., 2012; Dsikowitzky et al., 2015). Moreover, diphenyl sulfones are organosulfur compounds mostly used as monomers in the polymer industry, but also formed as TPs in the synthesis of benzenesulfonic acids and chlorides (Bueno et al., 2009). For context, industrial influent treated at the Darvill WWTP are from sources including paper, oil and dye industries, etc., and therefore, were deemed as probable origins of these compounds.

In the secondary treatment stage, diverse compounds were detected, and these included: N–Aminopyrrolidine, 4–Pyridinamine, N,N–dimethyl–, 1–Pyrrolidinamine, 4,5–Dichloro–1,3–dioxolan–2–one, 1,3–Dioxolane, 2–heptyl–4–phenyl–, 4–Quinolinol, 8–chloro– and 6–Chloro–4–quinolinamine. These compounds are categorised as carcinogenic and mutagenic to animals and humans (Hirao et al., 1976; Minako, et al., 1977; LaVoie, et al., 1984). Quinolinols and its derivatives are nitrogenous organic compounds used as raw materials in the chemicals, dye manufacturing, and pharmaceutical industries (Zhu et al., 2008). Other compounds detected in the biological reactor included 2,4,6 –trichlorobenzyl alcohol, methyl ether; nitrosobenzene; 3–Nitro–N'–[(E)–4–pyridinylmethylidene] benzohydrazide; N–aminopyrrolidine; 1,3–DIPN; 1,4–DIPN; 1,7–DIPN; 2,6-DIPN; Diphenyl sulfone; Benzaldehyde, 2,4–dihydroxy– ; 1,3–Dioxolane, 2–heptyl–4–phenyl– and 2,4–Difluorobenzene, 1–benzyloxy. One notable characteristic of these compounds is the breadth of their uses, and so is their sources. For example, 1,3–Dioxolane is an industrial solvent and typically used widely in the production of coating materials, strong adhesives, lithium–sulfur battery electrolyte, textile, electroplating, polymer, and gasoline (Aurbach, 2000; Yabueng and Napathorn, 2018). And, Nitrosobenzene is used as an intermediate in the synthesis of azomethine derivative, allylamines, and oxazines.

After the influent went through variant treatment stages, diphenyl sulfone, 1,3–di–iso–propylnaphthalene, 1,3–Dioxolane, and 2–heptyl–4–phenyl were also detected at the effluent stream before the chlorination process. This implies these compounds were incompletely removed. Polychlorinated biphenyls (PCBs) were also detected in the final effluent after chlorination, and these were 1,1'–Biphenyl,2,3,4,4',6–Pentachloro–, and 2,2',3,4',5,6–Hexachloro–1,1'–biphenyl. PCBs are manufactured for different industrial uses and are still in use, although were banned in 1977 in the USA (USEPA, 2005). These compounds are widely incorporated in dielectric fluids in capacitors and transformers, adhesives, heat transfer fluids, hydraulic fluids, lubricating oils, as additives in paints, carbonless copy paper, adhesives, and sealants (Breivik *et al*., 2002; Korytar et al., 2002). PCBs are persistent in the environment, carcinogenic, bioaccumulate in terrestrial ecosystems, and toxic to the ecosystem and human (Manodori *et al*., 2006; Xing *et al*., 2005). Notably, PCBs sources to the environment and WWTPs includes illegal releases from industries, historical stocks in building materials, and electrical transformers. A summary of chemicals detected in the final effluent are listed in Table 4.1.

Table 4.1: Diverse compounds detected qualitatively at the Darvill WWTP final effluent using GC–MS.

Compound Name	Structure	Molecular Formula	Molecular Weight (g/mol)	CAS Number
1,3–di–iso–propylnaphthalene		$C_{16}H_{20}$	212	57122–1 –4
Diphenyl sulfone		$C_{12}H_{10}O_2S$	218	127–63–9
2–Heptyl –4 –phenyl –1,3 –dioxolane		$C_{16}H_{24}O_2$	248	55668–40–1
2,4–Difluorobenzene,1–benzyloxy–		$C_{13}H_{10}F_2O$	220	152434–86–1
1,1'–Biphenyl,2,2',5,5'–tetramethyl–		$C_{16}H_{18}$	210	3075–84–1
1,1'–Biphenyl,2,3,4,4',6–Pentachloro–		$C_{12}H_5Cl_5$	324	74472–37–0

These results offer qualitative evidence that chemicals of emerging concern used in diverse industries as raw materials and additives eventually end up into the Darvill WWTP sewer network, and eventually into the ecosystems following their incomplete removal during

treatment processes. Consequently, they may induce unknown deleterious impacts to biological wastewater treatment processes, and eventually the aquatic life. Therefore, there is need to characterise and quantify their levels of ecological risks. This is because such data are severely lacking, hence this should constitute future research agenda. The generated information from such efforts are essential to develop science evidence-based discharge standards (enforceable bylaws) from point sources, or industries in pursuit to protect the human health, and ecological integrity.

4.2. QUANTITATIVE ANALYSIS

4.2.1. Quantification of TCS and TCC in variant treatment processes

Concentrations of TCS and TCC were evaluated at selected stages of the treatment processes within the Darvill WWTP using GC–MS in SIM mode. Recoveries for both TCS and TCC were > 90%; hence, an indication of good method recovery (Thompson et al., 2002). Notably, both compounds were not detected from the blank samples during the validation tests. The LODs for TCS and TCC were 48.9 and 15.3 ng/L; whereas the LOQ were 163 and 51.1 ng/L, respectively (Table S7).

Results obtained at different treatment units during the sampling period of August to December 2020 for TCS and TCC are pictorially presented in Figure 4.1 and Figure 4.2, respectively. It was also observed that, both compounds were detected at all the treatment unit samples. The concentration ranges for TCS and TCC, respectively, were: Influent (1.02 – 3.37; 0.45 – 1.1 µg/L), reactor feed (< LOD–2.06; 0.15 – 1.2 µg/L), PST underflow (1 – 3.2; 0.45 – 0.74 µg/L), SST feed (0.71 – 1.39; 0.45 – 0.58 µg/L), SST effluent (0.74 – 1.45; 0.45 – 0.57 µg/L), RAS (0.99 – 3.42; 0.44 – 0.62 µg/L), WAS (0.66 – 1.42; 0.44 – 0.57 µg/L), final effluent (<LOD – 1.17; < LOD – 0.58 µg/L). Tabulated data are presented in Appendix (Table S10). The results equate to mean TCS and TCC influent flows into Darvill WWTP of 44.82 and 18.01 kg/a, respectively. Further, the quantities of TCS and TCC reaching the Msunduzi River were estimated to be 18.21 and 9.9 kg/a, respectively (Figure 4.3).

Highest influent concentrations were recorded in the month of September 2020 for TCS (3.37 µg/L), and October 2020 for TCC (1.1 µg/L). However, no variations were evident in other months over the period assessed for both compounds (Table 4.*4*). These high peaks were likely due to the first rains, and as a result entrained higher pollutant concentrations from the

catchment area. This in turn, may have settled and accumulated higher concentrations of TCS and TCC in the sewer network. Results herein are in agreement with previous works on spatial variation of pollutants where their highest concentration peaks of pollutants were observed at the start of a wet season (Sun et al., 2018).

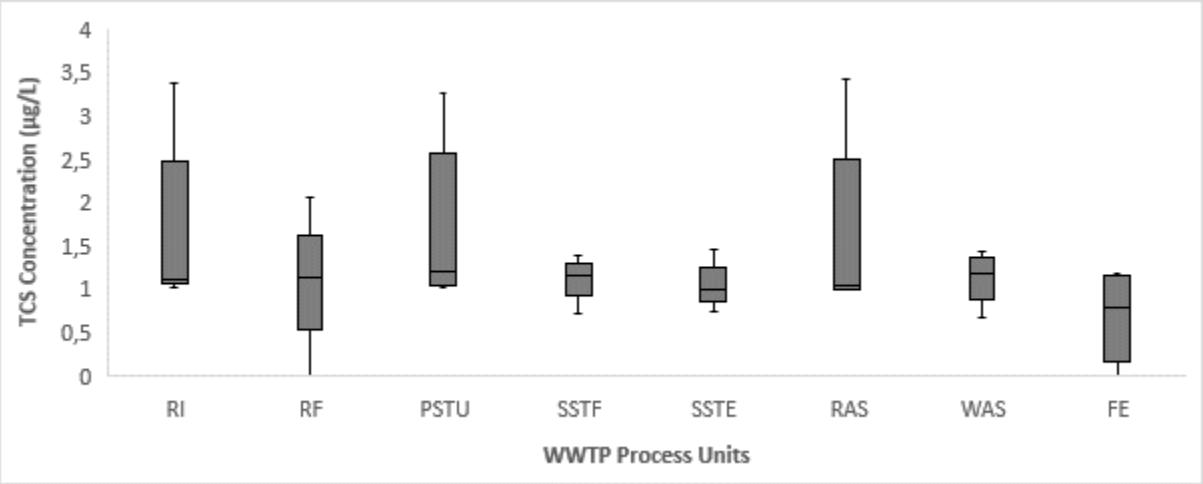


Figure 4.1: Measured concentrations (n = 5) of TCS across the Darvill WWTP at different treatment processes[1].

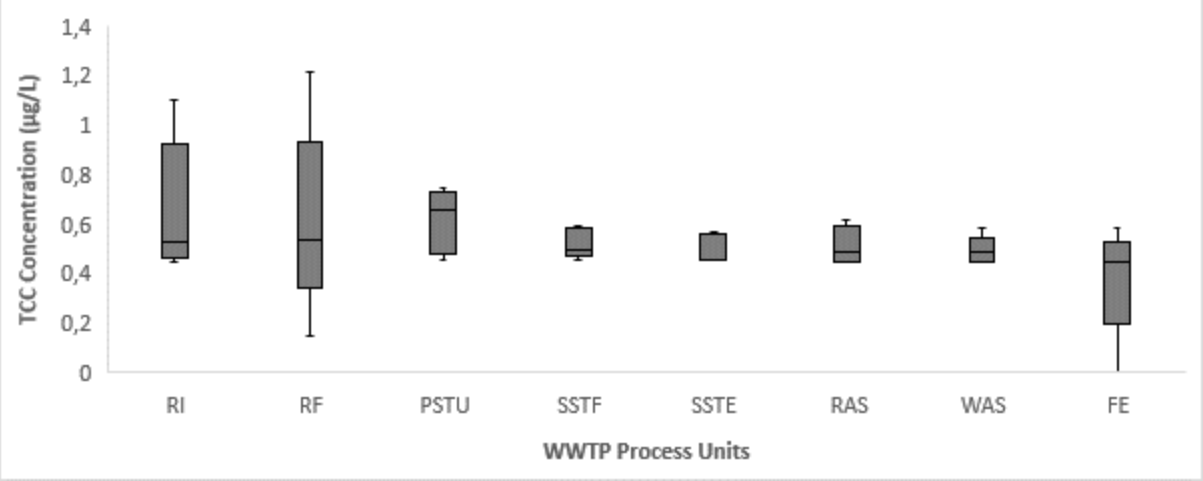


Figure 4.2: Measured concentrations (n = 5) of TCC across the Darvill WWTP at different treatment processes.

[1]RI – raw influent, RF – reactor feed, PSTU – primary settling tank underflow, SSTF – secondary settling tank feed, SSTE – secondary settling tank effluent, RAS – return activated sludge, WAS – waste activated sludge, and FE – final effluent.

