UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Prioritisation of emerging chemical pollutants in South African water resources

By

Fritz Petersen

10197762

Submitted in partial fulfilment of the requirements for the degree

MSc Water Resource Management

In the Faculty of Natural and Agricultural Sciences

University of Pretoria

Supervisor: Prof Patricia Forbes

Co-supervisor: Dr James Dabrowski

04 April 2016

Declaration

I, Fritz Petersen declare that the dissertation, which I hereby submit for the degree MSc Water Resource Management at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signature:……..

Date:……

Acknowledgements

Funding from the Water Research Commission (WRC) as part of WRC project no. K5/2438, the Photonics Institute of South Africa (PISA) and the National Research Foundation (NRF) is gratefully acknowledged.

I would further wish to acknowledge my study leaders, Professor Patricia Forbes and Doctor James Dabrowski, for their valuable input and the time they took to help me throughout this entire project.

Finally I would like to acknowledge and dedicate this dissertation to Ms Marie-Lou Petersen and Miss Michelle Bester as without their patience, support and encouragement it would have been extremely difficult for me to further my studies and complete this dissertation.

Table of Contents

List of Figures

List of Tables

Summary

Emerging chemical pollutants (ECPs) are defined as new chemicals which do not have a regulatory status, but which may have an adverse effect on human health and the environment. Sources and environmental pathways of these ECPs have been increasingly associated with waste and wastewaters arising from industrial, agricultural and municipal activities. The ECPs of current concern include a wide range of compounds including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), brominated flame retardants (BFRs), antivirals, antiretrovirals, pesticides, phthalates, disinfectants, psycho-stimulants, diuretics, cosmetics, contrast media, neuroactive compounds, blood lipid lowering agents, beta-blockers, antibiotics and, analgesics and anti-inflammatory drugs.

There is currently a lack of information regarding the nature, concentration, variability, transport and fate of these compounds in water, which is of global concern. A recent South African survey on emerging contaminants in drinking water in South Africa detected a total of 34 pharmaceuticals or pesticides, which indicates the need for more research in this area. In this study a prioritisation methodology for emerging chemical pollutants in water was developed and used. A group of 168 ECPs were prioritised based on various factors including toxicity (acute toxicity in rats), environmental persistence (half-life in water), relevant physicochemical data (partition coefficient) and global prevalence. The ECPs were then ranked by assigning weightings to these factors. The ranks each substance obtained were then summed across all the factors in order to obtain a final weighting for each substance. Each substance was then ranked in accordance with its final summed total which resulted in a ranked list of priority ECPs. After the prioritisation process, it became apparent that pesticides were a class of compounds that warranted further studies as they accounted for many of the highest ranked ECPs. The full list of ranked ECPs generated can prove to be an invaluable starting point for further research into ECPs in South African water bodies and to compare various ECPs with each other in term of their persistence, bioaccumulation and toxicity and thus the hazard they pose to the environment.

Additionally, relevant surface water sampling sites in the Gauteng Province of South Africa were identified utilising a geographic information system (GIS) to generate maps. The sites were identified by identifying potential sources of ECPs, including hospitals and clinics, sewage treatment plants, and areas with high population densities or areas that were vulnerable from an environmental point of view. Buffers were drawn around these areas to identify the water sources which have the highest probability of containing the relevant ECPs. The wards that are located along the identified at-risk river areas were also identified in an attempt to aid decision and policy makers within both the private sector and government in making informed decisions regarding ECPs.

List of Abbreviations

AOPS - Advanced Oxidation Processes

ARV - Anti-Retroviral

BFR - Brominated Flame Retardant

CNS -Central Nervous System

DDD - Dichlorodiphenyldichloroethane

DDE - Dichlorodiphenyldichloroethylene

DDT - Dichlorodiphenyltrichloroethane

DEET - N,N-diethyl-meta-toluamide

EC – Environment Canada

ECP – Emerging Chemical Pollutant

EDC – Endocrine Disrupting Chemical

ENVI - Environment for Visualizing Images

EPA – Environmental Protection Agency

ESRI - Environmental Systems Research Institute

FDA - Food and Drug Administration

FR – Flame Retardants

GABA - Gamma-Aminobutyric Acid

GIS – Geographic Information System

ICM - Iodinated Contrast Media

LOAEL - Lowest Observed Adverse Effect Level

MP – Medium Pressure

NOAEL – No Observed Effect Level

NSAIDS - Nonsteroidal Anti-Inflammatory Drugs

PA – Phthalic Acid

PAH - Polycyclic Aromatic Hydrocarbon

PBT – Persistence Bioaccumulation and Toxicity

PE – Phthalate Esters

PCP – Personal Care Products

QSAR - Quantitative Structure–Activity Relationship

SANBI - South African National Biodiversity Institute

SQL – Structured Query Language

SSRI - Selective Serotonin Re-Uptake Inhibitors

TA – Terephthalic Acid

TCC - Triclocarban

TCS - Triclosan

USGS – United States Geological Survey

UV – Ultra-Violet

WRCS – Water Resource Classification System

WWTP – Waste Water Treatment Plant

Chapter 1

1.1 Introduction

Humanity is facing major problems in the twenty-first century related to water quantity and/or water quality issues (Jackson, et al. 2005). The focus on maintaining clean usable water will likely be intensified in the future by climate change, resulting in higher water temperatures, melting of glaciers, and an intensification of the water cycle, in terms of more intense and more frequent extreme weather events (Huntington 2006), with potentially more floods and droughts (Oki and Kanae 2006). A lack of good sanitation, and related to it a lack of safe drinking water, currently affects more than a third of the people in the world, and therefore is a threat when considering potential human health impacts (Schwarzenbach et al. 2010). An additional related potential threat is: exposure to pathogens or to chemical toxicants via the food chain (e.g., the result of irrigating plants with contaminated water or the bioaccumulation of toxic chemicals by aquatic organisms) or during recreation (e.g., swimming in polluted surface water) (Schwarzenbach et al. 2010), as the aquatic environment has been termed the ultimate sink for natural and anthropogenic chemicals (Sumpter 1998).

Improvement in the fields of science and technology holds many advantages; however there can be detriments that accompany these improvements as well, especially when one considers the negative impacts such advances can have on the environment. Modern science and technology often develops and utilizes new chemicals for the benefit of the human race such as in the fields of health and agriculture. These chemicals can, however, have unintended effects after they have served their main purpose especially when they end up in water bodies and other natural ecosystems and start to negatively influence the organisms that live within these habitats. Once these chemicals enter ecosystems they are known as Emerging Chemical Pollutants (ECPs) and can be defined as new chemicals which do not have a regulatory status, but which may have an adverse effect on human health and the environment (Liu et al. 2014).

There is no standardised definition of what an ECP is, as different agencies define it differently. It has at times been defined to include regulated chemicals such as polychlorinated biphenyls (PCBs), as PCBs have the potential to cause endocrine disruption, which is why they are currently regulated (Diamond et al. 2011). Other definitions state that ECPs are chemicals that are currently unregulated, and this lack of a concise definition means that each study monitors its own subjective list of chemicals (Diamond et al. 2011). This can lead to questions being raised over how efficient the efforts of monitoring agencies are with regards to accurately and successfully assessing, and where possible circumventing or mitigating, negative effects associated with ECPs.

Pharmaceuticals are designed to target specific metabolic and molecular pathways in humans and animals, but they often have important side effects too. This is an example of how a chemical that is intended to be beneficial might end up causing harm to both the environment and humans, which can occur when ECPs are introduced into the environment and start potentially affecting the metabolic and molecular pathways in animals and other organisms that have identical or similar target organs, tissues, cells or biomolecules (Fent et al. 2006). For example, during the 2000s it was discovered that an unusually high death rate among various species of vulture in Asia was caused by a widely used analgesic and anti-inflammatory drug namely diclofenac (Meteyer et al. 2005). Renal failure and visceral gout resulted in population loss as uric acid accumulated throughout the body cavity following kidney malfunction (Meteyer et al. 2005). Residues of diclofenac leading to renal failure were reported by both experimental oral exposure and through feeding vultures the diclofenac-treated livestock. Thus it is apparent that diclofenac shares a direct relationship with renal failure in vultures (Meteyer et al. 2005).

Many ECPs are characterized poorly in terms of their presence in the aquatic environment and their potential effects on aquatic wildlife and humans (Diamond et al. 2011). That being said, acute toxicity for ECPs are unlikely to occur at environmental concentrations, as concentrations at which acute effects occur are usually 100-1 000 times higher than residues found in the aquatic environment (Farré et al. 2008). The only exception to these findings would be in the case of a spill of these chemicals (Fent et al. 2006). Although the reported concentrations of ECPs are generally low, questions have been raised over the potential impacts of these chemicals in the environment on human and animal health after long-term (chronic) exposure (Thomaidis et al. 2012). Thus the chronic effects of ECPs (e.g., pharmaceuticals) are more relevant, because many aquatic species are continually exposed over long periods, even throughout their entire life cycle. However, there has been little information reported to date on different effects and end points (Farré et al. 2008).

In the study of ECPs there is a lack of chronic toxicity data and when it is available the chronic toxicity data is mostly limited to certain species and as such comparison of toxicity between different species becomes difficult. Comparison between substances are also complicated as the toxicity of the substances are not always tested on the same organisms. Studies on the chronic toxicity often do not investigate the important key targets, nor do they address the question of different organisms (Fent et al. 2006). Toxicity experiments are usually performed according to established guidelines whereas specific investigations including analysis of possible targets of various ECPs, or over the different life stages of the aquatic organisms, are lacking or extremely rare (Fent et al. 2006). Life-cycle analyses have largely only been reported for ethinylestradiol (EE2) (Parrott and Blunt 2005) and toxicity to benthic and soil organisms have very rarely been evaluated (Fent et al. 2006).

Acute toxicity is the main focus of the available literature on the ecotoxicological effects of ECPs and it is generally focused on aquatic organisms (Fent et al. 2006). The effects of environmental parameters, such as pH, on the toxicity of ECPs have only been rarely explored. Studies like the aforementioned would be of importance when, for example, one considers the case where ambient pH can induce different toxicities for acidic pharmaceuticals (Fent et al. 2006).

It should be noted that ECPs can undergo chemical transformations in the environment and can thus have varying properties (Farré et al. 2008). This largely depends on the compartment in which the ECPs are present in the environment (e.g., groundwater, surface water or sediment) or in the technosphere (e.g., waste water treatment plants (WWTPs) and drinking-water facilities). Diverse transformations can take place, sometimes producing products that can differ in their environmental behaviour and eco-toxicological profile (Farré et al. 2008). For example, transformation products of some pollutants are often more persistent than their corresponding parent compounds or exhibit greater toxicity (e.g., the major biodegradation product of nonylphenolethoxylates, nonylphenol, which is much more persistent than the parent compound and can mimic estrogenic properties (Boxall et al. 2004)).

A biologically active compound's effect is typically the result of an interaction with a receptor and the particular moiety of the molecule (Boxall et al. 2004). If the active moiety remains intact during degradation, then the degradate may have the same mode of action as the parent (Boxall et al. 2004). There is also, however, the possibility that a transformation process could occur, which can result in a degradate that has a different and more potent mode of action than the parent, meaning the degradate will likely be more toxic than the parent (Boxall et al. 2004). The effects of drug metabolites and breakdown products have also rarely been investigated, however the relevance of studying compounds can be seen if the phototransformation products of naproxen are considered. This is due to the fact that they showed higher toxicities than the parent compound, though genotoxicity was not found (Isidori et al. 2005).

After being introduced into the environment, degradates may be transported and distributed between the major environmental compartments (Fent et al. 2006). The concentrations in these compartments can vary greatly depending on numerous factors and processes, including how the parent compound is released to the environment; how fast it degrades; the half-lives of the degradates; partitioning to sludge, soil, and sediment; and subsequent movement to air and water (Fent et al. 2006).

1.2 ECPs in a South African Context

Water pollution and the potential problems associated with ECPs are of particular concern to South Africa as it is a water scarce country where only 8.6% of the rainfall is available as surface water

(Haarhoff et al. 2015). South Africa's freshwater resources are already being utilised to capacity and the amount of available freshwater could become a limiting resource in determining the success of the goal of continued socio-economic development in the future (Haarhoff et al. 2015).

A large proportion of South Africa's population lives in rural or poorly developed areas that have inadequate infrastructure which includes a diminished water value chain (Ncube et al. 2012). This leads to undesirable scenarios and increases the risk of these people either contaminating the water or relying on and using water that has already been contaminated. In these areas there can be either no formal treatment or distribution of the water resource, which leads to consumers taking their drinking water directly from the water resource (Haarhoff et al. 2015). These areas can also suffer from the lack of a protected distribution system to direct treated water from the source to a tap in the homes of the consumers. This leads to scenarios where the inhabitants of these areas are forced to carry water in buckets (at times from unsanitary sources) to be used and stored in their homes. This form of water transport has been referred to as the "human pipe'' (Ncube et al. 2012).

Transporting water in this manner (via a "human pipe") can entail many hazards for the people who then use and consume this water in their daily lives. In addition to the pollution (both ECPs and conventional pollution) that was initially in the water, the quality of the water may be further diminished by the inappropriate use of materials for buckets (Haarhoff et al. 2015). These buckets can be plastic cans or poorly cleaned containers which contain bio-films on the inside. Lack of formal schooling and education in these regions also increases the risk of water recontamination occurring in the homes of consumers. In areas where there is this described lack of formal water infrastructure and there is a decreased water value chain, the ECPs and all pollutant concentrations in the raw water should ideally be strictly monitored and controlled to minimize the potential damage that these substances can cause (Haarhoff et al. 2015).

The rapid rate of industrialisation coupled with population growth and climate change has led to an increase in the awareness of the harm that humans can do to the environment. As such there is a growing cognizance of the accumulative amounts of chemicals being discharged into the environment from wastewater treatment effluents as well as industrial and agricultural sources.

South Africa has approximately 930 water supply systems thus sampling and analysing all these systems regularly for the thousands of potentially harmful chemicals would not only be extremely costly, it would also be very time consuming (Haarhoff et al. 2015). This is a problem faced by all policy makers and regulatory bodies around the world, but it cannot be used as an excuse for inaction. A possible solution to the problem can be found by implementing geographic information systems (GIS) as a tool to reduce the amount of sampling sites by determining hotspots based on relevant variables. These sampling hotspots can then be sampled regularly to determine the health

of the water body within which it is located and it can also be used to test for the presence of specific ECPs in the aquatic system.

Sampling for ECPs in South Africa usually only occurs at sites which are located within areas that are perceived to have high levels of pollution. It is worth noting that even with this being the case there are few instances where concentrations are found to be high enough to cause concern (Haarhoff et al. 2015). However there exists a distinct lack of information on the current status of ECPs and ECP contamination in South Africa and although the National Toxicity Monitoring Program is available, its efficiency is diminished due to limited sampling sites, analysis and budget (Haarhoff et al. 2015). Another problem that occurs in South Africa is the lack of periodic and ongoing data collection. This is especially important in South Africa as it is a developing country (Haarhoff et al. 2015)

The WHO has stressed the importance of gaining more knowledge and data on ECPs. Six aspects have been highlighted which they view as the most important with regards to ECPs and the influence that ECPs can have on both the environment and humans. These 6 aspects are as follows: 1) Strengthening knowledge of ECPs particularly in developing countries where there is a lack of data; 2) Enhanced testing (mixtures and effects); 3) Reducing exposure and susceptibility to disease; 4) Identifying Endocrine Disrupting Compounds; 5) Promoting scientific advances, innovation and disease prevention by creating suitable conditions for this to occur; and 6) Finding clear methods to assess the strength of the evidence between exposures to chemicals and adverse health effects (Bergman et al 2013).

A workshop on ECPs was held in Pretoria in 1999, where the need for reliable and relevant data on ECPs and especially EDCs in South African water systems was expressed. Consequently the WRC initiated a research programme on EDCs in 2001. This led to the development and publication of a strategic research plan by the WRC in 2005 (Burger and Nel 2005). This plan included the compilation of a list of priority compounds (for effects on both humans and animals).

More recent studies on ECPs found evidence of these compounds in one of Gauteng's largest water bodies, namely the Rietvlei Dam and the adjoining Rietvlei Nature Reserve (Barnhoorn et al, 2011). Evidence of intersex fish and wildlife that had calcified testes was found and the authors linked this with elevated levels of lindane, DDT and PCBs that they found in the fatty tissues of the organisms. These findings indicated that ECPs can be present in a multitude of environments and as such they cannot be ignored.

South Africa has a large agricultural sector which is also related to certain ECPs, due to the use of several herbicides, insecticides, nematocides and fungicides on crops, as well as substances that stimulate growth as well as veterinary products in animal husbandry (Haarhoff et al. 2015). The

detection, monitoring, control and treatment of these substances are more complex than other substances, due to the fact that these chemicals are non-point pollutants (Haarhoff et al. 2015).

1.3 Objective

The purpose of this study is to identify relevant ECPs that may be found in South African water bodies. These ECPs will then be prioritized based on multiple aspects including toxicity, quantity of use, environmental persistence, relevant physicochemical data and local (or global) prevalence to determine which of them are of greatest concern specifically to South Africa. Risk maps identifying areas of greatest concern in the province of Gauteng will be created by utilising a geographic information system (GIS). The sites will be identified by determining potential sources of ECPs, including hospitals and clinics, sewage treatment plants and areas with high population densities. Water sources which have the highest probability of containing the relevant ECPs will thereby be determined.

Chapter 2

2.1 Classes of Emerging Chemical Pollutants

ECPs can be categorized into groups of substances: pesticides, pharmaceuticals (including analgesics and non-steroidal anti-inflammatory drugs (NSAIDs), antibiotics, beta-blockers, blood-lipid lowering agents, neuroactive compounds, endocrine disrupting hormones, steroids, diuretics, psycho-stimulants and antidepressants), contrast media, personal care products (including disinfectants and phthalates), polycyclic aromatic hydrocarbons (PAHs) and flame retardants (Fent et al. 2006). These substances are briefly discussed to highlight their beneficial uses, the hazards they might pose and their primary characteristics. A number of inorganic ECPs have been mentioned in the literature (for example certain heavy metals and metalloids), but this dissertation focuses on organic ECPs.

2.2 Pesticides

The importance of agriculture in Africa, and the fact that South Africa is the highest user of pesticides in sub-Saharan Africa (Dalvie et al. 2009), means that pesticides have to be taken into account when discussing and prioritising ECPs under a South African context. Pesticides were included in this study owing to the fact that there are, as previously mentioned, multiple definitions for the term “emerging chemical pollutant”. These definitions can at times include or exclude pesticides based on the author’s discretion. The decision to include pesticides in this study was ultimately made to incorporate as many substances as possible and was also influenced by the size of the agricultural sector of South Africa.

The uninterrupted use of pesticides can result in: damage to the environment, human toxicity, reduced agricultural production and reduced agricultural sustainability. Both plants and animals can be adversely affected by numerous short- and long-term effects already on record, including human deaths (Wilson and Tisdell 2001). Pesticides can cause numerous health problems in humans including the following: chronic neurotoxicity, endocrine disruption, immune impacts, genotoxicity, mutagenicity and carcinogenesis (Dabrowski et al. 2014).

Pesticides can move throughout the environment via runoff, leaching and spray drift (Schulz 2001) causing pesticides to occur in non-target environments, especially in ground and surface water resources (Dabrowski et al. 2002). The amounts of pesticides that can be transferred to surface waters from runoff are reliant on the time interval between the application of pesticides and the first heavy rainfall event, the slope and soil types of the catchment, the quantity of applied pesticide, the chemical nature of the pesticide and the size and characteristics of buffer strips (Dabrowski et al. 2002).

The unintended devastation of vital agricultural predators of pests as a result of pesticide use has led to the spread of several pests and diseases (Wilson and Tisdell 2001). Initially the use of pesticides was very effective in reducing pest infestations and in increasing agricultural production and productivity. However, over time targeted pests developed resistance to pesticides necessitating increasing applications or resulting in rising populations of pests or both (Wilson and Tisdell 2001). After a point, resistance of pests can grow to such an extent that the application of pesticides is no longer an economically viable solution. Once application stops, the population of pests may climb to levels in excess of those pre-dating the use of pesticides. They may remain permanently above levels prior to the use of the pesticides. This can occur as a direct consequence of the pesticides eliminating the beneficial predators of pests (Wilson and Tisdell 2001). Pesticides are among a number of proposed causes for the decline in amphibian populations globally (Hayes et al. 2006). In South Africa, atrazine, mancozeb and acetochlor have been ranked as the top three priority pesticides in terms of their persistence, toxicity and usage information (Dabrowski et al. 2014).

Malaria is a disease that kills many people each year. Dichloro-diphenyl-trichloroethane (DDT) (a pesticide) is used in effort to control the threat posed by the malaria-carrying mosquito (Bornman et al., 2010). The efficacy that DDT has shown in decreasing cases of malaria as well as malaria related deaths when sprayed indoors has led to its continued use in efforts to control malaria (Bornman et al., 2010). The Stockholm Convention has granted South Africa restricted use of DDT for indoor residual spraying even though the use of DDT has been banned internationally (Bornman et al., 2010). DDT is not only harmful towards the environment due to its toxicity, but it is also an EDC (Bornman et al., 2010).

DDTs acute toxicity within the majority of mammals is low, however very limited information is available on the effect that chronic exposure (sufficient to cause hormone disruption) has on humans and animals (Bornman et al., 2009). This is especially true in South Africa as studies investigating the effect that chronic low dose exposure of DDT in the environment will have on aquatic as well as human health is severely lacking (Bornman et al., 2009). Bornman et al. (Bornman et al., 2009) has reported that the residues of DDT were found in fish fat samples taken from South African water bodies, thus it is known that DDT does occur in South African water bodies, which warrants further investigation. In a South African study completed in 2009 (De Jager et al., 2009) a correlation between DDT/DDE (Dichlorodiphenyldichloroethylene) and the occurrence of sperm with chromatin defects in young men was reported. The disruption of normal hormone function and DDT/DDE has widely been reported to cause adverse health effects.

2.3 Pharmaceuticals

2.3.1 Non-steroidal Anti-inflammatory Drugs (NSAIDs)

NSAIDS are commonly used to treat inflammation and pain and to relieve fever, and sometimes they are also used for long-term treatment of rheumatic diseases (Fent et al. 2006). NSAIDs act by inhibiting either reversibly or irreversibly one or both of the two isoforms of the cyclooxygenase enzyme (COX- 1 and COX-2), which catalyse the synthesis of different prostaglandins (active lipid compounds that cause hormone like effects in mammals) from arachidonic acid (Vane and Botting 1998). Since NSAIDs inhibit non-specific prostaglandin synthesis, most side effects after long-term treatment are related to the physiological function of prostaglandins (Fent et al. 2006). Renal (kidney) damage and renal failure after chronic NSAID treatment have been known to occur and seems to be triggered by the lack of prostaglandins in vasodilation-induction (Fent et al. 2006).

Paracetamol (acetaminophen) is a popular over-the-counter pain reliever and fever reducer. Paracetamol's mode of action is not yet fully understood but it is thought that this drug acts mainly by inhibiting the cyclooxygenase of the central nervous system (Fent et al. 2006). The lack of inhibition of peripheral cyclooxygenase involved in inflammatory processes is the reason behind why paracetamol is thought to lack anti-inflammatory effects (Fent et al. 2006). Adverse effects of paracetamol are mainly due to formation of hepatotoxic metabolites, primarily *N*-acetyl-*p*-benzoquinone imine, synthesized when the availability of glutathione is diminished in liver cells (Fent et al. 2006).