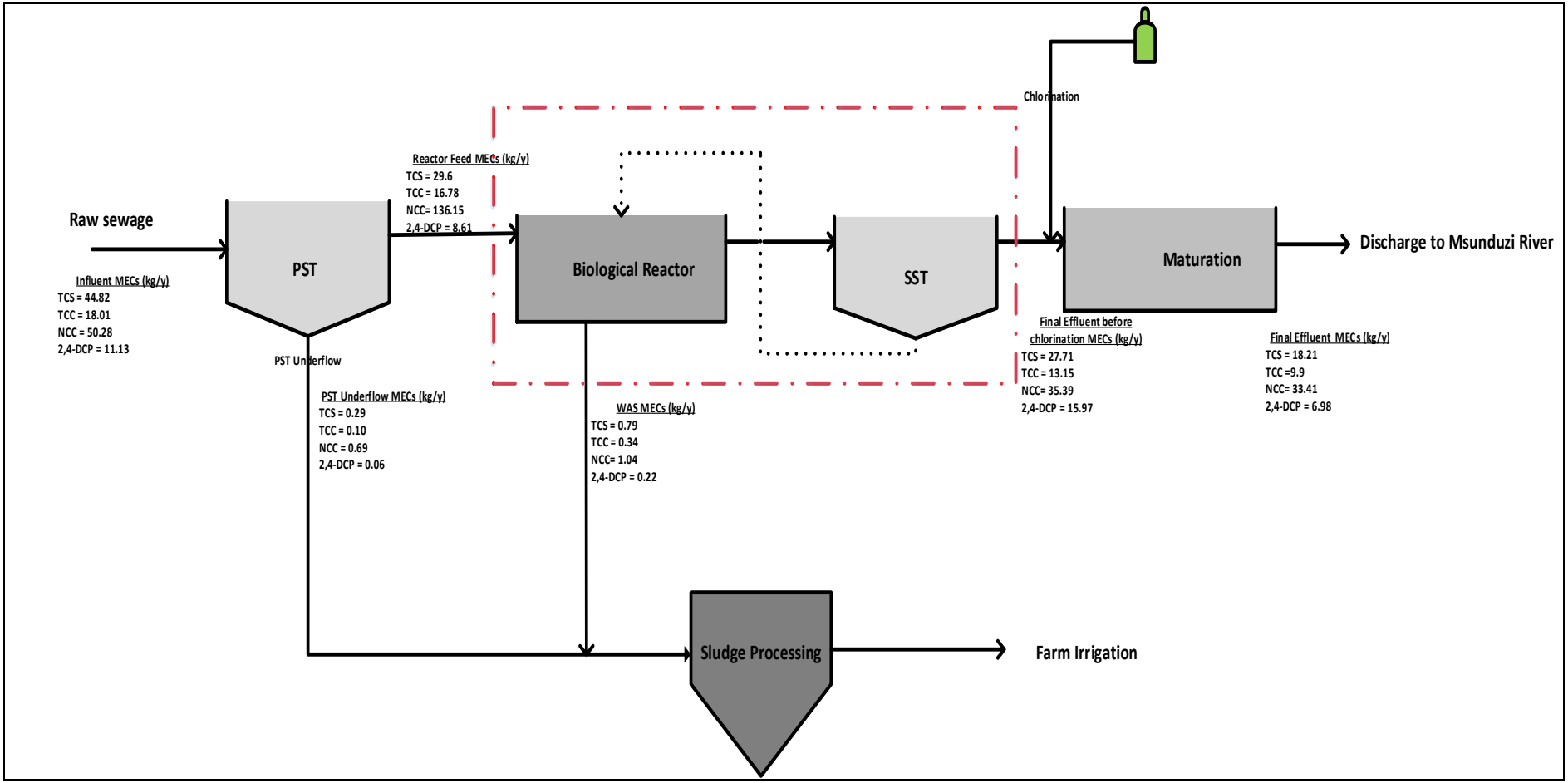


Figure 4.3: Schematic of the wastewater treatment train showing annual flows of TCS, TCC, MCC, and 2,4–DCP at different process unit calculated from measured environmental concentrations.

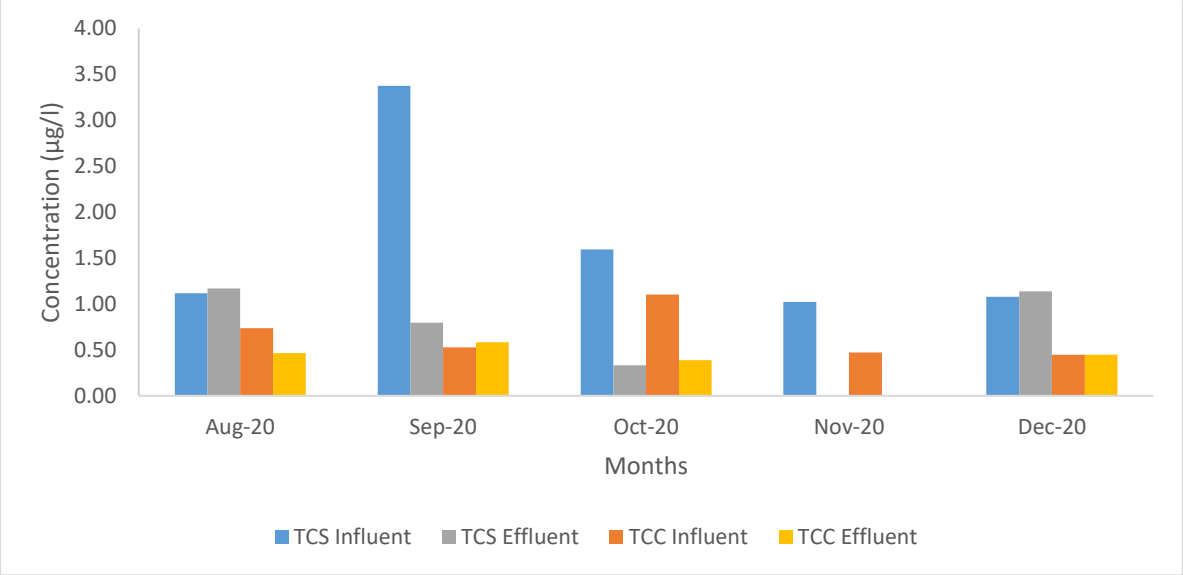


Figure 4.4: Measured monthly concentrations of TCS and TCC in Darvill WWTP both for the influent and treated effluent.

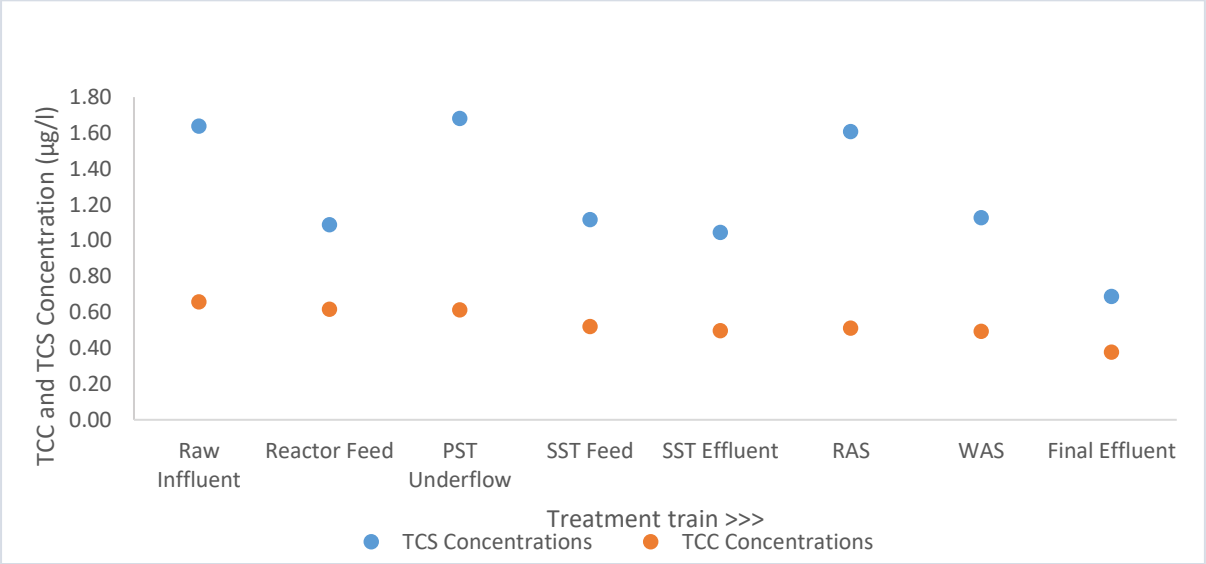


Figure 4.5: Mean TCS and TCC concentrations across the Darvill WWTP over a five month period (August – December 2020) sampled once per month. Standard deviation ranged from 0.2-1 and 0.05-0.3 µg/L for TCS and TCC, respectively. >>> signifies the flow of influent process treatment train

Results indicated low removal efficiencies for both compounds across the treatment plant. The overall removal efficiency for TCC was 45%, while TCS had an overall removal efficiency of 59%. Highest removal for TCS was from the primary sedimentation with the efficiency of 34%, whilst the biological system yielded very low removal of 6%. Conversely, TCC was mostly removed from the biological system (22%) with primary sedimentation reaching only 6.8% removal efficiency. The results also demonstrates that TCS concentrations were considerably 2–fold higher relative to TCC. These findings are in agreement with measured concentrations previously reported by Lehutso et al (2017) from six wastewater treatment plants in Gauteng, South Africa where TCS was observed to be higher relative to TCC. Further, the concentration range for TCS is on the lower end of the range previously reported by Madikizela, et al (2014) from a study conducted in Durban, KwaZulu Natal Province (1.02–3.37 versus 2.1–9 µg/L). Both TCS and TCC concentrations detected in this study were lower relatively to maximum influent wastewater concentrations reported elsewhere in South Africa (Amdany et al, 2014; Madikizela, et al 2014; Lehutso et al, 2017).

Of the three studies, two were in Gauteng Province (Amdany et al, 2014; Lehutso et al, 2017) and one in Durban, KwaZulu Natal Province (Madikizela, et al 2014). Overall, the results on the detected TCC and TCS concentrations point to likely dependency on the income per capita in the region in question. Hence, owing to steep income distribution disparities in South Africa – with Gauteng Province per capita relatively higher than KwaZulu Natal Province (Statistics South Africa, 2018; Musee, 2018) – and wide spatial population densities among regions (e.g., 116 versus 726 persons/km2 for KwaZulu Natal and Gauteng, respectively, may among other factors partly account for the differences on detected concentrations observed.

The occurrence of TCS, TCC, DIPNs, 2–Heptyl–4–phenyl –1,3–dioxolane, and PCBs in the final effluent at the Darvill WWTP point to urgent need to identify suitable technologies to improve their removal, and in turn, minimize risks to the aquatic species in the receiving ecosystems. This aspect is not just isolated at Msunduzi LM, but across South Africa as similar sources are across the country. Such technologies when considered should include plausible retrofitting into the existing WWTPs e.g., as a pre–treatment step (especially for industrial effluent stream), and to polish the final effluent before release into the Msunduzi River, or any other surface systems. Among plausible candidate technologies may include advanced oxidation processes (AOP), activated carbon absorption, coagulation-flocculation, and membrane filtration as they are known to effectively remove a variety of micropollutants

including PCPs from wastewater (Röhricht et al.,2009; Hernández–Leal et al., 2011; Gerrity et al., 2011; Yangali–Quintanilla et al.,2011; Matamoros and Salvadó, 2013).

Various studies have documented acute toxicity of TCS to algae, crustaceans and fish (Orvos, et al., 2002; Ishibashi, et al., 2004; Franz, et al., 2008). Moreover, TCC has been shown to bioaccumulate in aquatic species and cause lipid weight in fish (Houtman et al., 2004). In addition, results on risk assessment investigations using RQ method (described in Section 3.4) indicated both compounds can induce deleterious impacts to aquatic life, terrestrial organisms, and wastewater microorganisms (Musee, 2018; Mohan and Balakrishnan, 2019). This necessitates risk assessment studies of both contaminants to generate data essential to develop guidelines, and benchmarks that can aid to inform set effective wastewater and biosolids discharge limits. To achieve this overarching goal, further monitoring and analysis of these pollutants need to be done across the Msunduzi River catchment area, and other regions across South Africa. The data and knowledge base can serve as sound scientific basis to develop strategies aimed to improve the management of both pollutants in the environment, and also to protect the human health.

4.2.2. Removal efficiencies of TCC and TCS

The removal efficiencies of the target analytes was monitored from the primary, secondary, and tertiary treatment stages of the Darvill WWTP. During the sampling period, the overall performance of the plant with respect to COD and suspended solids (SS) removal were 86% on average (range of 20–426 mg/L) and 80% (range of 10–316 mg/L), respectively. The average mass flows of TCS, TCC, and their TPs are summarized in Figure 4.3. In the primary treatment, influent wastewater flows into three PSTs through a splitter box. The PSTs allows solid/liquid separation by settling suspended solids present in the wastewater. The PSTs are designed to partially reduce the COD, total Kjeldahl nitrogen (TKN), and phosphorus loads before release into the activated sludge reactors by 30%, 15%, and 20%, respectively. Settled solids are continuously removed, and then taken to the sludge treatment, while the supernatant flows into the bioreactors for further treatment. From the detected TCS and TCC concentrations in the influent yielded mass flows of 44.8 and 18 kg/a. And, in the primary treatment their concentrations can be reduced to mass flows of 29.6 and 16.8 kg/a, respectively, for TCS and TCC resulting to removal efficiencies of 34 and 6.8%. The resultant mass flows removed from

the PST underflow with the primary sludge were 0.29 and 0.1 kg/a for TCS and TCC, respectively. Hence, TCS removal was relatively higher to that of TCC.