2.3.2 Antibiotics

Following from penicillin's discovery in 1928 by Sir Alexander Fleming, antibiotic use in human and veterinary medicine has become a common therapeutic practice that has led to both high consumption and the gradual accumulation of antibiotics in the environment (Manzetti and Ghisi 2014). Antibiotic contamination can have a multitude of sources which includes the following: wastewater, landfills, urban sites as well as industrial and hospital effluents (Renew and Huang 2004; Watkinson et al. 2009). Antibiotic compounds are largely composed of structures encompassed by cyclic components, represented by benzene rings, piperazine units, hexahydropyrimidines, as well as sulfonamides, quinolone and morpholine groups (Renew and Huang 2004). These compounds have meta-stable properties and yield both activated metabolites, conjugates and hydroxylated forms after being metabolised by humans and animals (García-Galán et al. 2008). These characteristics of antibiotics mean that when they are continuously released into the environment a range of diverse active chemical compounds enter the environment with possible reactive properties and largely unknown consequences. It should also be mentioned that there exists a lack of data on the potential increased resistance of clinically relevant microbes found in water bodies associated with antibiotic contamination of these water bodies (Cizmas et al. 2015).

Antibiotics can enter the environment in a variety of ways, from their production (direct discharges as a result of production can be extremely high) as active pharmaceutical ingredients, through to the excretion of residues after usage or through the discarding of unused medicines (Sarmah et al. 2006). Considerable amounts of active residues can be found in the urine and faeces of individuals who use antibiotics, thus waste waters can be rich in antibiotic residues, however they have also been found in marine environments (Kümmerer 2009). The degradation rates of different antibiotics in the environment can be vastly different. For example, penicillins are easily degraded whereas fluoroquinolones and tetracyclines are much more persistent meaning they will have a greater capacity to accumulate in the environment (Larsson 2014). It should, however, be noted that only a fraction of the total amounts probably remains bioactive as many antibiotics tend to bind strongly to particles. The precise amount of bio-available fractions of antibiotics in solid matrices is an important consideration in order to assess risks, but accurately determining this is still a major challenge (Boxall et al. 2012).

Antibiotics can be biologically converted to solubilized forms, including glucuronated, glutathione-conjugated and possibly arachidonated conjugates, as well as hydroxylated and nitro reduced forms (Farkas et al. 2007). Some of these forms have an increased capacity to be assimilated and accumulated in the environment (Farkas et al. 2007) and are therefore potentially absorbed in more advanced species, such as fish, animals and humans through nutrition and diet. This has recently been experienced where chloramphenicol glucuronic-conjugates have been found in the tissues of poultry, in bee-honey, and shrimp from Asian countries (Ferguson et al. 2005). Most species, particularly vertebrates, feature pathways and systems that metabolically break down xenobiotics and exogenous molecules in similar manners (Thomas 2007). The chemical properties, functional groups and the reactive atoms in the structures of antibiotics determine their metabolic fate. Thus diverse types of antibiotics can be treated differently by the body and therefore precede different types of metabolites in the excretion (urine/faeces) (Manzetti and Ghisi 2014).

Metabolites of antibiotics are sources of pollution in the environment particularly if thought is given to the water compartment and ground-water reserves. With the ever growing use of antibiotics and the poor regulation of their metabolites in the environment, the accumulation of antibiotics and their metabolites in animals and humans can thus be considered an environmental and toxicological threat. An estimated 100,000–200,000 tons of antibiotics are consumed each year, and large quantities of their residues are released into the environment, feeding the cycle of biotransformation and bioaccumulation of antibiotics in the environment (Kümmerer 2009). Wastewaters are the major carriers of antibiotics in heavily populated areas and the effective decontamination of wastewaters is critical for water purification and avoidance of their accumulation in the environment (Hu 2013). It is worth noting that antibiotics have also been reported in drinking water (Schaider et al. 2014).

Antibiotics are a group of emerging pollutants which require constant monitoring in the environment with particular focus on heavily populated urban areas (Manzetti and Ghisi 2014). Ideally, antibiotics should not affect humans and should only be toxic to bacteria and microbes, however reality is more complicated, as several classes of antibiotics used for therapy have direct toxic effects at prescribed doses (Larsson 2014). Research indicated that metabolites of antibiotics can be persistent, and accumulate in food and drinking supplies, including groundwater (which was originally thought to be resistant to substantial contamination (Manzetti and Ghisi 2014). As previously mentioned, wastewater is the most prominent environmental compartment impacted by these contaminants, and modern decontamination approaches (within waste water treatment plants) do not remove the antibiotic compounds fully, resulting in a low but never diminishing concentration remaining present in the environment (Manzetti and Ghisi 2014).

In a study by Martinez Bueno et al (2012) ECPs in waste water were typically detected in the range of a few ng L^{-1} to few hundred ng L^{-1}, although there were some exceptions to this as more frequently used compounds were detected in the mg L^{-1} range. These ECPs included atenolol, gemfibrozil, galaxolide, caffeine, acetaminophen, diclofenac, ofloxacin, ibuprofen, codeine, naproxen, paraxanthine and fenofibricacid (Bueno et al. 2012). Antibiotics as well as analgesics and anti-inflammatories were found most commonly and typically had the highest detection ranges as compounds classes (Bueno et al. 2012).

2.3.3 Beta-blockers

Beta-blockers typically act by competitively inhibiting beta-adrenergic receptors with the purpose of lowering high blood pressure (hypertension), and to circumvent the repetition of heart attacks in people who have already experienced one (Fent et al. 2006). Depending on the medical needs of a patient, beta-blockers may selectively inhibit one or multiple receptor types, where this selectivity is based on dissimilarity in chemical groups added to compounds that are able to enhance the interactions with amino acids of the trans membrane domains (Fent et al. 2006). Some beta-blockers (e.g. propranolol) have the ability to cause cell membrane stabilization, while others (e.g. metoprolol) have no membrane stabilizing qualities (Doggrell 1990). Side effects of beta-blockers are mainly bronchoconstriction and disrupted peripheral circulation.

Antilipidemic drugs (which promote the reduction of lipid levels in the blood) can be divided into two groups namely statins and fibrates. Fibrates are detected in the aquatic environment more often than the former (Fent et al. 2006). Both types work within the blood plasma to decrease the concentration of cholesterol (statins and fibrates) and triglycerides (fibrates) (Fent et al. 2006). Statins inhibit cholesterol synthesis by impeding the 3-hydroxymethylglutaril coenzyme A (HMG-CoA) which plays a vital part in limiting cholesterol synthesis, during the step where the conversion

of HMG-CoA to mevalonate takes place (Laufs and Liao 1998).The resorption of LDL (Low Density Lipoprotein)-cholesterol from blood plasma then takes place as a result of the intracellular cholesterol depletion which occurs when the expression of LDL receptors in hepatocyte membranes is increased (Fent et al. 2006). Fibrates likely act by activating the lipoprotein lipase enzyme, which is mainly responsible for the conversion of very low density lipoprotein (VLDL) to high density lipoproteins (HDL), which will therefore lead to a decrease in plasma triglycerides concentration (Staels et al. 1998).

Antilipidemic drugs, like the majority of all drugs, can also pose certain risks to the health of organisms. Fibrates stimulate cellular fatty acid uptake, conversion to acetyl-CoA derivatives, and catabolism by the beta-oxidation pathways, which, combined with a reduction in fatty acid and triglyceride synthesis, results in a decrease in VLDL production (Staels et al. 1998). Hepatic damage may occur after chronic exposure to fibrates (Qu et al. 2001) and this is thought to be related to inhibition of mitochondrial oxidative phosphorylation (Keller et al. 1992). Furthermore, fibrates can cause a massive proliferation of peroxisomes and there exists a strong correlation between fibrate exposure and hepatocarcinogenicity in rodents, however this was not the case in humans (Cajaraville et al. 2003).

2.3.4 Neuro-active compounds

Antiepileptic drugs act on the central nervous system (CNS) by reducing the overall neuronal activity (Fent et al. 2006). This can be achieved in two ways which are the blocking of voltage-dependent sodium channels of excitatory neurons (e.g. carbamazepine), or by intensifying the inhibitory effects of the GABA (gamma-aminobutyric acid) neurotransmitter (which is an amino acid which acts as a neurotransmitter in the central nervous system) by binding on a specific site in the gamma subunit of the corresponding receptor (e.g. diazepam) (Rogers et al. 1994).

Lately several studies have found that antidepressants and anxiolytic drugs alter the behaviour of fish, molluscs and crustaceans even at extremely low concentrations (Fong and Ford 2013).The intended targets of antidepressants, anxiolytic and neuropathic drugs for example TA (SSRI), drugs blocking voltage-gated sodium channels and GABA agonists, and specific antihypertensive compounds, are highly maintained across vertebrates and 61% of them are also found in the invertebrate crustacean *Daphnia* (Gunnarsson 2006; Rivetti et al. 2015). It then follows that neuro-active drugs may adversely affect aquatic invertebrates.

Several neuro-active compounds are intended to affect neurotransmitters (serotonin, dopamine, epinephrine, GABA, which control multiple physiological and behavioural processes (Fong and Ford 2013). The tendency of antidepressants at low concentrations to not follow a monotonic responses is increasingly being reported (Rivetti et al. 2015).

Similar findings have been reported for both endocrine and neuro-active compounds, as while they are present at low concentrations they act specifically on their target sites, however if they are present at high concentrations they become toxic thus impairing the survival, growth and reproduction of organisms, regardless of its original intended purpose (Rivetti et al. 2015). There is thus a necessity to study the continuous effects of neuro-active compounds at varying concentrations levels in non-target organisms.

Selective serotonin reuptake inhibitors (SSRIs) function by blocking the re-uptake of serotonin in the nerve synapses. SSRIs are prescribed universally to treat clinical depression in humans (Rivetti et al. 2015) which leads to these compounds becoming continuously more prevalent throughout the environment.

It was recently theorised that increased levels of synaptic serotonin found in water bodies was caused by SSRI treatment increased post-synaptic neuronal activity in *D. magna*, which alters the organism's view of the food environment and switches its life-history responses towards those usually only found during times of the highest levels of food availability (Rivetti et al. 2015). In invertebrates SSRIs can thus affect serotonin transporters, serotonin and other receptors. This can then negatively affect numerous organisms including for example crustaceans whose serotonin regulates neuro-secretory organs that release neuro-hormones that control reproduction, growth, maturation, immune function, metabolism, behaviour and colour physiology (Fong and Ford 2013).

Diazepam (Valium) is generally used to treat anxiety as it augments the effect of the neurotransmitter GABA. It does so by binding to the benzodiazepine site on the GABA receptor which leads to a depression of the central nervous system (Rivetti et al. 2015).

Carbamazepine is usually prescribed for the treatment of epilepsy and neuropathic pain (Rivetti et al. 2015). It achieves this by stabilizing the inactivated state of voltage-gated sodium channels, which reduces the number of these channels that are available to open leaving the targeted cells less reactive until the drug dissociates (Ambrósio et al. 2002). Carbamazepine is moderately persistent in water and can be found at concentrations ranging from 1 to up to 3000 ngL^{-1} in rivers receiving waste water treatment effluents (Muñoz et al. 2009). It was reported that in *Daphnia* carbamazepine decreased population growth rates at 200 μgL^{-1} and propranolol and fluoxetine impaired reproduction at 110 $\mu gL^{-1}$and 125 μgL^{-1},respectively (Dzialowski et al. 2006; Hansen et al. 2008).

Carbamazepine and diazepam can start effecting the phenotypic responses (e.g. behaviour) shortly after an organism is exposed to them, whereas a different neuro-active compound such as fluoxetine required at least one week to induce the same response (Rivetti et al. 2015). Certain neuro-active compounds can alter reproduction by delaying the time of the first reproduction and as

such it will negatively affect population growth rates (Rivetti et al. 2015). This contributes to the potential risk that these substances an pose to the environment.

2.3.5 Endocrine disrupting chemicals

An endocrine disrupting substance is an exogenous substance or mixture that alters the function of the endocrine system and therefore causes negative effects in an intact organism, or its offspring, or subpopulations (Mills and Chichester 2005). Numerous classes of chemicals show endocrine-disrupting properties. Endocrine-disrupting chemicals (EDCs) have the potential to interfere with normal reproduction and development, which are controlled by an array of hormonal signals, in a number of ways. This includes mimicking endogenous hormones, antagonizing normal hormones, altering the natural pattern of hormone synthesis or metabolism, or modifying hormone receptor levels (Sonnenschein and Soto 1998).

When interference by exogenous substances occurs to the internal endocrine signalling pathways of an organism, endocrine disruption has occurred (Cheek et al. 1998). The similarity of the reproductive physiology of mammalian and non-mammalian vertebrates in so far as the broad structure and function of the reproductive axis involving the hypothalamus, pituitary and gonads is concerned lead to the fact that many different species are susceptible to EDCs (Mills and Chichester 2005). EDCs can impact organisms living in various aquatic environments as they have been found in freshwater, estuarine, and marine environments (Mills and Chichester 2005). Interference with the normal synthesis, storage, release, transport, metabolism, binding, action or elimination of endogenous hormones are how EDCs are likely to influence these susceptible organisms (Kavlock et al. 1996). It is worth mentioning that anti-estrogenic activity has even been displayed by several PAHs in a yeast-based oestrogen receptor binding assay (Tran et al. 1996).

Evidence for endocrine disruption from the natural environment has been commonly reported in studies that focus on animal species that either live in water or are very water dependent (Aneck-hahn et al. 2009). Thus the aquatic environment generally forms the basis for endocrine disruption studies and sampling. The vulnerability of aquatic ecosystems is further incited by the fact that the majority of EDCs as well as their breakdown products will inevitably end up in an aquatic ecosystem somewhere in the world (Aneck-Hahn et al., 2009). These aquatic ecosystems can simply be the habitat of various organisms or it can be used as a drinking source for humans.

Evidence for endocrine disruption in fish in the form of intersex has been reported in both freshwater and marine environments (Aneck-Hahn et al. 2007). Male rats dosed with ecologically applicable concentrations of p-nonylphenol resulted in harmful effects on both the Sertoli cells and the testes (Aneck-Hahn et al. 2009). DDT is still utilized in certain areas of South Africa as a malaria vector control (such as in the Limpopo Province) and it was discovered that non-occupational exposure to DDT damaged the semen of human males (Aneck-Hahn et al. 2007). The threat of EDCs in South

Africa has not been avoided or mitigated and thus is similar to other countries of the world in that both animals as well as humans are at risk (Aneck-Hahn et al. 2009). The threat that EDCs pose to the South African environment as well as to human health in general is thought to be more severe and widespread than originally predicted. Thus there is a dire need to inform the general public about the risk as well as further scientific study especially in order to gather more epidemiological information (Aneck-Hahn et al. 2007).

2.3.6 Antiretrovirals

The use of antiretrovirals (ARVs) per capita in South Africa is elevated and higher than any other nation due to the number of people living with HIV/AIDS in this country (Wood et al. 2015). It has been reported that approximately 2 150 880 people living in South Africa were receiving treatment by ARVs in 2012 in contrast to the estimated 199 000 people who are treated using ARV therapy in Eastern Europe (World Health Organization et al. 2013a). As such these compounds should be considered as emerging pollutants, especially in South Africa.

The greater number of people who use and rely on ARV treatment in South Africa have been speculated to possibly lead to an increased number of these compounds that ends up in the environment (Wood et al. 2015). This could lead to a unique and possibly detrimental scenario with regards to the presence and transformation of these compounds once they have entered the environment. The potential impact that these compounds can have on the environment and the water resources of the country can be aggravated by the overall low rainfall and water scarcity in sub-Saharan Africa; which would mean that there will be little or no dilution of these target compounds that can occur naturally in the environment. The sheer number of compounds that are used for the treatment of HIV/AIDS and thus the breadth of the compound class also present analytical challenges (Peng et al. 2014). These compounds include the following: nucleoside and non-nucleoside reverse transcriptase inhibitors, protease inhibitors, fusion inhibitors, entry inhibitors and integrase strand transfer inhibitors, which are used to treat HIV (Peng et al. 2014) and to prevent mother-to-child transmission (Mofenson 2010). Compounds include Zalcitabine, Tenofovir, Abacavir, Efavirenz, Lamivudine, Didanosine, Stavudine, Zidovudine, Nevirapine, Indinavir, Ritonavir and Lopinavir (Wood et al. 2015; Peng et al. 2014).

Unlike with substances such as antibiotics, which promote drug resistance in the naturally occurring microbes in the environment, the consequences, impacts and environmental relevance of ARVs in water supplies might not be immediately apparent (Peng et al. 2014). HIV does not have a non-human host and cannot occur in the environment, as is the case with other viruses or bacteria. The model for the transfer of resistant genes between species is also not relevant and cannot be applied when considering the nature and characteristics of this virus (Wood et al. 2015). The effects that ARVs can have on other environmental retroviruses is largely unknown and literature on the topic is

lacking (Wood et al. 2015; Peng et al. 2014). It should be mentioned that even if the presence of these compounds in the environment does not affect the target virus, they could still stimulate the development of drug resistance in other pathogens (Wood et al. 2015; Peng et al. 2014).

2.4 Personal Care Products

Due to the direct route that personal care products (PCPs) follow from being discharged into domestic wastewater, which travels from residential areas into the water resources and passes through wastewater treatment plants, they form an essential group of compounds to consider (Haarhoff et al. 2015). PCPs are typically also used in considerable quantities and as such their potential to cause significant damage to both human beings and the environment is greatly enhanced.

Personal care products (PCPs) are a varied group of compounds that are generally used to make products such as soaps, lotions, toothpaste, fragrances, and sunscreens (base) (Brausch and Rand 2011). The primary classes of PCPs include disinfectants (e.g. triclosan), fragrances (e.g. musks), insect repellants (e.g. *N*,*N*-diethyl-*meta*-toluamide (DEET)), preservatives (e.g. parabens) and UV filters (e.g. methylbenzylidene camphor) (Brausch and Rand 2011). PCPs are products intended for external use on the human body and thus are not subjected to metabolic alterations (which pharmaceuticals are subject to); therefore, large amounts of PCPs move into the environment unchanged and in their unaltered forms (Ternes and Hansruedi 2004). Many PCPs are utilized in large quantities and many have been found to be environmentally persistent, bioactive, and have the potential for bioaccumulation (Peck 2006).

PCPs comprise some of the most commonly detected compounds in surface water throughout the world (Peck, 2006); however, unlike the case with pharmaceuticals, there is a lack of knowledge on PCP toxicity (Daughton and Ternes 1999). Multiple studies have been published on the topic of pharmaceutical occurrence and toxicity (Jorgensen and Halling-Sorensen 2000; Crane et al. 2006; Fent et al. 2006), but a significantly smaller number of studies have determined the potential risk that the release of PCPs into aquatic environments pose. However, when reported, the risk posed by PCPs in water bodies to human health has commonly been reported as being inconsequential (Cizmas et al. 2015).

2.4.1 Triclosan (TCS) and triclocarban (TCC)

Triclosan (TCS) and triclocarban (TCC) are used in soaps, deodorants, skin creams, toothpaste and plastics as antimicrobials (McAvoy et al. 2002). TCS and TCC are amongst the 10 most regularly detected organic wastewater compounds when considering both frequency and concentration (Brausch and Rand 2011). The methyl derivative methyl triclosan (M-TCS), usually found in WWTP effluent, is relatively stable and lipophilic and as such is likely to bioaccumulate in biota (Brausch

and Rand 2011). TCS already has known ecological effects for example it has been found to induce alterations in swimming performance of fish such as *Oncorhynchus mykiss, Danio rerio*, and *Oryzias latipes* at low concentrations (71 μgL^{-1}). These measured concentrations are considerably greater than other endpoints indicating that this behaviour is not a sensitive endpoint for identifying TCS effects (Orvos et al. 2002). It is worth mentioning that TCS is also weakly estrogenic and exposure to TCS has been associated in changes in fin length and sex ratios of medaka fish (*O. latipes*) (Brausch and Rand 2011). These estrogenic effects have been attributed to its similarities in structure to the non-steroidal estrogen diethylstilbestrol (Ishibashi et al. 2004).

2.4.2 Fragrances

The most widely studied class of PCPs are possibly fragrances as they are suspected of being nearly omnipresent contaminants in the environment (Daughton and Ternes 1999). Synthetic musks are the most commonly used fragrances and are utilized in a wide range of products including deodorants, soaps, and detergents (Brausch and Rand 2011). Synthetic musks can be divided into two classes namely: nitro musks (which were introduced in the late 1800s) or polycyclic musks (which were introduced in the 1950s) (Daughton and Ternes 1999). Active efforts are underway to phase out nitro musks due to their environmental persistence and potential toxicity to aquatic species (Daughton and Ternes, 1999). This means that polycyclic musks are currently used in higher quantities with especially celestolide (ABDI), galaxolide (HHCB) and toxalide (AHTN) seeing widespread use.

Both types of musks are water soluble, but the typical high octanol– water coefficient which are common for polycyclic musks (Schramm et al. 1996) indicate the high possibly for these musks to bioaccumulate in aquatic species (Brausch and Rand 2011). This potential has been confirmed by numerous studies which found high concentrations of musks in lipids from fresh- and saltwater fish and mollusks (Schramm et al. 1996).

Nitro musks have a negligible propensity to cause acute toxicity to aquatic taxa studied to date. It has been suggested that nitro musk transformation products possess the potential to be highly toxic to aquatic organisms although there is little data to support this (Daughton and Ternes, 1999). Polycyclic musks are more acutely toxic than nitro musks based on published literature (Brausch and Rand 2011). However, limited research has been conducted on the effects of musks on algae and benthic invertebrates, and therefore the potential risk cannot be accurately determined (Brausch and Rand 2011).

Synthetic musks possess high octanol–water coefficient and as such benthic invertebrates are suspected to be exposed to high concentrations of synthetic musks located within the sediment and ought to be tested to evaluate potential toxicity of musks released in WWTP effluent (Brausch and Rand 2011). Very few studies have scrutinized synthetic musk toxicity to sediment/soil organisms

although there is a potential risk of exposure to musk for benthic invertebrates (Brausch and Rand 2011).

2.4.3 N,N-diethyl-m-toluamide

N,N-diethyl-m-toluamide (DEET) is the most common active ingredient in insect repellants (Costanzo et al. 2007) and is consistently identified in surface waters (Brausch and Rand 2011). DEET was developed during the 1940s and its method of action relies upon interfering with insects' capability to detect lactic acid on hosts. DEET is currently registered for use in 225 products and it is estimated annual usage exceeds 1.8 million kg in the United States of America alone (USEPA, 1998). DEET is moderately persistent in the aquatic environment, however unlike the case with many other PCPs (e.g. fragrances) DEET has a low bio-concentration factor (BCF) and is not likely accumulated into aquatic organisms (Costanzo et al. 2007). There is currently a lack of data pertaining to acute toxicity of DEET to aquatic organisms (Brausch and Rand 2011).

Studies found that DEET is only marginally toxic to aquatic organisms (Brausch and Rand 2011). Even though DEET is fairly resistant to breakdown and is commonly found in surface water, no studies could be found that specifically examined chronic toxicity of DEET to aquatic organisms. DEET has been found to impede cholinesterase in rats however, and DEET had no effect on sperm count, morphology, or viability in male rats after 9 weeks exposure (Brausch and Rand 2011).

Costanzo et al. (2007) performed a preliminary risk assessment based on available data and concluded that DEET is unlikely to produce biological effects at environmentally relevant concentrations in aquatic ecosystems. Due to the lack of chronic toxicity information, a definitive assessment could not be made. Analogous conclusions surrounding the biological risk posed by DEET are still pertinent while the chronic toxicity of DEET to aquatic organisms remains undetermined.

2.4.4 Parabens

Parabens (alkyl-p-hydroxybenzoates) are antimicrobial preservatives found in cosmetics, toiletries, pharmaceuticals, and certain types of food (Daughton and Ternes, 1999). Seven different types of parabens are currently in use benzyl, butyl, ethyl, isobutyl, isopropyl, methyl, and propyl and that number is expected to grow in the future. Methyl- and propylparaben are the most commonly used in cosmetics and are usually co-applied to increase preservative effects (Peck 2006). Only a limited number studies have inspected paraben concentrations in WWTP and surface water (Brausch and Rand 2011).