TCS and TCC concentrations entering the reactor were 1.09 and 0.61 µg/L, whereas those of the effluent were 0.69 and 0.37 µg/L, respectively. Hence, the concentrations of both TCS and TCC did not change significantly (p = 0.3 and 0.55, respectively) over the secondary treatment processes (biological reactor and SST). The resultant removal efficiencies were low at 6% and 22% for TCS and TCC, respectively. However, a notable increase in the concentration of TCS in the RAS stream was observed (Table 4.1). These findings suggest probable accumulation of TCS within the system, and low degradation over 12-h HRT (both reactor and SST), and 12-d SRT. Further, the accumulation may pose detrimental impacts to the microorganisms essential for wastewater treatment, and hence, induce adverse implications on the overall WWTP performance. This, in turn raises the need to conduct risk assessment on the implications of TCS and TCC to specific microorganisms present in the WWTP at current and future compounds concentrations in the biological reactor. Such data can inform decision(s) on whether to include process units/technologies with capabilities to adequately remove micropollutants in future designs to protect microorganisms essential to treat wastewater.

Studies have documented that the key transformation mechanisms of TCS and TCC in wastewater are chlorination/dechlorination and hydroxylation processes, and in turn, leading to formation of variant TPs (Armstrong et al., 2018; Wang and Wang, 2019). Herein, four common TPs, viz.: MeTCS, 2,4–DCP, 4–CA, and NCC of TCS and TCC were monitored during the assessment period. Results showed that MeTCS and 4–CA were below LOD in all samples, and irrespective of the treatment stage investigated. Conversely, 2,4–DCP and NCC were detected in all samples (Table S10) including at the influent. For example, a concentration of 0.34 and 1.52 µg/L for the 2,4–DCP and NCC, respectively, were detected in the influent during the month of August 2020. The presence of these TPs at the influent suggest likely transformation of TCS and TCC occurred upstream in the collection system before reaching into the WWTP.

Additionally, degradation and photolysis of other compounds from industrial sources may have also contributed to the formation of both 2,4–DCP and NCC. Results herein demonstrates that the concentrations of the TPs did not significantly change ($p > 0.56$ and $p > 0.32$ for 2,4-DCP NCC, respectively) during the assessment period and throughout the WWTP process. Previously, formation of 2,4–DCP was observed in studies conducted in simulated benchtop

nitrifying reactors at pH range of 6.5–7.5 (Armstrong et al., 2019), a pH comparable to one of 6.8–7.9 of the influent at the time of this study.

The overall TCS mass loss was 26.7 kg/a (difference between influent and effluent quantities), but the formation of 2, 4–DCP increased at the SST effluent (before chlorination) with a mass gain of 4.84 kg/a, but decreased following the chlorination process. In addition, the possibility that 2,4–DCP may have been further chlorinated or converted to other TPs e.g., 2,4,6–trichlorophenol cannot be ruled out. From these findings, about 15.6% of the overall TCS loss may be attributed to the formation of 2,4–DCP, and the rest to removal through adsorption onto the sludge. In previous works, up to 50% of TCS removal through adsorption on the sludge has been reported owing to its high octanol-water coefficient (4.8 at 25 °C) (Bester, 3003; Haidler and Halden, 2007), and the findings are in agreement with this study. This is attributed partly to particle settling due to high suspended solids associated with the activated sludge process.

Other works have documented the detection of 2,4–DCP in the Eastern Cape Province, South Africa in wastewater, and receiving rivers at a concentration of 657 ng/L (Yahaya et al., 2019). 2,4–DCP is an endocrine disrupting chemical that affects sex hormone synthesis in fishes, for example, it has been observed to induce estrogenic effects in zebrafish (Zhang et al., 2008; Ma et al., 2012; Xiao et al., 2017). In addition, 2,4-DCP is among listed priority toxic pollutants by USEPA (USEPA, 2002), and thus raises the need for its quantification along the Msunduzi and Mgeni Rivers (in the catchment area of the downstream WTPs). The generated data will aid to determine potential impacts to drinking water quality, human health, and aquatic life. The high levels of NCC at Darvill WWTP requires a further assessment of the sewer system, for example, to aid trace the major contributors and/or point sources (e.g. industries, or variant commercial activities, or settlements). Notably, the overall TCC loss of 8.02 kg/a did not correlate to a gain in NCC throughout the WWTP given that the NCC/TCC ratio was relatively constant at about 3. These results indicated that NCC had an overall removal efficiency of 46%, similar to that of TCC (45%).

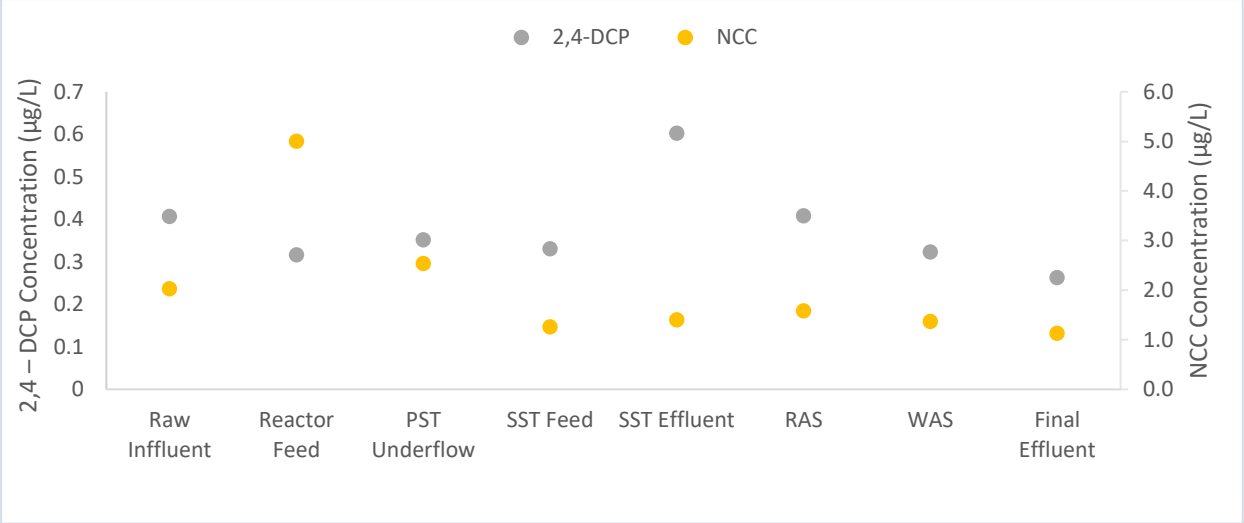


Figure 4.6: Mean concentrations of the TPs 2,4–DCP and NCC across the WWTP over a five month period (August – December 2020) sampled once per month. Standard deviation ranged from 0.05-06 and 0.3-6.6 µg/L for 2,4-DCP and NCC, respectively.

4.3. MODELLING ANALYSIS

Modelling analysis performed herein was motivated by the limited data of MECs for the TCS and TCC not just in South Africa, but across Africa partly owing to analytical analysis being highly costly (Ebele et al., 2017). The objective was to model TCS and TCC flows from PCPs, their likely concentrations into different environment matrixes, and potential risks to taxa at variant levels of biological organizations. And, to test the robustness of the proposed model based on the MFA approach, the estimated PECs were compared with MECs derived from this study.

4.3.1. Inventory analysis

To develop an inventory for this study, first, products containing TCS and TCC were searched online, in scientific literature, and thereafter, physically were confirmed by visits to the retail shops within the Msunduzi LM. The number of products containing TCS and TCC were 90 and 36, respectively (Table S14 and Table S15). These products were lower relative to the inventory developed for the Gauteng Province (GP), South Africa, which had 128 and 52 products for TCS and TCC, respectively (Musee, 2018). Gauteng Province has the second highest income per capita in South Africa after the Western Cape Province whilst KwaZulu

Natal is number five (Table S11). For both TCS and TCC, all products identified and recorded in the inventory were in the PCPs category.

The distribution of TCS-containing products were as follows (Table S14 and Table S15): 67 deodorants (74.4%) in eight brands, 7 were liquid hand soaps (7.7%) in three brands, 7 were toothpastes (7.7%) in one brand, 4 facewashes (4.4%) in one brand, 3 hair products (3.3%) in one brand, and 2 bar soaps (2.2%) in one brand. The results are in agreement with previous studies where PCPs were the highest product category incorporating TCS with deodorants and liquid hand being the highest and second dominant products, respectively (SCCP, 2009; QYResearch, 2015; Musee, 2018). The distribution of TCC-containing products were as follows (Table S13 and Table S15): 29 bar soaps (80.5%) in four brands, 4 liquid hand soaps (11.1%) in one brand, and 3 shower gels (8.3%) in one brand. These results are also in agreement with previous inventories reported elsewhere (Perencevich et al., 2001; Halden and Paull, 2005; European Commission, 2005; Musee, 2018).

4.3.2. Flows of TCC and TCS

The TCS and TCC flows into the Msunduzi LM environment from different PCPs were estimated based on daily usage data for product categories (extracted from ECB, 2003, and modified as per Musee (2018) proposed protocol), income per capita, population, and the compounds concentrations in a given product article. The results (Table 4.2) showed different income groups usage per day, and were lower relative to data for developed countries (ECB, 2003; USEPA, 2011), and Gauteng Province (Musee, 2018). This is for two-fold reasons. First, South Africa is a developing country; hence, the purchasing power per capita is lower relative to that of developed countries e.g., Europe or USA (World Bank, 2020). And secondly, the Msunduzi LM is a semi-rural municipality within the KZN province, and hence, has lower income per capita in comparison to GP (Table S11) (Statistics SA, 2016).

Table 4.2: Estimated daily usage rates for different PCPs in Msunduzi Local Municipality, KwaZulu Natal, South Africa based on their incomes per capita.

Product category	Usage per Income Groups (g/c/d)		
	Lower	**Middle**	**Upper**
Bar soaps	0.06	0.47	1.88
Liquid soups	0.06	0.47	1.90
Hand wash	0.02	0.18	0.71
Shower gel	0.12	0.98	3.91
Aftershave	0.02	0.16	0.63
Toothpaste	0.03	0.27	1.10
Body lotion	0.19	1.50	6.00
Hand lotion	0.01	0.05	0.21
Deodorants	0.10	0.78	3.13
Face treatments	0.06	0.46	1.85
Hair products	0.12	0.98	3.94

The estimated quantities of TCS and TCC flows into the Msunduzi LM environment were 87 and 120 kg/a, respectively (Table 4.3). Further, the resultant consumption per capita of TCS and TCC, respectively, were estimated as 128.5 and 176.2 mg/c/a, and significantly lower relative to developed countries (McAvoy, et al., 2002; Heidler & Halden, 2007; Heidler & Halden, 2009; Huang, et al., 2014). Herein, TCS concentration used was 0.3% (maximum allowable value in SA) (FCDA regulations, Act No. 54 of 1972; Amendment Act, No. 39 of 2007) due lack of available data on the products' list of ingredients, and also due to lack of information from online sources. For the TCC, the concentrations ranged from 0.02 to 1.5%. Although the number of products containing TCS exceeded two and half-folds to those of TCC-containing products, however, total TCC flows into the environment were higher. The maximum allowable concentrations of TCS and TCC found in PCPs in South Africa were 0.3 and 1.5%, respectively, (Musee, 2018). Plausibly this may account for the higher TCC estimated consumption per capita relative to TCS. It should be noted, however, that the daily consumption estimated values are likely to be lower since in certain products, the actual

concentration in a given product may have been lower (below 1.5% recommended maximum value).

Deodorants (77.5%) followed by toothpaste (12.5%), and the bar soaps (98.7%) contributed the highest flows of TCS and TCC, respectively. These product categories are widely used for bathing and body freshening, and also affordable including by low and middle income earners relative to other product categories considered as luxurious and non-essentials. This assertion is supported by higher market penetration of these product types (e.g., at 0.3, 0.99, and 0.51%, correspondingly, for deodorants, and. toothpaste, and bar soaps) (Table S14 and Table S15) compared to other product categories where market penetration were in the lower range of 0.04 to 0.31%.

Table 4.3: Estimated aggregate quantities of TCS and TCC released from different PCPs categories into the Msunduzi LM environment.

Product Category	TCS (kg/a)				TCC (kg/a)			
	Lower Income	Middle Income	Upper Income	Total	Lower Income	Middle Income	Upper Income	Total
Bar soaps	0.06	0.34	0.05	0.5	15.9	79.59	22.13	117.62
Hand wash	0.28	1.41	0.39	2.1	0.01	0.06	0.02	0.08
Shower gel	-	-	-	–	0.26	1.32	0.37	1.95
Toothpaste	1.48	7.4	2.05	10.9	-	-	-	–
Deodorants	9.12	45.67	12.7	67.5	-	-	-	–
Face treatments	0.59	2.99	0.83	4.4	-	-	-	–
Hair products	0.25	1.25	0.34	1.9	-	-	-	–

In Msunduzi LM, some 52% of the households were connected to the sewer system with the rest using pit latrines (Statistics SA, 2016). As a result, the estimated quantities of TCS and TCC flows into the Darvill WWTP were 45 and 62 kg/a, respectively. The rest (TCS and TCC as 42 and 58 kg/a, respectively) were assumed to be released through run-offs, and directly into the aquatic environment. The sewage from pit latrines are collected in trucks and eventually discharged into the Darvill WWTP for treatment, however, these were not taken into account in the model calculations as they were assumed to contribute negligible concentrations of TCS and TCC (from low income groups). Using the Equations (reference the range of equations in

chapter 3 that led to the results in Table 4.4), the final effluent discharged into the Msunduzi River was estimated to contain 7 and 9 kg/a for TCS and TCC, respectively. Quantities in the final effluent were observed to be dependent on removal efficiencies, as well documented in literature previously (Heidler et al., 2006; Lozano et al., 2013) with lower values used in this study to account for poor WWTP efficiency in comparison to other countries (Musee, 2011; Musee, 2018). And, the quantities estimated in the soil through sludge use for irrigational purposes were 14 and 19 kg/a for TCS and TCC, respectively.

Table 4.4: Estimated quantities of TCS and TCC released into different environmental matrixes in the Msunduzi LM based on model inputs used in this study.

Variable	**TCS**	**TCC**
Total flows into Msunduzi LM (kg/a)	87	120
Fraction of treated wastewater (Statistics SA, 2016)	0.52	0.52
Quantity released into Darvill WWTP (kg/a)	45	62
Quantity in the sludge (kg/a)	14	19
Quantity in the final effluent (kg/a)	7	9
Quantity degraded (kg/a)	25	34
Quantity released through run –off (kg/a)	42	58
Total quantity reaching freshwater (kg/a)	49	67

4.3.3. Predicted environmental concentrations

The PECs of TCS and TCC released into Darvill WWTP were computed from the estimated quantities (Table 4.4), and plant inflows data (Table S16), and results are summarised in Table 4.6. PECs estimates for TCS in the influent ranged from 1 346 to 2 043 ng/L (see Figure 4.7) with an average of 1 645 ng/L. These values were computed using annual average plant flow for the year 2020). For the TCC, higher estimates of PECs in the effluent ranged from 1 845 to 2 800 ng/L, and with an average of 2 254 ng/L (Figure 4.7). The lowest concentrations were observed for the month of February 2020 due to high rainfall and inflow (higher dilution factor effect), and the highest concentrations for August 2020 as was the driest month, hence with least rainfall (Table S16). The model results were deemed to be in good agreement with the

MECs (Table 4.5). This is because the ratios of PEC to MEC were in the range of 0.7-5 and 0.2-1.8, respectively, for TCC and TCS. Notably, model results for estimated PECs are considered good if are within the established criteria, thus; ranked as accurate (0.5 < PEC/MEC< 2), and acceptable (2 < PEC/MEC < 10) (Tauxe –Wuersch et al., 2005; Ort et al., 2009; Morasch et al., 2010).

Notably, PECs for the TCC were relatively higher than the MECs. This was attributed to two-fold reasons. First, although there were only three product categories found containing TCC in the market with bar soaps contributing 80.5% to the model, however, the upper limit of 1.5% concentration per article was used for most products. For example, the bar soaps due to lack of available data in products list of ingredients or from patent information sourced online a concentration per article of 15% was used. This dependency on fewer product categories and upper limit of concentration may have skewed the model outputs. And secondly, the PECs are based on average plant inflows for each month; whereas MECs were based on samples collected on specific days. Conversely, PECs for the TCS were comparable to the MECs plausibly owing to wide variety of products used in the model.

Table 4.5: Calculated PEC/MEC ratios for TCC and TCS for Influent and effluent streams at Darvill WWTP for the period of assessment.

	PEC/MEC – TCC		TCS – PEC/MEC	
Month	Influent	Effluent	Influent	Effluent
Aug-20	3.8	0.9	1.8	0.3
Sep-20	5.0	0.7	0.6	0.4
Oct-20	2.3	1.0	1.2	0.9
Nov-20	4.2	-	1.4	-
Dec-20	4.4	0.7	1.3	0.2

Table 4.6: Estimated PECs for TCS and TCC in Darvill WWTP, soils irrigated with sludge, and Msunduzi River water based on average annual flows.

Environmental matrix	Variable	TCS	TCC
	PEC – Influent (ng/L)	1645	2254
Wastewater	PEC – Effluent (ng/L)	247	338
	PEC – Sludge (µg/kg)	28	39
	PEC at DF1 = 1 (ng/L)	247	338
Freshwater	PEC at DF2 = 3 (ng/L)	82	113
	PEC at DF3 = 10 (ng/L)	25	34

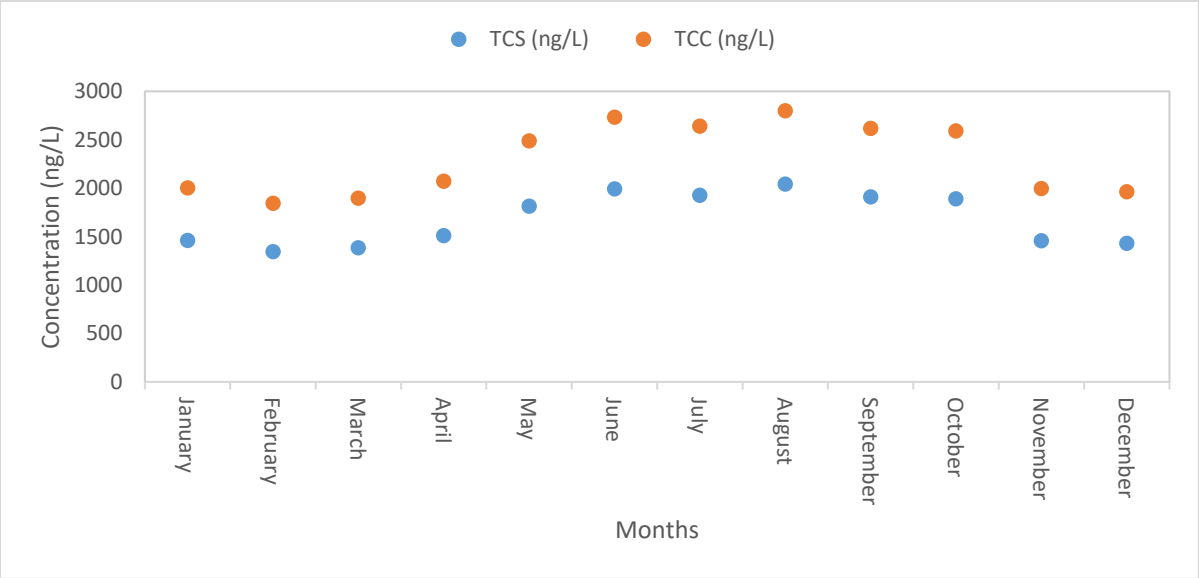


Figure 4.7: Estimated PECs for TCS and TCC at the Darvill WWTP influent based on average monthly flows.

Overall, results indicate that the estimated PECs in this study were relatively lower compared to MECs reported from developed countries, and in other regions in SA (Table S1 and Table S2). This was attributed to lower household income per capita in Msunduzi LM (since in KwaZulu Natal province), for instance, relative to other regions (e.g., Gauteng Province) (Table S11), and in turn, had low market penetration, or none for certain product categories. The model results suggest that in the absence of MECs for contaminants, mathematical models can be employed to evaluate possible environmental concentrations based on sales, income per capita, among other data for a given product categories. In turn, such model results can serve as first screening-tier approach to contaminants in variant environmental systems. Further,

based on MECs and PECs herein using TCS and TCC as case study contaminants; the model can be refined as can be developed rapidly, is less expensive relatively to analytical approaches, and possible application over large geographical spatial regions as opposed to analytical approaches that are expensive, laborious, and time consuming.

And finally, the models can facilitate to map regions likely to be hot spots for contaminants of focus, and therefore, aid to identify areas where MECs should be determined. Consequently, monitoring of TCS and TCC in the Msunduzi River and agricultural land is recommended to determine the contamination levels. Furthermore, the removal efficiency of the planned water reclamation plant under construction at Darvill WWTP site necessitates further investigations to ensure minimal/no adverse impacts to humans from the reclaimed water. The model PECs, herein, therefore offer a baseline on the potential contaminant levels that necessitates removal during the water reclamation process planned for Darvill WWTP treated effluent. Therefore, can serve as a valuable source of information for input design parameter(s) for the reclamation plant.

4.3.4. Predicted non effect concentrations

Both acute and chronic toxicity data retrieved from the literature were used to estimate the PNECs for organisms in surface water, wastewater, and terrestrial systems. The lowest dilution factor (DF = 1) was used for the risk assessment calculations to account for worst case scenario in freshwater system; especially to reflect the dry season where PECs were found to be the highest. For TCS exposure, both chronic and acute toxicity results showed algae as the most vulnerable species (lowest PNEC as 0.00067 µg/L using AF = 1 000), followed by wastewater microorganisms and fish, respectively (Figure 4.8). Terrestrial organisms and crustaceans were the least sensitive, and showed lower variability of PNEC values. The PNEC ranges for TCS were: fish (0.054–1 800 µg/L), algae (0.00067–93.75 µg/L), crustacean (0.263–20 µg/L), microorganisms (0.00028–182 µg/L), and terrestrial (1–100 µg/L). For TCC, results showed that fish and crustaceans were the most sensitive species *(*Figure 4.9). Wastewater microorganisms exhibited the highest variability of PNECs plausibly due to many different bacterial strains present in wastewater (Musee, 2018). The PNEC ranges for TCC were: fish (0.0021–1800 µg/L), algae (0.017–3 µg/L), crustacean (0.025–40 µg/L), microorganisms (0.00028–182 µg/L), and terrestrial (0.04–33.8 µg/L).

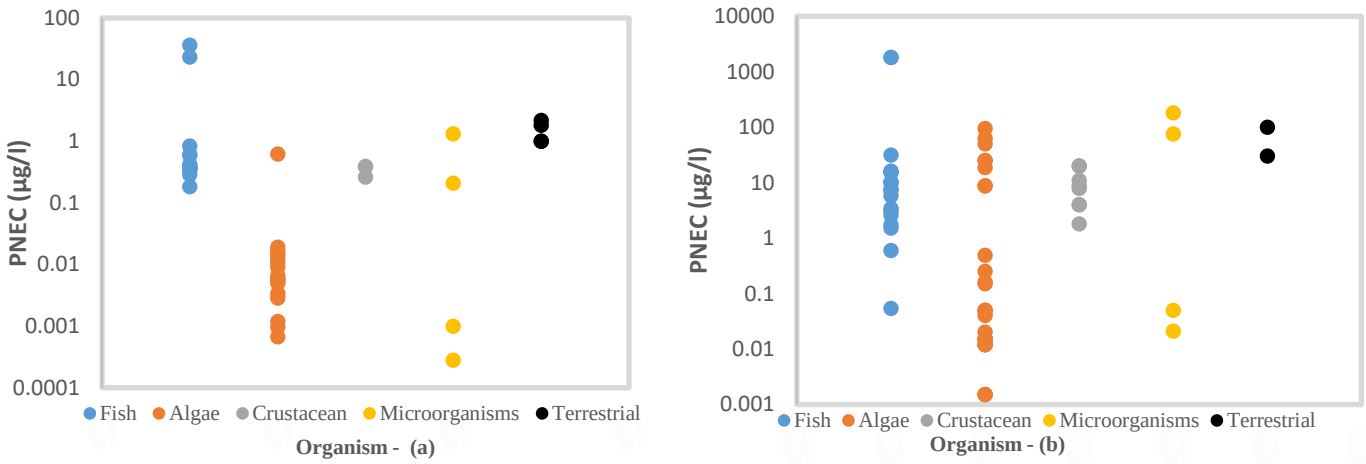


Figure 4.8: Estimated PNECs of TCS in freshwater, wastewater, and terrestrial environments for acute (a) and chronic (b) toxicity.