Methyl- and ethylparaben seem to be least acutely toxic of the different types of parabens with LC_{50} values approximately three times greater than benzylparaben (Terasaki et al. 2009) and benzylparaben appears to be most acutely toxic (Terasaki et al., 2009). It has been reported that

increasing chain length of parabens' substituents can increase paraben acute toxicity to bacteria and this appears to be true for other trophic groups as well (Brausch and Rand 2011).

The only data on the chronic effects of parabens to aquatic organisms comes from a single known study examining toxicity in *D. magna* and *Pimephales promelas* (fathead minnow) (Dobbins et al. 2009). This study found that benzyl- and butylparaben had the highest toxicity to invertebrates and fish whereas methyl- and ethylparaben appeared to possess the lowest toxicity. This correlates well with the findings of acute toxicity studies, as well as previous studies that indicated increased chain length of parabens increases toxicity. It must be noted that chlorination also considerably enhances the toxicity of parabens to both bacteria and *D. magna* (Terasaki et al. 2009).

Benzyl-, butyl- and propylparaben might possibly cause adverse effects to aquatic organisms based on available environmental concentration and toxicity data. Dobbins et al. (2009) reported that parabens incur a limited hazard to aquatic organisms. They did however mention that certain parabens namely: benzyl-, butyl- and propylparaben, can stimulate low-level estrogenic responses in organisms that are chronically exposed to parabens. Analysis of environmental concentrations suggest that the risk to aquatic organisms is only minimal. This is due to the fact that effect concentrations tend to be a thousand times higher than observed concentrations within surface waters (Brausch and Rand 2011).

2.4.5 UV filters

Recent understanding of the various hazards that are posed by ultraviolet (UV) radiation to humans has caused an amplification in the usage of UV filters (Brausch and Rand 2011). UV filters are contained within sunscreen products and cosmetics to provide fortification against UV radiation and can be either organic (absorb UV radiation, e.g. methylbenzylidene camphor) or inorganic micro-pigments (reflect UV radiation, e.g. ZnO, TiO_2) (Brausch and Rand 2011). For the purpose of this project focus will be given to organic (absorbent) products.

UV filters tend to enter the environment in one of two manners namely directly or indirectly. This can be directly from being washed off the body while swimming or during other recreational activities or it can enter the environment indirectly via WWTP effluent (Brausch and Rand 2011). While UV filters are used at high levels and are thus likely to enter aquatic environments, there is a lack of data on actual occurrence information largely due to a lack of suitable analytical methods (Brausch and Rand 2011).

A study indicated that UV filters do not appear to be acutely toxic to aquatic organisms (Fent et al. 2010). UV filters tend to bioaccumulate and recent studies have also shown that they also possess the potential for estrogenic activity. These studies utilized fish (*P. promelas* and *O. mykiss*) to

indicate that several UV filters have the capability to cause estrogenic effects and also adversely affect fecundity and reproduction (Brausch and Rand 2011).

Even though PCPs can be released at levels exceeding other compounds, including pharmaceuticals, there is a lack of research conducted on the identification of environmental concentrations and potential toxicity (Brausch and Rand 2011). PCPs in the environment are also repeatedly replenished through normal usage and are thus persistent or at the very least pseudo-persistent compounds that warrant acute and chronic studies (Brausch and Rand 2011).

Studies into both acute and chronic toxicity are also needed to fully elucidate the potential effects and risks that the release of PCPs into surface waters entails. As is the case with pharmaceuticals, studies examining the effects of PCPs on benthic invertebrates are severely lacking (Brausch and Rand 2011). The potential for PCPs to bioaccumulate and their propensity to cause estrogenic and endocrine effects need to be studied and investigated as these are the areas of greatest concern as the majority of completed studies reported little short- or long-term toxicity (Brausch and Rand 2011).

2.5 Contrast Media

The majority of these iodinated X-ray contrast media (ICM) are derivatives of 2,4,6- triiodobenzoic acid with polar carboxyl and hydroxyl moieties in their chains. Some have one or several free carboxyl groups, while others are neutral compounds as they are amide derivatives (Pérez and Barceló 2007b). They all have the shared characteristic of featuring iodine atoms in the molecule, as these are responsible for absorption of X-rays, which is what makes these compounds suitable for use during X-ray diagnostic processes (Pérez and Barceló 2007b).

The most commonly used pharmaceutical (approximately 3.5×10^6 kg per year (Pérez and Barceló 2007b)) that is administered intravenously is iodinated X-ray contrast media (ICM). ICM are perfectly suited for use during diagnostic tests (the imaging of organs or blood vessels) due to its stable metabolic characteristics whilst inside the body which allows for rapid elimination via urine or faeces after use (Pérez and Barceló 2007b). It should be noted that belated side effects can still occur at frequencies of 1–3% in patients who have been exposed to ICM. These side effects are allergic/allergy-like adverse effects which includes the *de novo* synthesis of cysteinyl-leukotrienes (Pérez and Barceló 2007b). The negative effects associated with ICM were discovered in hospital wastewater where these compounds contributed considerably to organically bound halogens which could be absorbed onto activated carbon (AOX) (Kümmerer et al. 1998).

2.6 Flame Retardants

Flame-retardants (FRs) are anthropogenic environmental contaminants that are utilised at relatively high concentrations for numerous purposes (Segev et al. 2009). Brominated flame retardants (BFRs) (the most common and popular FRs currently available on the market) are considered toxic, persistent and bio-accumulative (Segev et al. 2009). FRs are used at reasonably high concentrations (5-30%) in numerous applications (both indoor and outdoor) which include the manufacture of electronic equipment, textiles, plastic polymers, televisions, computers, microwave ovens, copy machines, lamp shades, textiles, furniture and in the car industry (Alaee et al. 2003). Globally the demand for BFRs continues to rise and it is estimated that more than 200 000 tonnes of BFRs are produced in the United States alone each year and that more than 1.5 million tonnes are produced globally each year (Alaee et al. 2003). The primary use of FRs (as their name suggests) are to protect materials against ignition and to minimize fire-related damage (Segev et al. 2009).

As is the case with the majority of halogenated organic compounds, BFRs tend to have restricted biodegradability, thus they are persistent and tend to accumulate in the environment (Segev et al. 2009). It is worth mentioning that the toxicity of the compounds towards fauna, flora and humans can be naturally altered to be less or even more toxic than the original compound (Segev et al. 2009). FRs are introduced into the environment in a multitude of ways. They can, for example, be present in wastewaters from industrial facilities that manufacture FRs (including facilities that integrate these compounds into the products they produce) (Birnbaum and Staskal 2004). The volatilization and leaching from products during manufacture or usage and the breakdown of foam products are also ways that FRs can enter the environment (Segev et al. 2009). In addition, the disposal of products (e.g. electronic equipment), leaching from landfills, the burning and recycling of waste or adsorption onto dust particles can also result in FRs ending up in the environment (Birnbaum and Staskal 2004).

Additive FRs tend to be released into the environment at a greater rate than reactive FRs (Alaee et al. 2003). When a FR enters the environment, attachment to particles can lead to these compounds being able to travel great distances (recent studies have even found levels of BFRs in the Arctic) if they travel with airborne dust particles or via water bodies such as rivers (Segev et al. 2009). During transport in the water body these molecules can adhere to solid particles and can thus become part of the suspension load and later the deposition load (Segev et al. 2009). After being deposited these compounds will form part of the sediment of the region. The above mentioned are cited as the reasons why traces of FRs (halogenated and organophosphorous-containing) can be found in terrestrial, freshwater and marine environments, often at great distances from the site of their production/release (Birnbaum and Staskal 2004).

Increased lipid solubility and reduced water solubility are directly associated with the halogen moiety of organic compounds. Additionally, the toxicity of compounds can be increased by the halogen substituent and its potential organohalide metabolites (Birnbaum and Staskal 2004). Thus many BFRs are toxic (acute and chronic), persistent and bio-accumulative in the environment, due to bromide substituents (Birnbaum and Staskal 2004). BFRs have been found in plants and animals (including humans) throughout the food chain (Segev et al. 2009).

Human tissue, blood serum and breast milk of exposed individuals (e.g. people working in the production of BFRs) have all been known to contain BFRs (Sjödin et al. 2003). BFRs have numerous hazardous qualities such as immunotoxicity, cytotoxicity, neurotoxicity, endocrine disrupting capabilities, genotoxicity, mutagenicity, carcinogenicity and teratogenicity (Birnbaum and Staskal 2004). Despite their potentially devastating attributes, limited data is available on BFRs, particularly regarding the effects of BFRs on the environment (including environmental fates and biodegradability potential), plants, animals and humans (Segev et al. 2009).

2.7 Phthalates

Phthalate esters (PEs) or phthalates are the dialkyl or alkyl aryl esters of 1,2-benzendicarboxylic acid (phthalic acid). The name phthalate is derived from phthalic acid, referring to three isomers namely the ortho-isomer or phthalic acid (PA), para-isomer or terephthalic acid (TA), and meta-isomer isophthalic acid (IA) (Liang et al. 2008). Phthalates can be found in multiple environments which include the following: air (Wensing et al. 2005), soils, sediments, landfill leachate (Schwarzbauer et al. 2002), and natural waters (Stales et al. 1997). The diversity of the environments within which phthalates can be found is attributed to the popularity and widespread use of plastic. Phthalates are not chemically bonded to the plastic polymer when utilised as plastizers, thus rendering them able to transfer from the plastics into the environment (after a sufficient time period).

Phthalates are produced in massive quantities during the manufacturing of various plastics and as a result of their release during these processes, including use and disposal, have become widely distributed throughout the environment (Liang et al. 2008). This is cause for concern as phthalates and their metabolites are hepatotoxic, teratogenic, and carcinogenic by nature, thus they have the potential to cause serious damage to the environment and humans (Matsumoto et al. 2008).

2.8 PAHs

PAHs are composed of carbon and hydrogen atoms arranged in the form of fused benzene rings (linear, cluster or angular arrangement) (Maliszewska-Kordybach 1999). They feature strong mutagenic, carcinogenic and toxic properties. PAHs consist of thousands of compounds in the environment and 16 of these are defined as EPA priority PAH compounds. Individual PAHs can

feature substantial differences in their physical and chemical properties (Maliszewska-Kordybach 1999). Generally PAHs with a lower molecular mass are more water-soluble, more volatile and less lipophilic than higher molecular mass PAHs (van Jaarsveld et al. 1997).

Some PAHs are resistant to environmental degradation and can thus remain in the environment for long periods of time which give them ample opportunity to cause environmental impacts. The dispersion of these chemicals are also a concern as some of them are semi-volatile, meaning that under normal environmental conditions they are in constant motion between the surface and atmosphere of the earth in repeated, temperature-driven cycles of deposition and volatilisation (Maliszewska-Kordybach 1999).

PAHs are produced and released during all processes of incomplete combustion of organic materials and as such they occur over a wide area. The size of this area and the concentrations of PAHs in the environment were greatly expanded during the last century of industrial development (Wild and Jones 1995). Before being deposited via atmospheric precipitation on soils, vegetation or sea and inland waters, PAHs can travel great distances through the air (Wild and Jones 1995). The presence of PAHs in all the various compartments of the environment may pose a threat to all living organisms (Maliszewska-Kordybach 1999).

Anthropogenic PAHs can be separated into two categories based upon their origin: the combustion of materials for energy supply and combustion for waste removal (Wild and Jones 1995). The first category includes both stationary and mobile sources. Examples of mobile sources include industries (mainly coke and carbon production, petroleum processing, aluminium sintering, etc.), residential heating (furnaces, fireplaces and stoves, gas and oil burners), power and heat generation (coal, oil, wood and peat power plants) whilst mobile sources include examples that are mainly part of the transport sector like cars, trains, airplanes and ships (Maliszewska-Kordybach 1999). Means of transport can affect a country's estimated annual PAH emission quantities as there is a difference between gasoline and diesel engines (Maliszewska-Kordybach 1999). The second category covers the incineration of both municipal and industrial wastes (Maliszewska-Kordybach 1999). Miscellaneous sources of PAHs include unregulated fires (which includes the burning of biomass) such as agricultural burning, recreational fires and crematoria (Wild and Jones 1995).