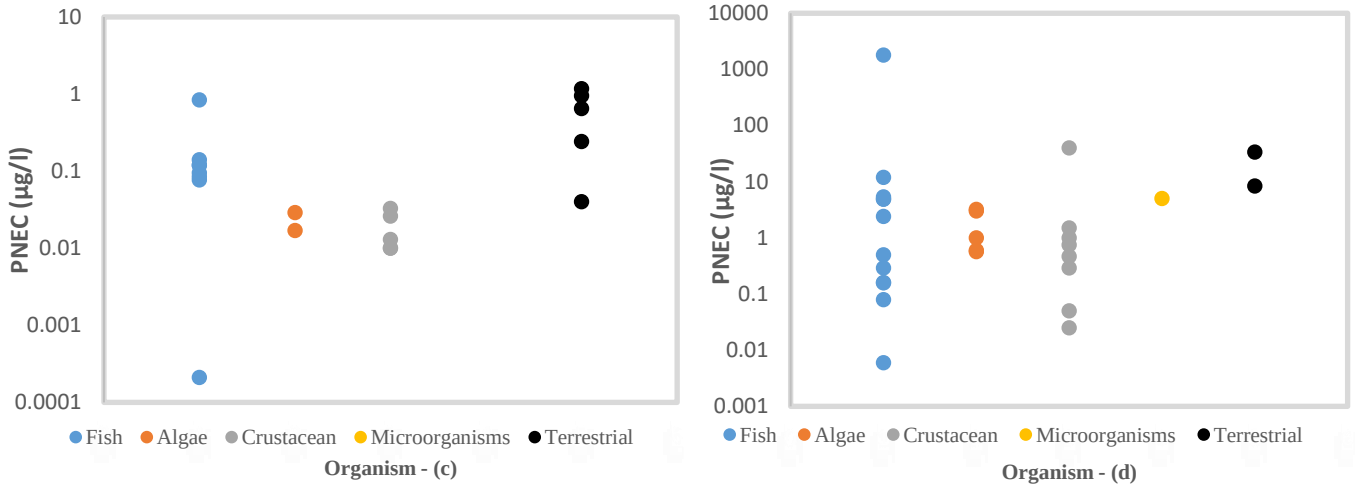


Figure 4.9: Estimated PNECs of TCC in freshwater, wastewater, and terrestrial environments for acute (c) and chronic (d) toxicity.

4.3.5. Environmental risk assessment

The risk quotient methodology was applied following the calculation of PNECs for both acute and chronic toxicity data sets to determine potential risk levels to organisms in the different environmental compartments. Results demonstrates that TCS poses significant risks to wastewater microogarnisms (RQ = 881 for acute toxicity), followed by algae (highest RQ = 254 for acute toxicity) and fish (RQ = 4.5), respectively (Figure 4.10). The calculated RQs are comparable to previous studies where fish and algae were the most sensitive species to TCS

contamination in freshwater (Dos Santos et al., 2016; Musee, 2018; Mohan and Balakrishan, 2019). TCS results showed low (0.1 ≤ RQ < 1) to moderate (1 ≤ RQ <10) risk to fish and crustaceans when applying the stricter evaluation criteria of Lemly (1996).

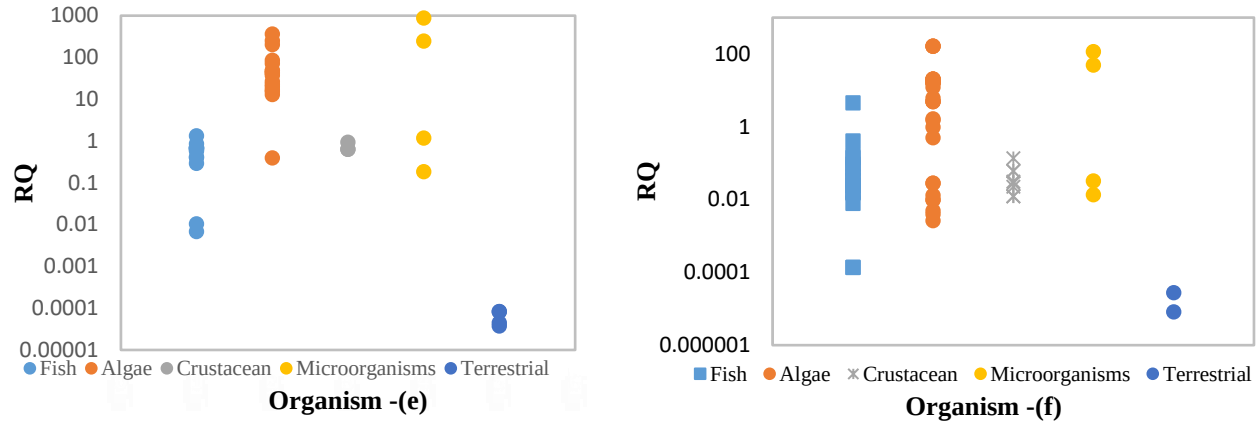


Figure 4.10: Calculated RQs of TCS in freshwater, wastewater, and terrestrial environments for acute (e) and chronic (f) toxicity.

Table 4.7: Calculated risk quotients for TCS using both PECs and MECs for selected wastewater microorganisms.

Wastewater Microorganism	RQ – TCS (PEC)		RQ – TCS (MEC)	
	Acute	Chronic	Acute	Chronic
Activated sludge-mixed liquor	-	0.01	-	0.05
Nitrifying bacteria	-	0.03	-	0.14
Vibrio fischeri	881	117	3750	500
Aphanizomenon flosaquae	246	-	1050	-
Tetrahymena pyriformis	1.17	-	5	-
Tetrahymena thermophila	0.18	-	0.78	-
Paramecium aurelia	-	49		210

MECs in the reactor were used to calculate RQs to make a comparison with those computed using PECs to further validate the model (Table 4.7). Only wastewater microorganisms were used for this comparison because the effluent receiving river was not sampled for the analysis of TCS and TCC MECs. Further, only results for TCS are shown due to lack of toxicity data for TCC in wastewater microorganisms. This further necessitate the need for TCC toxicity studies in wastewater microorganisms to enable risk assessment analysis of wastewater treatment processes. The results were found to be comparable for all the species assessed with the RQs for MECs fourfold higher than those calculated using PECs. This is because the MECs used were from the reactor whilst the PECs used were modelled for final effluent after treatment. The results suggest that modelling approaches can be further utilized to conduct risk assessments for TCS in wastewater in the absence of time consuming laboratory results to make informed decisions with respect to plant performance and effluent compliance.

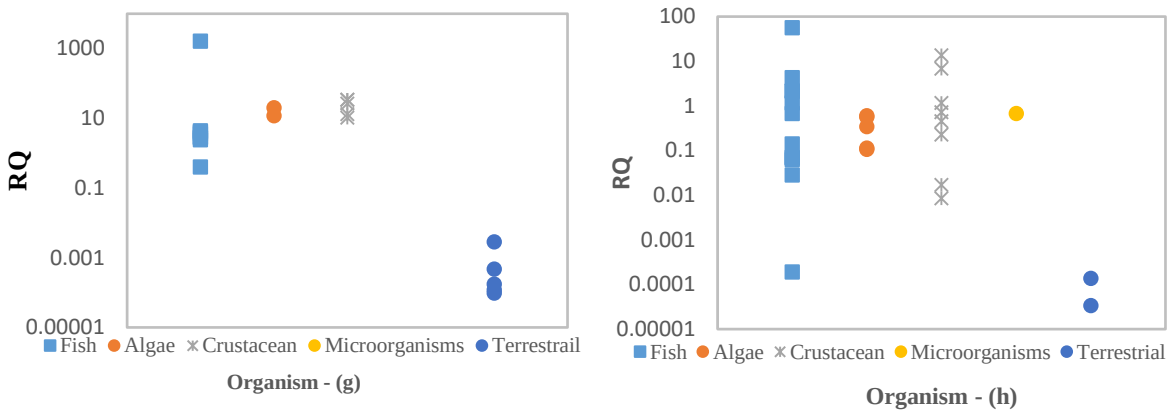


Figure 4.11: Calculated RQs of TCC in freshwater, wastewater, and terrestrial environments for acute (g) and chronic (h) toxicity.

For TCC, the highest RQ was recorded for fish (RQ = 1610), followed by crustacean (RQ =13.5) and algae (RQ = 0.56), respectively (Figure 4.11). In terrestrial environment, both TCS and TCC showed no adverse impacts at current levels with RQs < 1. The higher RQ values relative to other parts of the world are attributed to lower contaminant (TCS and TCC) removal efficiencies resulting to higher residual concentrations in the effluent. Further, precipitation is very low in South Africa compared to other countries in Europe and America resulting to none and/or low effluent dilution in the receiving rivers. The higher PEC values for TCC may have led to overestimation of RQs due to higher concentrations per article (1.5%) used in the model calculations. This was due to the lack of TCC concentration data in products from the market

and online. Overall, the WWTP did not effectively remove TCS and TCC to low levels before the effluent was released into the aquatic environment, and especially on a worst case scenario of DF =1 (non-dilution) used for this study.

Moreover, the accumulation of these compounds in the biological reactor system may further exacerbate reduction of the plants performance linked to their deleterious impact on microorganisms. As such, this may not only affect the removal of tri-based compounds, but also other forms of pollutants – with resultant poor overall performance of the treatment plant. Also, the agricultural application of sludge may result to groundwater contamination over time, and therefore merits to be monitored to ensure their levels remain low, and plausibly adopt sludge pre-treatment processes before use as soil conditioner. The latter approach merits cost-benefit analysis to achieve the fine balance of protection ecological integrity, and sustainable use of sludge as resource.

CHAPTER 5:

CONCLUSIONS AND RECOMMENDATIONS

In this study, the objective was to determine the concentrations in the Darvill WWTP of two antibacterial agents, triclosan (TCS) and triclocarban (TCC) widely used in household personal care products (PCPs). Two approaches used entailed: first, detection of both chemicals using analytical approaches (by means of sampling and analysing both the influent and effluent matrixes). This led to the determination of measured environmental concentrations (MECs). The second approach comprised of using sales data of PCPs containing TCS and TCC in the catchment area served by Darvill WWTP – by means of employing a mathematical model to estimate the predicted environmental concentrations (PECs), again both in the influent and effluent.

Initially, the influent and effluent samples were qualitatively screened to aid identify general organic contaminants using GC–MS, and later quantified to determine the concentrations of TCS, TCC, and four of their TPs. The contaminants of environmental concern qualitatively identified were in three broad chemical classes, viz., DIPNs, 2–Heptyl–4–phenyl–1,3–dioxolane and PCBs, and were detected across different treatment stages of the WWTP. The presence of these chemicals were mainly attributed to industrial effluent discharges to the sewer network as are utilised in the manufacturing processes of industries in the Darvill WWTP catchment.

The environmental concentrations of TCS and TCC entering the Darvill WWTP were significant and ranged from 1.02–3.4 µg/L and 0.45–1.1 µg/L, respectively. The overall removal efficiency of TCS (59%) and TCC (45%) were satisfactory and poor, respectively. The resultant residual concentrations at the final effluent were < LOD–0.58 µg/L and <LOD–0.58 µg/L, respectively, for TCS and TCC. The formation of TPs, namely, 2,4–DCP (for TCS) and NCC (for TCC) was observed at concentration ranges of 0.26–0.4 µg/L and 1.13–2.02 µg/L, respectively. MeTCS and 4–CA were not detected above limit of detection in all the samples analysed. Only 15.6% of TCS removal could be attributed to the formation of 2,4–DCP, with no direct correlation of TCC removal to the formation of NCC.

The modelling approach used in this study successfully predicted TCS and TCC concentrations with average PEC/MEC ratios of 1 and 3, respectively. According to the scientific literature,

these ratio values are within a range of 1 to 10. In turn, this indicates the modelled results are acceptable, and therefore, the developed predictive model was robust and reliable. As such, MECs were not determined in the river system. Rather, models were applied to determine PEC values under different dilution factors (DF) for the concentration of TCS and TCC in the river systems. The ecotoxicological risk assessment performed quantified the potential risks of TCS and TCC to the aquatic and terrestrial organisms. Overall, TCS had high RQs for wastewater microorganisms, and thus an indication of potential adverse effects to the functioning of the Darvill WWTP. In the aquatic environment, TCS and TCC exposure to the selected organisms were dependent on market data (market penetration), population size, provision of sanitation services, and economic dynamics of the study area.

Findings of this study suggests that during the dry season when the river has low flows (DF =1), both the TCS and TCC may pose elevated risks to the aquatic organisms especially fish and algae. In turn, this has significant implications in maintaining ecological integrity. Secondly, from the study, it is possible to derive reasonable results on the potential concentrations of a given pollutant in the aquatic systems if sales data of its sources are known (e.g., captured in inventory). This is fundamentally crucial, as the models are cheaper, versatile, and rapid to apply over a wide breadth of pollutants and geographical regions, for example, in an attempt to identify potential "hotspots" of environmental pollution for focused remediation efforts. This is desirous as analytical methods to generate MECs are expensive, laborious, and time consuming.

So in future environmental management, inventory of products as potential sources of chemical pollutants in a given catchment can therefore play a key role, as they would serve as source of data to estimate risks using computer simulation models as demonstrated in this study. Finally, the developed model can be extended to other treatment works to identify and sharpen on pollutants of emerging and/or significant concerns. This can form the basis of undertaking future targeted monitoring programmes to pollutants identified to be of considerable concern.

Overall, the study showed that the wastewater sampled at different treatment units in the Darvill WWTP contained variant contaminants, which potentially may pose environmental threat to aquatic life, and potentially compromise the human health. In view of this, there is a need to incorporate technologies at various treatment units at the WWTP with capability to remove most organic contaminants before discharge into the receiving surface water as well las pre-treat sludge before use e.g., for irrigational purposes. At present, various technologies are

available for deployment for both pre- and post-treatment of wastewater in WWTPs to aid effective removal of the contaminants of concern. These technologies includes activated carbon absorption, membrane filtration, coagulation-flocculation, and AOPs. And, it is recommended that the target contaminants be continuously monitored throughout the treatment processes to aid better decision–making on process technology selection, but also generate information essential for regulators to set science-evidence based environmental discharge standards as at present are not available for most emerging contaminants.

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APPENDIX

SUPPLEMENTARY INFORMATION

Table S1: Global occurrence of TCS in different environmental compartments.

Continent	Country	Wastewater (ng/L)		Removal Efficiency (%)	Freshwater (ng/L)	Sediment/Soil/Sludge (µg/kg)	Reference
		Influent	Effluent				
Africa	Durban, SA	2 100 – 9 000	1 300 – 6 400	28 – 38			Madikizela, et al 2014
	Pietermaritzburg, SA	1 020 – 3 370	<LOD – 1 170	59			This study
	Gauteng Province, SA	2 010 – 17 600	990 – 13 000	26 – 50	880 – 8 720	2.16 – 13.5	Lehutso et al, 2017
	Gauteng Province, SA	197 – 650	30 – 270 [2]	58 – 84	4.7 – 348		Musee, 2018
	Kabwe, Zambia				0.02 – 0.03		Sorensen et al., 2015

[2] Predicted Environmental Concentrations (PEC)

	Johannesburg, SA	78 460 – 127 700	10 700 – 22 900	82 – 86			Amdany et al, 2014
Asia	China	104 – 122					Chen et al., 2012
	China (100 WWTPs)					<0.004 – 4.8	Chen et al., 2019a
	Chennai, India	920 – 1757	443 – 800	51 – 54			Mohan and Balakrishnan, 2019
	Shanghai, China					475 – 1048	Yu et al., 2019a
	Tone Canal, Japan				11 - 31		Nishi et al, 2008
	China				49.9		Wang et al., 2012
	China				35 – 1023		Peng et al., 2008
	China				<LOD – 64		Lv et al., 2014
	China				<LOD – 478		Zhao et al., 2010
	China				1329		Zhao et al., 2013
	Japan				11 – 134		Nishi et al., 2008
America	Canada	870–1830					Lee et al., 2005

	USA	7580 –8520					Lozano et al., 2013
	USA	6178 – 38 255					Kumar et al., 2008
	USA					0.4 – 85	Venkatesan, et al., 2012
	Ohio, USA	3 800 – 16 600	500 -2700	83 – 86			McAvoy et al, 2002
	USA	2800 – 7400	10 – 240	96 – 99			Heidler and Halden, 2007
	Mid-Atlantic, USA	4 700	70	98			Heidler & Halden, 2007
	USA	712–2301					Yu et al., 2011
	USA				8.8 – 34.9		Zhang et al., 2007
	USA				1 – 3		Wilson et al., 2009
	Brazil				415		Dos Santos et al., 2016
	Grand Rapids, USA					90 – 7060	Cha and Cupples, 2009
Europe	Germany	142–214					Wu et al., 2007
	Greece	170 – 23 900					Stasinakis et al. (2008)
	UK	33 – 463					Kasprzyk–Hordern et al., 2009

Switzerland	500 – 1 300	70 – 650	50 – 86			Lindström et al, 2002
Ruhr, Germany	4 800 – 7 300	10 - 600	91 – 95	3-10		Bester, 2005
UK	7500 – 21900	340 – 1100	95	0.2 – 80		Sabaliunas et al., 2003
Dortmund, Germany	1 200	51	95			Bester, 2003
Spain	< LOQ –936					Gonzalez –Marino et al., 2009
Spain				2		Gorga, Petrovic and Barcelo, 2013
France	2140 – 5260					Gasperi et al., 2014
Switzerland		42 - 213		11 - 98	53 - 125	Singer, 2002

Table S2: Global occurrence of TCC in different environmental compartments

Continent	Country	Wastewater (ng/L)		Removal Efficiency (%)	Freshwater (ng/L)	Sediment/Soil/Sludge (µg/kg)	Reference
		Influent	Effluent				
Africa	Gauteng Province, SA	86–2840	<LOD–1 890	33		2.59–8.23	Lehutso et al, 2017
	Gauteng Province, SA	1590–1840	270–770	–	39–998		Musee, 2018[3]
	Pietermaritzburg, SA	450–1 100	<LOD-390	45			This study
Asia	China	249–285					Chen et al., 2012
	China		342		<LOD–338	426–2 633	Zhao et al., 2010
	China					0.05–14.1	Lv et al., 2014
	China (100 WWTPs)					<0.003–43	Chen et al., 2019a
	Shanghai, China				11-31	975–2 194	Yu et al., 2019a
	India	10 000	860			28 000	Subedi et al., 2017
	India				2.2–1119	<LOD–26.3	Vimalkumar et al., 2018

[3] Predicted Environmental Concentrations (PEC)

America	USA	920–5 920			Lozano et al., 2013
	USA	157–1372			Kumar et al. (2008)
	USA			5–822	Venkatesan, et al., 2012
	Ohio, USA		48–330		Klein et al., 2010
	USA	1 217–2 354			Yu et al. (2011)
	Grand Rapids, USA			4 890–9 280	Cha and Cupples, 2009
Europe	France	97–140			Gasperi et al., 2014
	France			0.17–492	Souchier et al., 2015
	Ireland			80	Healy et al., 2017

Table S3: Occurrence of personal care products in developing countries in waters.

Continent	Country	PCP Category	Compounds	Extraction	Analytical instruments	Wastewater [ng/L]	River Water [ng/L]	Groundwater [ng/L]	Reference
Africa	Kenya	Preservative	Butylparaben	SPE–Oasis HLB	UPLC/HS–MS	–	20		Koreje et al., 2016
		Preservative	Ethylparaben	SPE–Oasis HLB	UPLC/HS–MS	–	100		Koreje et al., 2016
		Preservative	Methylparaben	SPE–Oasis HLB	UPLC/HS–MS	–	120		Koreje et al., 2016
		Preservative	Propylparaben	SPE–Oasis HLB	UPLC/HS–MS	–	10		Koreje et al., 2016
		UV filters	Oxybenzone	SPE–Oasis HLB	UPLC/HS–MS	–	5		Koreje et al., 2016
		Insect repellent	N,N –diethyltoluamide (DEET)	SPE–Oasis HLB	UPLC/HS–MS	–	2	–	Koreje et al., 2016
	SA	Antimicrobial	Triclosan	SPE–Oasis HLB	HPLC	27 000	–	–	Amdany et al., 2014
		Preservative	Methylparaben	SPE–Oasis HLB	UPLC/TQD–MS	58.7–146.1	–	–	Acher et al., 2017
		Preservative	Propylparaben	SPE–Oasis HLB	UPLC/TQD–MS	31.8–136	–	–	Acher et al., 2017
		UV filters	Benzophenone – 3	SPE–Oasis HLB	UPLC/TQD–MS	56.2–64.3	–	–	Acher et al., 2017

		UV filters	Benzophenone – 4	SPE–Oasis HLB	UPLC/TQD–MS	441–1 076	–	–	Acher et al., 2017
		Antimicrobial	Triclosan	LLE and SPE	LC–MS/MS	990–17 600	880–8 720	–	Lehusto et al., 2017
Africa		Antimicrobial	Triclocarban	LLE and SPE	LC–MS/MS	86–2 840	ND-360	–	Lehusto et al., 2017
		Antimicrobial	Triclosan	SPE–Oasis HLB	HPLC–PDA	1 300–9 000	ND–900	–	Madikizela et al., 2014
	Zambia	Insect repellent	N,N –diethyltoluamide (DEET)	LLE	GC–MS	–	–	0.4–1.8	Sorensen et al., 2015
		Food additives	Triacetin	LLE	GC–MS	–	–	ND–0.04	Sorensen et al., 2015
	Zambia	Antimicrobial	Triclosan	LLE	GC–MS	–	–	0.02–0.03	Sorensen et al., 2015
		Food additives	Butylated hydroxytoluene	LLE	GC–MS	–	–	0.3–0.4	Sorensen et al., 2015
		UV filters	Homosalate	LLE	GC–MS	–	–	ND–0.05	Sorensen et al., 2015
		UV filters	Octocrylene	LLE	GC–MS	– –	–	0.04–0.12	Sorensen et al., 2015
South America	Chile	Preservative	Propylparaben	SPE–Oasis HLB	GC–MS	D	D	–	Arismendi et al., 2020
		Preservative	Ethylparaben	SPE–Oasis HLB	GC–MS	430–620	380	–	Arismendi et al., 2020
		Preservative	Triclosan	SPE–Oasis HLB	GC–MS	0.7–1.02	ND	–	Arismendi et al., 2020

Europe	Poland	Preservative	Methylparaben	USAEME	GC–MS	20–5 300	–	4 – 2 880	Kapelewska et al., 2018
		Preservative	Ethylparaben	USAEME	GC–MS	2 – 4 150	–	1–3	Kapelewska et al., 2018
	Poland	Preservative	Propylparaben	USAEME	GC–MS	1–2 730	–	470	Kapelewska et al., 2018
		Preservative	Buthylparaben	USAEME	GC–MS	1–710	–	10–40	Kapelewska et al., 2018
		UV filters	Benzophenone	USAEME	GC–MS	3– 2 320	–	10-3 450	Kapelewska et al., 2018
		UV filters	Benzophenone 2	USAEME	GC–MS	50–70	–	110	Kapelewska et al., 2018
	Poland	UV filters	Benzophenone 3	USAEME	GC–MS	1–1 260	–	40–1 120	Kapelewska et al., 2018
		UV filters	3–(4-methylbenzylidene) camphor	USAEME	GC–MS	10–18 010	–	10	Kapelewska et al., 2018
		Insect repellent	N,N–diethyltoluamide (DEET)	USAEME	GC–MS	1–2 620	–	0.03–17 280	Kapelewska et al., 2018

Table S4: Toxicity data for TCS and TCC in aquatic organisms (fish, algae and crustacean), wastewater and terrestrial organisms.