2.9. Disinfection By-products

Disinfection by-products are formed by the interaction between the chemicals used as a part of water sanitation and biotic as well as abiotic matter (Diamond et al. 2011). Strong oxidising agents such as chlorine and chloramine are often used as disinfection agents in water for the purpose of pathogen removal, odour elimination and to form a lingering disinfectant presence to ensure the safe transport of water to consumers. It should be noted however that these strong oxidising agents

can react with fulvic and humic acids, amino acids, and other organic tissues once it has been ingested (Diamond et al. 2011).

The negative health effects associated with disinfectant by products (DBPs) can be quite severe (Nieuwenhuijsen et al. 2000). The risk this class of ECP possesses cannot be ignored as it has been linked to numerous problems in pregnant women specifically. These problems include low birth weight, preterm delivery, spontaneous abortions, stillbirth, and birth defects, major cardiac defects, oral cleft, and respiratory, and neural tube defects (Nieuwenhuijsen et al. 2000).

Nieuwenhuijsen et al. (2000) recommended that large methodically designed epidemiological studies be carried out to determine if the risks that have been attributed to DBPs, especially in the case of pregnant women, are factual and correct. The authors did, however, note that these studies could prove costly, but that these costs can be minimised through proper planning (Nieuwenhuijsen et al. 2000).

2.10. Sources and Environmental Pathways of Emerging Chemical Pollutants

Certain organic chemicals have been proven to be harmful to fish, other animals and potentially also humans (Diamond et al. 2011). Due to this reason there has been a great effort to study the fate, occurrence and ecotoxicology of ECPs in the aquatic environment. Sources and environmental pathways of ECPs have been increasingly associated with waste and wastewaters arising from industrial, agricultural and municipal activities (Jorgensen and Halling-Sorensen 2000). Residues of these biologically active compounds can enter the environment via different transport pathways such as: emissions during manufacture, disposal of products and unused or expired medicines, human and animal excretion in urine and faeces, direct discharge of aquaculture products, and manure and slurry spreading (Jorgensen and Halling-Sorensen 2000) (Fig. 2.1).

Veterinary drugs (that are used for treatment and prevention of diseases in farming) and their metabolites are prone to contaminate soil and groundwater, but they are intentionally introduced into the environment when liquid manure is sprayed on agricultural fields. The transport of veterinary drugs to groundwater can be through leaching or run-off from livestock slurries, while sorption of the drug onto soil particles can delay its distribution. Human pharmaceuticals enter aquatic systems after ingestion and subsequent excretion in the form of the non-metabolized parent compounds or as metabolites through waste water treatments plants (WWTPs) (Pérez and Barceló 2007a). If the pharmaceuticals and their human or animal metabolites pass through WWTPs, they can then enter into rivers or streams. Alternatively they can undergo leaching and enter the groundwater. In addition, run-off from fields treated with digested sludge can cause pharmaceuticals to reach surface waters.

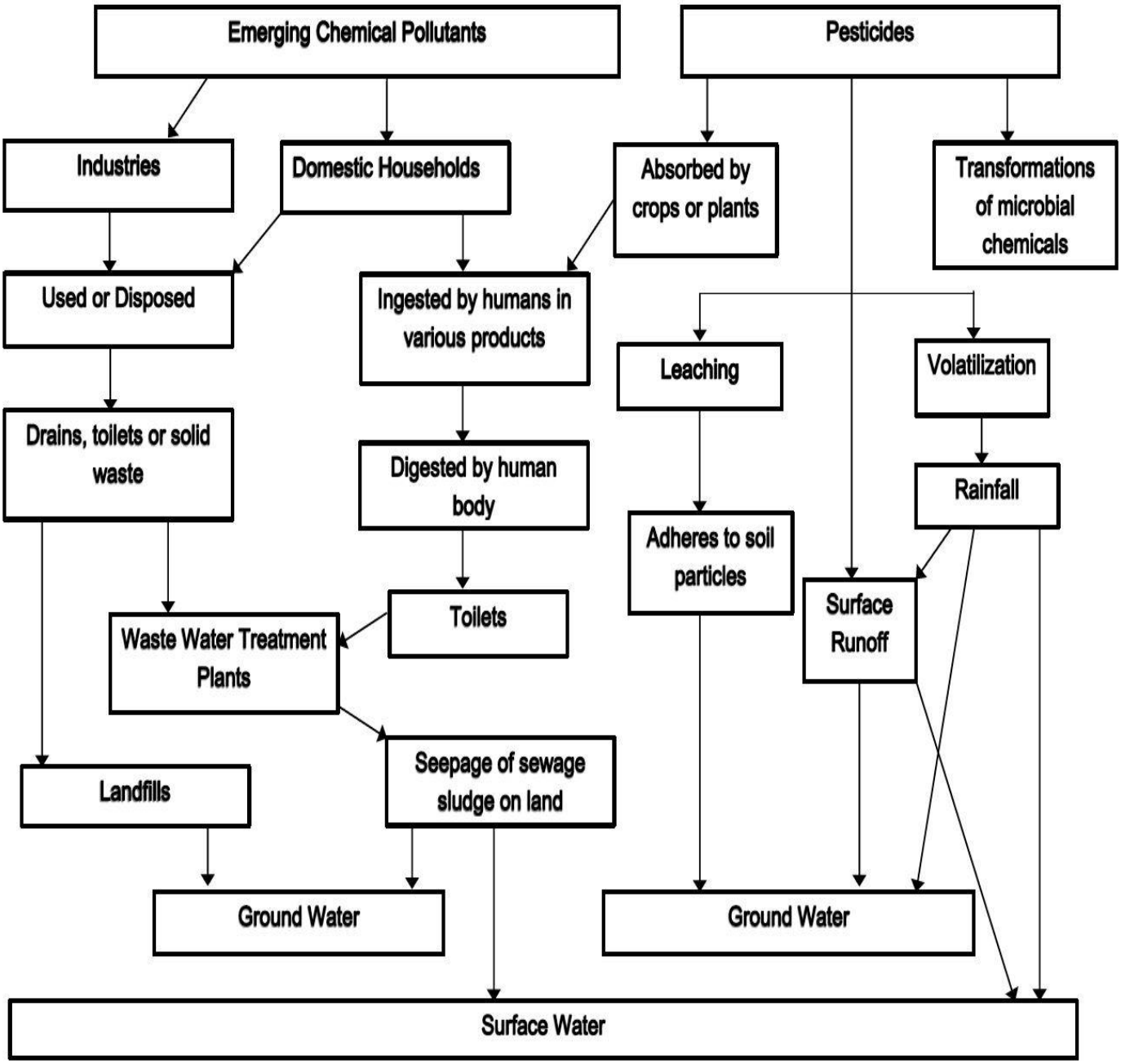

Figure 2.1:Sources and environmental pathways of emerging chemical pollutants to surface waters (Adapted from numerous literature sources)

2.11. Movement and Degradation of ECPs in the Environment

Once ECPs enter a water resource they can follow multiple pathways which may alter their concentration. Certain of these pathways involve the partitioning of these chemicals, meaning that they remain intact but can escape into the gas phase or be adsorbed and become part of the sediment of the water body (García et al. 2011). Degradation can also occur in some of the possible pathways. These chemicals can be degraded by light (photolysis) or they can be ingested and broken down by organisms (metabolisation) (Gavrilescu et al. 2014).

The degree to which partitioning and degradation takes place depends on numerous physical factors including: retention time in various media, sediment properties, pH, water temperature, light penetration, and degree of eutrophication (Haarhoff et al. 2015). If the exact details of partitioning and degradation rates are required for a study, a site-specific investigation will be required that takes the uniqueness of the aforementioned physical factors of the specific site into account.

2.11.1 Bioaccumulative Potential, Ingestion and Metabolisation of ECPs by organisms

ECPs are readily absorbed by organisms through their skin, respiratory and gastrointestinal tracts, before being distributed throughout the tissues of the organism (Gavrilescu et al. 2014). The bio-accumulation potential of ECPs tends to be relatively low, thus there generally tends to be low concentrations of these chemicals found in tissue (Haarhoff et al. 2015). It is worth noting that ECPs are often times more concentrated in specific areas, organisms and tissues within the organism than in others. The liver and kidneys of organisms can have high levels of ECPs within them whereas the body fat, brain, and muscle tissue usually has lower levels of ECPs (Haarhoff et al. 2015). There are exceptions to this, however, as certain ECPs will accumulate in the body fat as they are lipophilic.

The potential for a substance to accumulate or to be retained within the body is also an important consideration when assessing the risk that it poses. The properties of these substances are such that the body cannot readily remove them, consequently they steadily build up with successive exposures and the threat they pose to the organism can thus be sustained for long periods of time (Joint Research Centre 2003).

Lipophilic substances are an example of substances that have the potential to accumulate within the body (Joint Research Centre 2003). While there exists no direct correlation between the lipophilicity of a substance and its biological half-life, substances with high log P (partition coefficient) values tend to have longer half-lives. Thus there is the potential for highly lipophilic substances (log P >4) to accumulate in individuals if they are frequently exposed to that substance (Joint Research Centre 2003). The concentration of the substance within the body will decline at a rate determined by the half-life of the substance after exposure has ceased. Other substances that can accumulate within the body include poorly soluble particulates that deposit in the alveolar region of the lungs,

substances that bind irreversibly to endogenous proteins and certain metals and ions that interact with the crystal matrix of bone (Joint Research Centre 2003).

Highly hydrophobic substances can accumulate in sediments to concentrations at which they might exert significant toxic effects (Joint Research Centre 2003; Gavrilescu et al. 2014) . This is of great concern in the marine environment, where the sediment may act as a permanent sink for highly hydrophobic substances that can be accumulated to a large extent. As marine sediment constitutes an important compartment of marine ecosystems, the accumulation of potentially harmful substances can have far reaching negative effects for numerous marine ecosystems (Farré et al. 2008).

2.11.2 Volatilisation of ECPs

The partitioning of an organic chemical between water and air is a physical property that is described by the Henry's Law Constant, H (Joint Research Centre 2003). The magnitude of H provides an indication of which of the two phases, water and air, a chemical will tend to partition into at equilibrium. Chemicals with low values of H will tend to partition into the aqueous phase (Joint Research Centre 2003). Since air and water are the major "compartments" of most model ecosystems and water is considered to act as the link between all of the compartments, knowledge of the value of H is very important in assessing the environmental risks associated with a chemical. The Henry's Law Constant is expressed either as the ratio of the partial pressure in the vapour phase and the concentration in water (H ($Pa.m^3.mol^{-1}$)), or as the ratio of the concentrations in air and water (H', dimensionless) (Joint Research Centre 2003).

The release of organic ECPs from the water phase to the atmosphere is dictated by its vapour pressure, which shares a direct relationship with temperature (Haarhoff et al. 2015). Thus at higher temperatures (elevated water temperature) an ECP will volatilise at an increased rate. Once the ECP enters the atmosphere, it can either remain as a vapour or it can be adsorbed by suspended atmospheric particles.

2.11.3 Photolysis as a process of degrading ECPs

Sunlight can break some of the chemical bonds of an ECP, when the ECP is directly exposed to sunlight (Haarhoff et al. 2015). This mechanism of degradation is of specific importance in two scenarios the first being once an ECP has volatilised and enters the atmosphere. The second scenario occurs in instances where sunlight penetrates a water body. South Africa receives significant solar radiation and as such photolysis can play a larger role in our ecosystems than in areas that receive less sunlight such as Europe, Canada and large parts of the U.S.A. (Haarhoff et al. 2015). The precise effect of photolysis on ECPs in South Africa is yet to be studied and accurately quantified.

2.11.4 Adsorption of ECPs into Sediments

Sediments have been identified as a major carrier of ECPs in water. The octanol-water partition coefficient of a substance describes the partitioning of the compound between the water and the surrounding sediment. The log *n*-octanol-water partition coefficient (log K_{ow}) is a measure of the hydrophobicity of a chemical. As such, log K_{ow} is a crucial parameter in the assessment of environmental fate (Joint Research Centre 2003). Many distribution processes are driven by log K_{ow}, e.g. sorption to soil and sediment, partitioning into air and bioconcentration. ECPs are commonly highly hydrophobic and very insoluble in water and thus they tend to be adsorbed onto finely-dispersed colloids and particulates (Amdany et al. 2014).The free dissolved concentrations of ECPs in water are therefore frequently several orders of magnitude lower than their total concentrations. These free dissolved concentrations are generally within the $ng \cdot L^{-1}$ to $pg \cdot L^{-1}$ range, which is usually too low for accurate quantitative chemical analysis by traditional methods (Amdany et al. 2014). This means that the reliable and accurate analysis of free dissolved ECPs in natural water can be challenging and difficult and it is quite common for many sampling problems to occur (Amdany et al. 2014).

The sorption to soil and sediment components is a determining factor for the mobility of chemicals (Gavrilescu et al. 2014). This property accounts for the distribution among soil, sediment and water phases, as well as for volatilisation from soil surfaces, and influences the chemicals bioavailability and hence its transformation by soil microbes, for example. The extent of sorption to soil and sediment is governed by a variety of physico-chemical properties of both the soil and the contaminant. The heterogeneous soil chemistry and physics due to the variant proportions of the major components - mineral and organic matter, water, air and (micro)organisms - account for the differences in the binding capacity of different soils (Joint Research Centre 2003). The relevant parameters include organic carbon content, clay content, humidity, pH-value, cation exchange capacity, and temperature (Joint Research Centre 2003). The underlying processes of sorption may be due to Van der Waals interactions, hydrophobic interactions, hydrogen bonding, charge transfer interactions, ligand exchange and ion bonding, direct and induced ion-dipole and dipole-dipole interactions and covalent bonding (Joint Research Centre 2003). The sorption of non-polar substances, generally to the organic matter of the soil or sediment can be regarded as a distribution process between the polar phase of the soil water and the organic phase of the soil components (Joint Research Centre 2003). The equilibrium constant of this partitioning between solid and solution phases constitutes the adsorption coefficient for soil and sediments (Joint Research Centre 2003).

2.12 ECPs and Legislation

Water quality legislation aims to protect, govern and manage water resources, in order to meet the needs of the current generation whilst not compromising the ability of future generations to meet their own needs pertaining to water resources. Acceptable limits determined through scientific inquiry are often communicated through these laws, which makes the relationship and communication channels that exist between scientists and legislators imperative for the effective protection of water resources.

How a river is utilised within South Africa will largely dictate what level of pollution is acceptable, thus leading to a scenario where different rivers can have different quality standards. This can be seen in the case where a river that flows through a densely populated area will typically be more polluted than a river that flows through an area with a lower population number. Studies on the hazards and risks that are posed by ECPs towards both human and ecological health are still relatively novel and as such more information is required regarding these negative impacts. There is also a need to find empirical and undeniable evidence for the impacts they can cause. Lack of empirical evidence creates a scenario where legislation is lacking surrounding ECPs and what the exact acceptable limits of ECPs in water resources should be. EDCs (endocrine disrupting chemicals) can be seen as an exception to this statement as some legislation surrounding EDCs does exist in some parts of the world, however if this is sufficient and how effectively it is being implemented remains questionable. EDC legislation has also not been universally ratified and many countries (including South Africa) lack legislation in this regard.

2.13 South African Legislation

The management of South African water resources is largely governed by the South African National Water Act which was published in 1998 (DWA, 1998). The restructuring of past discriminatory laws surrounding water resources forms the core of this piece of litigation, with a focus on equal ownership and right to South Africa's water resources by its citizens (DWA, 1998). The scarce and valuable nature of water in South Africa and thus the import of sustainable resource management was also a central consideration when the National Water Act was proposed and later written and ratified (DWA, 1998).

Circumventing the over exploitation of water resources and ensuring the effective sustainable social and economic development of these resources are governed by the National Water Act (DWA, 1998). Equity, sustainability and efficiency forms three central pillars around which the National Water Act is based (DWA, 1998). Universal access by the citizens of the country to the water resources of South Africa and to the benefits that can be attained from these water resources is the formative idea behind the equity pillar. The conservation of water resources for future generations

whilst still encouraging and facilitating the utilisation of water resources for economic and social development for the benefit of the current generation form the core philosophy of the sustainability pillar. Reduction in the wastage of water, as well as the promotion of the most efficient and equitable use of water for economic and social development, constituted the efficiency pillar.

Chapter 2 of the National Water Act describes the National Water Resource Strategy which is of import to all water users and institutions as it contains laws pertaining to them (DWA, 1998). It expedites the proper management of South Africa's water resources by thorough the establishment of guidelines surrounding the utilisation, management and development of the water resources within South Africa (DWA, 1998). These guidelines include measures on water resource management at both a catchment and regional level. There is provision for an obligatory five yearly update of the National Water Resource Strategy which may provide an effective mechanism to include ECPs and especially EDCs in South African water quality legislation, as these substances could potentially lead to hazardous conditions for the people of the country.

The level of conservation that a specific water resource requires is based on analysing and specifying definitive limits surrounding water quality and quantity. Quantity of water requires looking at how much water is available and how much is required and is extracted from the specific water resource. The physical, chemical and biological aspects of a specific water body will determine the quality of the water found within it. The health of various aquatic ecosystem components including the flora contained within and surrounding the water body, insects, birds and mammals must also be analysed to determine water quality.

Preventing pollution is a pivotal part of the conservation and management of water resources and the National Water Act supplies legislation surrounding pollution prevention in its 3rd chapter (DWA, 1998). This chapter also assigns culpability to water pollution by stating that the individual who caused the pollution is responsible for mediating it and that landowners are responsible for preventing the pollution of water bodies whenever possible. Failure of the responsible person to do so can mean that the relevant catchment management agency may take prevention or mitigation steps and that the entity that caused the pollution will be responsible for paying for the cost of both mitigation and prevention. This creates a problematic scenario surrounding ECPs that lack litigation, as there is no specified legal requirement about the removal of ECPs and EDCs from water resources. This means that nobody will be held legally accountable for the damage these substances can cause, they therefore will largely remain in the water resources as it is unlikely that additional effort or expense will be made for the sake of removing these substances from the water resource.

In order to find a balance between the need for the utilisation of water bodies for the purpose of economic and social development and the need to conserve water bodies, the Water Resource

Classification System (WRCS) was implemented. This system classifies water bodies on the grounds of the characteristics of the water bodies in term of their purpose in aiding the social and economic development of South Africa (requires lower levels of protection) as well as their ecological importance (requires higher levels of protection). Sustainability in terms of both development and conservation is key to the WRCS. The classification process involves numerous compromises between the goals of development and conservation and will form an imperative part of the overarching goal of the protection of water bodies. Compromises can also be at a smaller scale such as where during a river's flow water will be used (for development) and where it will be conserved. Using water upstream can reduce both the quality and quantity of the water that will be available for downstream use. The inverse of this scenario where water is only used downstream and not upstream can lead to a lack of socio-economic development occurring in the upstream areas as well as dissatisfied people.

The WRCS categorizes water resources into various classes and then assigns a specific management goal for each individual water body by taking its unique characteristics into account. These characteristics include the existing condition of the water resource and then surmising the developmental and ecological processes that are reliant on it. A cost benefit analysis is then conducted to analyse the available options of development and conservation of the relevant water body while taking into account the surrounding environmental and socio-economic conditions. Water resources are grouped into three classes by the WRCS that range from water bodies that are heavily developed and used for socio-economic development to water bodies that feature little or no development or exploitation for socio-economic purposes. A determination of the quantity and quality of water required for both optimal ecosystem functionality and socio-economic development will be included in the ensuing conservation process as well as the classification of the individual water resource.

Initiation of the WRCS involves the definition of the existing condition of the water resource from an environmental point of view. After the existing condition has been accurately determined a planning phase is implemented that is concerned with what the ideal envisaged future condition of the water resource should be. Consultation with relevant stakeholders forms an imperative part of this process. The ideal envisaged future condition of the water resource relies upon assigning preferred attributes that are epitomised within a Management Class. This Management Class is monitored and managed according to a pre-approved set of traits determined by the Department of Water Affairs and by the general public.

After the water resource classification has been concluded it will inform the decision of the Minister of Water Affairs surrounding the Management Class, the various reserves surrounding the relevant water resource, as well as the quality requirements of the resources. Management Classes will

include a description of the existing condition of the water resource and will use it to describe to what extent the water resource can be used, exploited or developed. Information surrounding the acceptable limits of the quantity, circulation and quality of the reserves surrounding the specific water resource and thus the percentage of the water resource that can be used will be included in the Management Class. The Management Class of a water resource can thus have substantial socio-economic and environmental consequences.

It should be noted that very few organic compounds have been included in the drinking and surface water guidelines of South Africa, therefore by definition most organic compounds could be considered as emerging chemical pollutants.

2.14 Summary of the Water Resource Classification Procedure within South Africa

The WRCS relies upon seven steps for the sake of ensuring a logical and impartial process. A summary of these steps is included in this report due to the significance of understanding how the South African government conceptualises and endeavours to conserve, develop, utilise and manage water resources (especially rivers) and other forms of surface water within South Africa. The WRCS will also be utilised during and form part of the GIS process in order to identify potentially vulnerable areas as well as areas that might be potential pollution hotspots.

The initial step of the WRCS deals with a description of the existing condition of the water resource. This is done firstly by analysing and describing the areas surrounding and relying upon the specific water resource in terms of their social and economic activities. Ascertaining the socio-economic and ecological value of the water resource constitutes a major part of the first step of the WRCS. This includes succinctly describing the condition, needs and reliance on the specific water resources of the surrounding societies.

The combination of the value and the condition of the water resource is the purpose behind the second step of the WRCS. Information surrounding both socio-economic as well as ecosystem aspects are taken into consideration. An analysis of how the socio-economic circumstances of the water body are influenced by ecological characteristics is then conducted. Various scenarios surrounding these ecological influences are then scored and weighted for the purpose of further examination.

Ecological benefit and service analysis is central to the third step of the WRCS. The water quality required for the sustained optimal environmental yield and benefit is determined within this step. The correct extrapolation of data that pertains to any proposed, implemented or existing management procedures surrounding the water body is vital for this step to be conducted efficiently as well as correctly. This extrapolated data is then summarised and conveyed in the form of tables for every conceivable relevant environmental category. In so doing the changes to the

environmental sector can be accurately measured and communicated and this is what the concluding phase of the third step of the WRCS consists of.

Initial and environmentally sustainable baselines surrounding the use and proposed management actions of the water body is what the fourth step in the WRCS process seeks to identify. As such this step is also concerned with the ideas surrounding the current and future utilisation and exploitation of the water body. Considerations surrounding any managerial inputs surrounding the water body must also serve to inform the process of the fourth step.

The required compromises between the socio-economic aspects and the environmental considerations are jointly dealt with by steps five and six of the WRCS. These steps result in a decision surrounding the proposed Management Class, the various reserves surrounding the relevant water body, as well as the quality requirements thereof. Steps number five and six are vitally important for anyone interested in or reliant upon the water body, as it is where the nature of the compromise between socio-economic and environmental considerations are made and will thus largely determine the future condition and state of the water body.

Step number five is quite a lengthy process as it consists of seven separate objectives that must be completed. The first of these is the construction of a model to determine the environmentally sustainable yield that can be extracted from the water body. It is worth noting that this initial process does not include data on the consumption of water from the water body as this data is analysed in a separate second step. The important environmental impacts are then summarised and communicated in a report. This report contains information surrounding any expected or predicted alteration surrounding the water that is available for use in all sectors as well as what the result of the altered water availability will be on socio-economic development as well as environmental sustainability. After further analysis the proposed management actions are presented to all relevant stakeholders who will then provide input for further analysis that will ultimately inform the selection of a management plan. Stakeholder consultation and feedback is what step six of the WRCS comprises of.