Species	Organism	Effect	Dosage (µg/l) - NOEC/LOEL		Dosage (µg/l) - LC50/EC50		Reference
			TCC	TCS	TCC	TCS	
Fish	Mysidopsis bahia		0.06		0.21		
	Pimephales promelas	Development		0.54			Schultz et al., 2002
	Pimephales promelas	Growth	1.6				Schultz et al., 2002
	Pimephales promelas	Reproduction	5				Villeneuve, *et al,* (2017)
	Pimephales promelas	Genotoxicity	0.79				Zenobio et al., 2014
	Pimephales promelas	Mortality	54	100	95	360	Mayer and Ellersieck (1986); EPA (1992c)
	Oryzias latipes	Growth		162.1			Ishibashi et al., 2004
	Oryzias latipes	Morphology		75.2			Ishibashi et al., 2004
	Oryzias latipes	Morphology		17.3			Ishibashi et al., 2004
	Oryzias latipes	Mortality				352	Foran et al., 2000
	Oryzias latipes	Mortality				602	Ishibashi et al., 2004
	Oryzias latipes	Mortality				600	Kim et al., 2009
	Oryzias latipes	Mortality				399	Ishibashi et al., 2004

Oryzias latipes	Mortality		313			Ishibashi et al., 2004
Oryzias latipes	Mortality		153			Ishibashi et al., 2004
Oryzias latipes		1.6	156	85	352	Tamura, et al (2012) Journal of Applied Toxicology 33; Foran et al. (2000)
Oncorhynchus mykiss	Mortality				23400	EPA (1992c)
Oncorhynchus mykiss	Mortality		31.6			Orvos et al. (2002)
Oncorhynchus mykiss	Mortality		15.1			Orvos et al. (2002)
Oncorhynchus mykiss	Growth		71.3			Orvos et al. (2002)
Oncorhynchus mykiss	Mortality		18000			EPA (1992c)
Oncorhynchus mykiss	Mortality		100			EPA (1992c)
Oncorhynchus mykiss	Mortality	49	34.1	120	288	Consortium (2002); EPA/OTS (1992); Orvos et al. (2002)
Lepomis macrochirus		18000		77	370	Consortium (2002);Orvos et al. (2002)
Salmo airdneri		49		120		
Gambusia affinis	Genotoxicity		101.3			Raut and Angus, 2012
Gambusia affinis	Reproduction		57.9			Raut and Angus, 2012
Lepomis macrochirus	Mortality				36200	EPA/OTS (1992)

	Lepomis macrochirus	Mortality				370	Orvos et al. (2002)
	Lepomis macrochirus	Mortality		18000			EPA/OTS (1992)
	Ceriodaphnia sp.		2.9	6		184.7	
	Ictalurus punctatus	Mortality	120		140		EPA/OTS (1992)
	Ictalurus punctatus	Mortality			840		EPA/OTS (1992)
	Danio rerio	Development				839	Padilla et al., 2012
	Danio rerio		24	26		420	Oliveira et al. (2009); Tamura et al. (2013)
Algae	Scenedesmus subspicatus	Population		1.2			Orvos et al. (2002)
	Scenedesmus subspicatus	Population		40			EPA (1992c)
	Scenedesmus subspicatus	Population		0.5			Orvos et al. (2002)
	Chlorella fusca var. vacuolata	Population				9.13	Vogs et al., 2013
	Chlorella fusca var. vacuolata	Population				5.71	Vogs et al., 2013

Chlorella fusca var. vacuolata	Population		14.77	Vogs et al., 2013
Chlorella fusca var. vacuolata	Population		5.83	Vogs et al., 2013
Chlorella fusca var. vacuolata	Population		12.5	Vogs et al., 2013
Chlorella fusca var. vacuolata	Population		6.6	Vogs et al., 2013
Chlorella fusca var. vacuolata	Population		5.08	Vogs et al., 2013
Chlorella fusca var. vacuolata	Population		5.16	Vogs et al., 2013
Chlorella fusca var. vacuolata	Population		2.85	Vogs et al., 2013
Closterium ehrenbergii	Reproduction		620	Ciniglia et al., 2005
Closterium ehrenbergii	Reproduction	937.5		Ciniglia et al., 2005
Closterium ehrenbergii	Reproduction	500		Ciniglia et al., 2005
Closterium ehrenbergii	Genotoxicity	250		Ciniglia et al., 2005
Closterium ehrenbergii	Reproduction	625		Ciniglia et al., 2005
Closterium ehrenbergii	Reproduction	250		Ciniglia et al., 2005

Closterium ehrenbergii	Genotoxicity	187		Ciniglia et al., 2005
Cyanophycota sp.	Population	87.2		Proia et al., 2012
Chlamydomonas sp.	Population	0.015		Wilson et al., 2003
Chlamydomonas sp.	Population	0.15		Wilson et al., 2003
Chlamydomonas sp.	Population	0.12		Wilson et al., 2003
Chlamydomonas sp.	Reproduction	0.12		Wilson et al., 2003
Chlamydomonas sp.	Population	0.015		Wilson et al., 2003
Chroococcus sp.	Population	0.12		Wilson et al., 2003
Chroococcus sp.	Population	0.12		Wilson et al., 2003
Chroococcus sp.	Population	0.15		Wilson et al., 2003
Chroococcus sp.	Population	0.015		Wilson et al., 2003
Diatoma sp.	Population	87.2		Proia et al., 2012
Dunaliella tertiolecta	Population	4.9		DeLorenzo and Fleming, 2008
Dunaliella tertiolecta	Population	1.6		DeLorenzo and Fleming, 2008
Anabaena fios-aquae	Population		0.67	Orvos et al. (2002)
Anabaena fios-aquae	Population		1.2	EPA (1992c); Consortium (2002); Orvos et al. (2002); Samosoe-Petersen et al. 2003

Anabaena fios-aquae	Population		0.5		0.97	Orvos et al. (2002)
Pseudokirchneriella subcapitata	Population	10	0.2	17	3.4	Tamura, et al (2012) Journal of Applied Toxicology 33, Yang et al., 2008
Pseudokirchneriella subcapitata	Population		2.5			Yang et al., 2008
Pseudokirchneriella subcapitata	Population		0.4			Yang et al., 2008
Pseudokirchneriella subcapitata	Growth	5.7		29		Tamura, et al (2012) Journal of Applied Toxicology 34
Sphaerocystis sp.	Population		1.5			Wilson et al., 2003
Sphaerocystis sp.	Population		0.15			Wilson et al., 2003
Synedra sp.	Population		0.15			Wilson et al., 2003
Selenastrum sp.		30				Consortium (2002)
Microcystis sp.		32				Consortium (2002)
Navicula pelliculosa	Population				10.7	Orvos et al. (2002)
Navicula pelliculosa	Population				19.1	Orvos et al. (2002)
Navicula pelliculosa	Population				16	EPA (1992)
Navicula pelliculosa	Population		0.5			EPA (1992)

	Navicula sp.		6				Consortium (2002)
Crustacean	Daphnia Magnia	Growth	10				Flaherty and Dodson, 2005
	Daphnia Magnia	Mortality	2.9	40	10	390	EPA (1992c); Consortium (2002); Orvos et al. (2002); Samosoe-Petersen et al. 2003
	Daphnia Magnia	Mortality				390	Orvos et al. (2002)
	Daphnia Magnia	Mortality				263.5076	Sengupta et al., 2016
	Daphnia Magnia	Mortality		78.8945			Sengupta et al., 2016
	Daphnia Magnia	Mortality		200			Orvos et al. (2002)
	Daphnia Magnia	Reproduction		200			Orvos et al. (2002)
	Daphnia Magnia	Reproduction		88			Orvos et al. (2002)
	Daphnia Magnia	Reproduction		108.87441			Sengupta et al., 2016
	Daphnia Magnia	Mortality	15				Consortium (2002)
	Daphnia Magnia	Mortality	7.5				Consortium (2002)
	Daphnia Magnia	Mortality	4.7				Consortium (2002)
	Daphnia Magnia	Mortality	0.5				EPA (1992c)
	Daphnia Magnia	Mortality	0.25				EPA (1992c)

	Daphnia Magnia	Mortality			13	Simon, *et al*, 2015 Ecotoxicology 24(6)
	Daphnia Magnia	Mortality			33	Simon, *et al*, 2015 Ecotoxicology 24(6)
	Daphnia Magnia	Mortality			26	Simon, *et al*, 2015 Ecotoxicology 24(6)
	Daphnia Magnia	Immobilization			10	Tamura, *et al* (2012) Journal of Applied Toxicology 33
	Daphnia Magnia	Reproduction		40		Orvos et al. (2002)
	Daphnia Magnia	Reproduction		18		Orvos et al. (2002)
	Chironomus tentans		400			Dussault et al. (2008)
	Hyalella azteca		200			Dussault et al. (2008)
Microorganisms/Bacteria	Activated sludge-mixed liquor			1820		
	Nitrifying bacteria			750		
	Vibrio fischeri			0.21	0.28	
	A. flosaquae				1	

	Tetrahymena pyriformis					210	
	Tetrahymena thermophila					1330	
	Paramecium aurelia		50	0.5			
Terrestrial	Glomus intraradices	Reproduction		1000		1000	Hillis et al., 2008
	Eisenia fetida	Mortality				1836	Schnug et al., 2014
	Eisenia fetida	Mortality	338		1177		Wyrwol et al., 2013
	Eisenia fetida	Reproduction	84		956		Wyrwol et al., 2013
	Eisenia fetida	Reproduction			243		Wyrwol et al., 2013
	Eisenia fetida	Mortality			40		Snyder et al., 2011
	Eisenia fetida	Mortality			652	2184	Wyrwol et al., 2013
	Daucus carota	Growth		300		1000	Hillis et al., 2008

Table S5: Income distribution in Msunduzi Local Municipality (Source: http://www.statssa.gov.za/?page_id=993&id=the –msunduzi –municipality , accessed 18 March 2021).

Household Income	**Fraction**	**Equivalent population**
None income	0.161	109,325
R1 – R4,800	0.046	31,236
R4,801 – R9,600	0.068	46,175
R9,601 – R19,600	0.161	109,325
R19,601 – R38,200	0.165	112,041
R38,201 – R76,4000	0.126	85,559
R76,401 – R153,800	0.103	69,941
R153,801 – R307,600	0.088	59,755
R307,601 – R614,400	0.057	38,705
R614,001 – R1,228,800	0.018	12,223
R1,228,801 – R2,457,600	0.005	3,395
R2,457,601+	0.003	2,037

Table S6: Qualitative analysis data for target analytes obtained using gas chromatography mass spectrometry after derivatization.

Targeted analytes	**Chemical formula**	**Molar Mass (g mol $^{-1}$)**	**Retention Time (min)**	**Fragment ions (m/z)**	**SIM ions (m/z)**
4 –CA	C_6H_6ClN	127.6	5.2	65, 92, 127	92, 127
2,4 –DCP	$C_6H_4Cl_2O$	163.0	6.1	124, 126, 159, 187	124, 187
TCC	$C_{13}H_9Cl_3N_2O$	315.6	6.9	90, 126, 101, 161, 177	126, 161
TCS	$C_{12}H_7Cl_3O_2$	289.5	11.7	218, 288, 303, 252, 367	218, 252
M –TCS	$C_{13}H_9Cl_3O_2$	303.6	11.9	200, 252, 302, 347, 362	200, 252
NCC	$C_{13}H_{12}N_2O$	212.25	13.3	66, 93, 117, 129, 358	66, 93

Table S7: Method limits of detection and quantification for target analytes.

Targeted analytes	Equation	Linearity µg /L	Linear regression	Instrument LOD µg/L	Method LOD µg /L	Method LOQ µg /L
4 –CA	y = 97089x + 36371	0.5 – 30	0.9950	0.5	0.0063	0.0212
2,4 –DCP	y = 51927x – 11839	0.5 – 30	0.9991	0.5	0.0392	0.1309
TCC	y = 30665x – 13189	0.5 – 30	0.9977	0.5	0.0153	0.0511
TCS	y = 13397x – 12635	0.5 – 30	0.9955	0.5	0.0489	0.1630
M –TCS	y = 22854x + 41489	0.5 – 30	0.9956	0.5	0.1230	0.410
NCC	y = 53256x – 56687	1.0 – 30	0.9943	1.0	0.012	0.0410

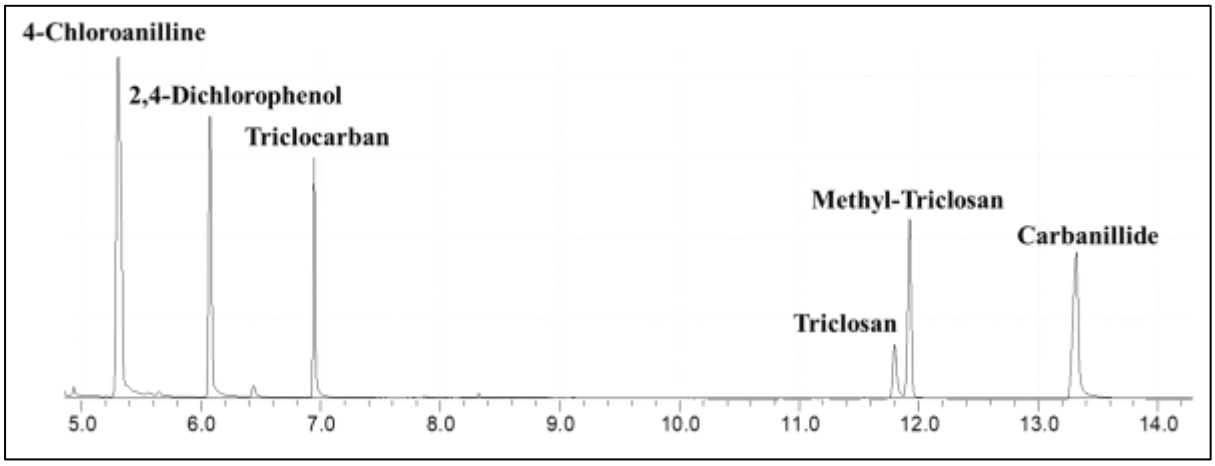

Figure S1: Chromatogram obtained by injecting 5 µL containing 1 µg L^{-1} mixture of target analytes.

Table S8: Population dynamics of Msunduzi Local Municipality (Statistics SA – KwaZulu – Natal [Community Survey 2016], Report 03 –01 –10).

Variable	**Quantity**
Total Population	6790,39
Population density – Persons/km^2	976
Area – km^2	696
No. of Households	180,469
Average household size	3.8
Toilets connected to sewer – (%)	51.6
Piped water inside dwellings – (%)	47.9

Table S9: Estimation of the assessment factor for PNEC calculation.

Available Data	**Assessment Factor**
At least one short term from each of the trophic levels of the base – set (fish, daphnia or algae)	1000
One long term NOEC (fish or daphnia)	100
Two long term NOECs from species representing two trophic levels	50
Long term NOEC from at least three species representing three trophic levels	10

Table S10: Detection and quantification of results in Darvill WWTP for the duration of assessment (August – December 2020) in µg/L.

Target analytes	**Month**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
NCC	August	1.52	2.92	4.68	1.11	1.71	2.72	2.13	1.17
	September	4.23	14.83	2.95	1.41	1.69	1.28	1.18	1.11
	November	1.26	1.20	1.34	1.14	1.11	1.23	1.10	1.06
	December	1.09	1.06	1.19	1.37	1.10	1.10	1.08	1.19
2,4–DCP	August	0.34	0.36	0.40	0.41	1.72	0.60	0.34	0.25
	September	0.37	0.23	0.23	0.23	0.23	0.23	0.23	0.23
	October	0.75	0.46	0.28	0.38	0.23	0.23	0.33	0.24
	November	0.31	0.31	0.39	0.32	0.34	0.51	0.35	0.23
	December	0.26	0.23	0.46	0.32	0.49	0.47	0.37	0.36
TCS	August	1.12	2.06	1.86	1.20	1.45	1.58	1.43	1.17
	September	3.37	1.18	3.26	0.71	0.74	3.43	1.07	0.80
	October	1.59	1.14	1.21	1.15	1.00	1.04	1.18	0.33
	November	1.02	1.05	1.01	1.39	1.05	1.00	1.29	< LOD
	December	1.08	0.00	1.06	1.12	0.98	1.00	0.66	1.14
TCC	August	0.74	0.65	0.65	0.45	0.55	0.62	0.48	0.47
	September	0.53	1.21	0.74	0.58	0.57	0.57	0.50	0.58
	October	1.10	0.54	0.50	0.59	0.46	0.44	0.58	0.39
	November	0.47	0.53	0.71	0.49	0.45	0.48	0.45	< LOD
	December	0.45	0.15	0.46	0.49	0.45	0.44	0.44	0.45

1: raw influent; 2: reactor feed; 3: PST underflow; 4: SST feed; 5: SST effluent; 6: RAS; 7: WAS; 8: final effluent.

Table S11: Average annual household income by province.

Province	Household Income (ZAR)	HI/HI(RSA)	Population
Eastern Cape	90,156	0.65	6,712,276
Western Cape	222,959	1.61	6,844,272
Northern Cape	103,912	0.75	1,263,875
Free State	98,529	0.71	2,887,465
KwaZulu Natal	101,088	0.73	11,289,086
North West	86,926	0.63	4,027,160
Gauteng	193,771	1.40	15,176,115
Mpumalanga	107,561	0.78	4,592,187
Limpopo	79,152	0.57	5,982,584
South Africa	138,468	1	58,775,020

Table S12: Criteria used to evaluate model results for PEC.

PEC evaluation criteria	PEC/MEC ratio	Reference
Unacceptably high	PEC/MEC > 10	Tauxe –Wuersch et al., 2005; Morasch et al.,2010
Acceptably high	2 < PEC/MEC < 10	Tauxe –Wuersch et al., 2005; Morasch et al., 2010
Unacceptably low	PEC/MEC < 0.1	Tauxe –Wuersch et al., 2005; Morasch et al., 2010
Accurate	0.5 < PEC/MEC < 2	Ortet al., 2009
Acceptably low	0.1 < PEC/MEC< 0.5	Ortet al., 2009

Table S13: Distribution of product categories containing TCS and TCC in Msunduzi LM market.

Product	Number of products containing	
	TCS	**TCC**
Deodorants	67	–
Bar soaps	2	29
Liquid hand soaps	7	4
Facewash	4	–
Hair products	3	–
Toothpastes	7	–
Shower gels	–	3
Total	**90**	**36**

Table S14: Inventory database for TCS containing products.

Product	**Concentration (% w/w)**	**Product weight (mg)**	**Product volume (ml)**	**Market penetration**	**Quantity (kg)**
Bar soap 1	0.3	100		0.09%	0.2
Bar soap 2	0.3	175		0.09%	0.2
Deodorant 1	0.3		150	0.26%	0.7
Deodorant 2	0.3		150	0.26%	0.7
Deodorant 3	0.3		90	0.21%	0.6
Deodorant 4	0.3		150	0.26%	0.7
Deodorant 5	0.3		150	0.26%	0.7
Deodorant 6	0.3		150	0.26%	0.7
Deodorant 7	0.3		150	0.26%	0.7
Deodorant 8	0.3		90	0.21%	0.6
Deodorant 9	0.3		90	0.21%	0.6
Deodorant 10	0.3		90	0.21%	0.6
Deodorant 11	0.3		90	0.21%	0.6
Deodorant 12	0.3		150	0.30%	0.8
Deodorant 13	0.3		150	0.30%	0.8
Deodorant 14	0.3		150	0.30%	0.8
Deodorant 15	0.3		150	0.30%	0.8
Deodorant 16	0.3		150	0.30%	0.8
Deodorant 17	0.3		150	0.30%	0.8

Deodorant 18	0.3	150	0.30%	0.8
Deodorant 19	0.3	90	0.11%	0.3
Deodorant 20	0.3	90	0.11%	0.3
Deodorant 21	0.3	90	0.11%	0.3
Deodorant 22	0.3	90	0.11%	0.3
Deodorant 23	0.3	90	0.11%	0.3
Deodorant 24	0.3	90	0.21%	0.6
Deodorant 25	0.3	90	0.21%	0.6
Deodorant 26	0.3	150	0.30%	0.8
Deodorant 27	0.3	150	0.30%	0.8
Deodorant 28	0.3	150	0.30%	0.8
Deodorant 29	0.3	150	0.26%	0.7
Deodorant 30	0.3	150	0.26%	0.7
Deodorant 31	0.3	150	0.26%	0.7
Deodorant 32	0.3	150	0.26%	0.7
Deodorant 33	0.3	90	0.21%	0.6
Deodorant 34	0.3	90	0.21%	0.6
Deodorant 35	0.3	90	0.21%	0.6
Deodorant 36	0.3	150	0.26%	0.7
Deodorant 37	0.3	150	0.26%	0.7
Deodorant 38	0.3	150	0.30%	0.8
Deodorant 39	0.3	500	0.30%	0.8
Deodorant 40	0.3	250	0.30%	0.8
Deodorant 41	0.3	150	0.30%	0.8
Deodorant 42	0.3	120	0.28%	0.8
Deodorant 43	0.3	120	0.28%	0.8
Deodorant 44	0.3	120	0.28%	0.8
Deodorant 45	0.3	90	0.28%	0.8
Deodorant 46	0.3	90	0.28%	0.8
Deodorant 47	0.3	90	0.28%	0.8
Deodorant 48	0.3	120	0.28%	0.8
Deodorant 49	0.3	150	0.28%	0.8
Deodorant 50	0.3	150	0.28%	0.8
Deodorant 51	0.3	150	0.28%	0.8
Deodorant 52	0.3	150	0.28%	0.8
Deodorant 53	0.3	90	0.28%	0.8

Deodorant 54	0.3		90	0.28%	0.8
Deodorant 55	0.3		250	0.13%	0.4
Deodorant 56	0.3		200	0.13%	0.4
Deodorant 57	0.3		125	0.13%	0.4
Deodorant 58	0.3		200	0.13%	0.4
Deodorant 59	0.3		125	0.13%	0.4
Deodorant 60	0.3		125	0.13%	0.4
Deodorant 61	0.3		50	0.11%	0.3
Deodorant 62	0.3		45	0.11%	0.3
Deodorant 63	0.3		100	0.11%	0.3
Deodorant 64	0.3		120	0.11%	0.3
Deodorant 65	0.3		120	0.11%	0.3
Deodorant 66	0.3		45	0.04%	0.1
Deodorant 67	0.3		45	0.04%	0.1
Facewash 1	0.3		150	0.41%	0.7
Facewash 2	0.3		375	0.41%	0.7
Facewash 3	0.3		375	0.41%	0.7
Facewash 4	0.3		150	0.41%	0.7
Hair Product 1	0.3		200	0.13%	0.5
Hair Product 2	0.3		250	0.13%	0.5
Hair Product 3	0.3		125	0.07%	0.2
Hand Wash 1	0.3		345	0.10%	0.1
Hand Wash 2	0.3		250	0.39%	0.2
Hand Wash 3	0.3		500	0.39%	0.2
Hand Wash 4	0.3		250	0.39%	0.2
Hand Wash 5	0.3		500	0.39%	0.2
Hand Wash 6	0.3		200	0.19%	0.1
Hand Wash 7	0.3		450	0.19%	0.1
Toothpaste 1	0.3		150	0.99%	1.0
Toothpaste 2	0.3	95	75	0.99%	1.0
Toothpaste 3	0.3	100	75	0.99%	1.0
Toothpaste 4	0.3	100	75	0.99%	1.0
Toothpaste 5	0.3	100	75	0.99%	1.0
Toothpaste 6	0.3	95	75	0.99%	1.0
Toothpaste 7	0.3	100	75	0.99%	1.0

Table S15: Inventory database for TCC containing products.

Product	Concentration (% w/w)	Product weight (mg)	Product volume (ml)	Market penetration	Quantity (kg)
Bar Soap 1	1.5	200		0.04%	0.33
Bar Soap 2	1.5	175		0.51%	4.29
Bar Soap 3	1.5	175		0.51%	4.29
Bar Soap 4	1.5	175		0.51%	4.29
Bar Soap 5	1.5	175		0.51%	4.29
Bar Soap 6	1.5	175		0.51%	4.29
Bar Soap 7	1.5	175		0.51%	4.29
Bar Soap 8	1.5	175		0.51%	4.29
Bar Soap 9	1.5	175		0.51%	4.29
Bar Soap 10	1.5	175		0.51%	4.29
Bar Soap 11	1.5	175		0.51%	4.29
Bar Soap 12	1.5	175		0.51%	4.29
Bar Soap 13	1.5	175		0.51%	4.29
Bar Soap 14	1.5	175		0.51%	4.29
Bar Soap 15	0.1	175		0.43%	0.24
Bar Soap 16	0.1	175		0.43%	0.24
Bar Soap 17	1.5	175		0.43%	3.63
Bar Soap 18	1.5	175		0.43%	3.63
Bar Soap 19	0.4	175		0.43%	0.97
Bar Soap 20	0.4	175		0.43%	0.97
Bar Soap 21	0.1	175		0.43%	0.24
Bar Soap 22	0.15	175		0.43%	0.36
Bar Soap 23	0.1	175		0.43%	0.24
Bar Soap 24	0.1	175		0.43%	0.24
Bar Soap 25	0.4	175		0.43%	0.97
Bar Soap 26	1.5	175		0.16%	1.32
Bar Soap 27	1.5	175		0.16%	1.32
Bar Soap 28	1.5	175		0.16%	1.32
Bar Soap 29	1.5	175		0.16%	1.32
Hand Wash 1	0.02		200	0.31%	0.01
Hand Wash 2	0.02		200	0.31%	0.01
Hand Wash 3	0.02		200	0.31%	0.01

Hand Wash 4	0.02	200	0.31%	0.01
Shower Gel 1	0.1	500	0.23%	0.27
Shower Gel 2	0.2	500	0.23%	0.54
Shower Gel 3	0.15	500	0.23%	0.40

Table S16: Sewage inflows and rainfall in Darvill WWTP.

Month	**Average Influent Flow – Ml/d**	**Average Rainfall – mm**
January	84.37	359
February	91.68	484
March	89.10	216
April	81.60	300
May	67.94	3
June	61.90	50
July	64.02	0
August	60.42	0
September	64.57	74
October	65.23	234
November	84.70	645
December	86.13	956