The decision surrounding the selection of the proposed management action will be communicated to the public via publication in the government Gazette. This process is what forms the backbone behind the seventh and final step of the WRCS process. This publication is initiated when the summary of the Integrated Water Resource Management is submitted to the relevant competent authority. This authority will then be responsible for publishing the management plan in the government Gazette, including all the relevant information surrounding the selection of the management plan, and all the socio-economic and environmental conditions, considerations and information surrounding the relevant water body. The WRCS process is then concluded by the application and monitoring of the management programme.

2.15 American Clean Water Act

As an example of international water quality legislation, as it pertains to ECPs, the American Clean Water Act will be briefly discussed for comparison purposes. This Act aims to ensure water quality is of a sufficient level to promote all forms of aquatic life. Ensuring water is safe for use by other animals, humans and for human leisure activities also forms part of this act (Lopez, 2010), which strives to prevent and mitigate water pollution on every level that it can potentially occur, and it strives to uphold the quality guidelines that are set forth by the National Recommended Water Quality Criteria (Lopez 2010).

Publishing data on water quality improvement or sustainment measures, as well as reviewing water quality standards at all levels of government, are enforced by the act and the Environmental Protection Agency (EPA) is responsible for the implementation and enforcement thereof (Lopez, 2010). The universal application of the Act throughout all the states that constitute the United States of America (USA) is governed by section 304 of this Act. This section also contains information surrounding the standard at which the country's water should be for a specified utilisation. The conservation and protection of the water bodies of the country against any form of degradation is also set forth in this Act (Lopes, 2010). Areas that require more stringent water quality protection can be identified by the states themselves, following which the state can then implement any reasonable water quality guidelines that are specific to these areas (Lopez, 2010). Any water resource that fails to meet the minimum quality requirements as set forth by this Act must be located and identified by the state within which it is found. The state is then forced to institute a limit for the total maximum daily loads as it pertains to further or continued pollution of the relevant water resource (Lopez, 2010). This enables the state to monitor and to a certain extent control the quality of its water resources.

As is the case with the South African Water Act, the American Clean Water Act mandates that it must be updated to ensure the continued incorporation of novel scientific information. This mandate is described in section 304 of the American Clean Water Act (Lopez, 2010). Failure to incorporate modern scientific findings in these laws will lead to a scenario where the law becomes entirely outdated and to a large extent irrelevant. It can also lead to hazardous scenarios where humans and the environment alike are exposed to danger without their knowledge and without sufficient protection from the law. This means that incorporation of novel scientific findings and data should be seen as an obligation of governments globally. The EPA plays a central role in efforts to maintain the quality of American water bodies. Despite the threat that outdated laws can entail, the EPA's criteria surrounding water quality has not been modernised to incorporate any new information surrounding EDCs or ECPs. This is despite the known risk that many of these substances can entail such as endocrine disruption as well as the potential to cause cancer (Lopez, 2010). It is worth

noting that there exists numerous other laws that aim to control and minimise human exposure as well as protecting the environment as a whole and all the organisms that live in it from harmful substances, including for example the Safe Drinking Water Act and the Toxic Substances Control Act (Lopez, 2010). These Acts nevertheless fail to specifically mention or make provision for EDCs and ECPs.

2.16. Efficiency of ECP Removal by Waste Water Treatment Plants

The occurrence of ECPs in wastewater effluent has been studied and it has been found that some of these chemicals are being effectively removed by the wastewater treatment process, although this process was not developed or intended to remove these chemicals (Haarhoff et al. 2015). There are, however, certain ECPs that are not removed (or only partially removed) by the traditional waste water treatment processes (Haarhoff et al. 2015). There is currently a lack of knowledge on precisely what the impact of each process within the wastewater treatment plant is on the removal of ECPs from the effluent. The presence of ECPs in water that is used for human consumption is of great concern due to the multiple potential chronic effects these chemicals can have on human health (Haarhoff et al. 2015).

An example of ECPs found in waste water effluent can be seen in a study done in South Africa in 2013 (Osunmakinde et al. 2013) which examined the presence of ECPs in wastewater effluent and found a multitude of chemicals present including: pharmaceutical products used to treat hypertension, antiretrovirals, analgesics and antibiotics as well as hormones from natural and contraceptive sources (Osunmakinde et al. 2013). These ECPs will then flow with the water and will unavoidably end up being used or consumed by humans. This idea is further strengthened by another study done in 2013 (Patterton 2013) which found certain ECPs to be present in South African drinking water.

Dilution is a vital consideration in the assessment of risk and potential impact that can be caused by ECPs (Deblonde et al. 2011). Differing volumes of waste water that enters a WWTP may lead to varying concentrations of the ECPs contained within the waste water. The volume of waste water that passes through a WWTP in conjunction with the number of households and businesses that is connected to the sewage system are thus key considerations in determining the likelihood of detecting ECPs in WWTPs (Deblonde et al. 2011). It also influences the chances that these ECPs will have adverse effects on the surrounding environment (Deblonde et al. 2011). The source of waste water is vital information that is required when sampling for specific pollutants (Deblonde et al. 2011).

Fluctuations in temperature, precipitation rate and solar radiation have been found to influence the number of molecules found suspended in wastewater (Deblonde et al. 2011). The precise process

behind the elimination of pharmaceuticals is largely unknown, however the processes of biodegradation and sorption are known to contribute to the process as a whole (Deblonde et al. 2011). It is worth noting that temperature influences both of these processes. Another elimination process of pharmaceuticals from waste water is photodegradation. This process as its name suggest relies on sunlight and as such it will be less prominent during the winter months when solar radiation is less intense (Deblonde et al. 2011). It is then very interesting to note that it has been reported that the elimination rate of Ibuprofen was reasonably constant even with seasonal weather changes (Deblonde et al. 2011).

A two year long analysis of WWTPs (Bueno et al. 2012) yielded valuable information regarding the various treatment processes for waste water in WWTPs, specifically surrounding their efficacy of removing ECPs. It was found that activated sludge biological treatment was the most efficient at removing stimulant compounds (>80%), UV filters (>86%) and some synthetic fragrances, analgesics/anti-inflammatories or disinfectants (>70%) (Bueno et al. 2012). Blood lipid lowering agents, diuretics as well as beta-blockers featured mean removal efficiencies of 50%. It should, however, be noted that certain ECPs, most notably some antibiotics and carbamazepine, featured very poor or no elimination at all (Bueno et al. 2012). This persisted even after the waste water was put through secondary treatment and it means that effluent from WWTPs can still contain ECPs and that these ECPs are thus continuously being discharged into water resources (Bueno et al. 2012).

These results confirmed that ECPs can remain present in water even after it has been treated by WWTPs. This can be due to two predominant reasons. The first being that certain ECPs are resistant to removal and that the current waste water treatment processes are insufficient at effectively removing them (Bueno et al. 2012). The second reason that ECPs can remain in water after it is treated is due to the fact that the chemicals are being discharged into waste water continuously and in large quantities (Bueno et al. 2012). This means that even if waste water treatment processes can remove the chemical it simply occurs in such large quantities that it remains a threat or potential problem even after the water has been treated. These two reasons explain why effluent from WWTPs is an important pathway for ECPs to be discharged and thus to potentially contaminate a country's water resources.

Both domestic and industrial waste chemicals that are disposed of via water will typically go through at least one wastewater treatment plant before they end up in either surface or ground water (Haarhoff et al. 2015). Mining and agricultural waste has an increased potential to end up in surface and ground water due to discharges directly into water ways (Haarhoff et al. 2015).

There is currently a lack of data on the efficiency of ECP removal from water by waste water treatment plants in South Africa (Haarhoff et al. 2015). The vast majority of South African water treatment plants are conventional plants which means that the processes they follow are

coagulation, flocculation, phase separation by settling / flotation and rapid filtration and lastly chlorination (Haarhoff et al. 2015). More modern and sophisticated processes are starting to come into general use, and as such they will also be briefly discussed.

Pharmaceutical residues, antibiotics, steroid hormones and fragrances have been reported to be the most commonly occurring trace organic compounds in secondary and tertiary treatment municipal effluents as well as water bodies receiving these wastewater discharges (Crook 2010). These chemicals are thus of specific importance in a South African context as South Africa utilizes mostly traditional wastewater treatment methods.

2.16.1 Coagulation and Flocculation

Coagulation and flocculation are generally ineffective at removing ECPs and specifically EDCs from drinking water (Snyder et al. 2009). There are a limited number of substances that can be effectively removed by coagulation and flocculation, however the removal efficiency is generally below 20% (Haarhoff et al. 2015).

2.16.2 Disinfection by means of oxidation

The most common oxidant in South Africa is chlorine and it is used for the process of disinfection in WWTPs (Haarhoff et al. 2015). Other oxidants that are less commonly used by WWTPs in South Africa include ozone, chlorine dioxide and UV irradiation. Chlorine has been found to be very effective at removing ECP and specifically EDCs from drinking water as it removes 95% of these substances (Haarhoff et al. 2015). Regardless of being sufficient for controlling a number of target compounds it does have a few limitations. Chlorine dioxide is a stronger oxidant than chlorine and it removes considerable proportions of many compounds (Haarhoff et al. 2015). It should however be mentioned that certain ECPs such as caffeine and ketoprofen are recalcitrant to chlorine dioxide oxidation. Chlorine and chlorine dioxide target and react mainly with functional groups like amines and phenols. It should be noted that concerns have been raised regarding potential adverse health effects (including reproductive effects) of the disinfection by-products of chlorination of water (Nieuwenhuijsen, 2000). Ozone, being the strongest oxidant, is very effective at removing and transforming ECPs and EDCs in water resources. Many of these substances can be oxidised by up to 90-99% by ozone, thus ozone is considered extremely efficient at eliminating these substances (Haarhoff et al. 2015). The efficiency of UV radiation at removing ECPs and EDCs is still a contested and debated subject. UV radiation, at the radiation doses normally used for the treatment of drinking water, is considered to be ineffective at removing these substances according to a review sponsored by the EPA (Snyder et al 2009). Other scientists have contrasting views and believe that medium pressure (MP) UV lamps (which are widespread at WWTPS internationally and

also finds use in a limited number of South African plants) are very proficient at eliminating certain ECPs by direct photolysis (Sharpless and Linden 2003).

2.16.3 Advanced Oxidation

The advanced oxidation processes (AOPs) consist of a combination of UV, hydrogen peroxide and ozone (UV / hydrogen peroxide; ozone / hydrogen peroxide; and UV / ozone) (Haarhoff et al. 2015). These combinations create hydroxyl radicals which bind to, react with and transform ECPs and EDCs non-selectively. This can lead to a drastic increase in removal efficiency, for example the removal efficiency of ibuprofen is doubled (Haarhoff et al. 2015). AOPs are consequently considered to be very effective processes for oxidising and removing ECPs and EDCs from drinking water; however they are only slightly more effective than ozone alone.

2.16.4 Activated Carbon Adsorption

Activated carbon adsorption has been found to be effective at removing ECPs and EDCs from drinking water when used in both powdered and granular form (Delgado et al. 2012), due to their hydrophobic properties. Activated carbon can however not successfully remove all polar compounds (Delgado et al. 2012).

2.16.5 Membrane Filtration

There are a wide variety of membrane types that are utilised during the process of membrane filtration and together they form a continuum. These include the following: microfiltration (MF – the coarsest pore size); ultrafiltration (UF); nanofiltration (NF) to the smallest pores in reverse osmosis (RO) (Haarhoff et al. 2015). Apart from the sizes of the membrane pores there is also a distinction between high pressure membranes and low pressure membranes.

Low pressure membranes typically have larger pore sizes than the size of the majority of the molecules of both ECPs and EDCs and as such these low-pressure membranes are typically ineffective at removing ECPs and EDCs from drinking water (Haarhoff et al. 2015). It should be noted that some elimination of these pollutants will occur but that is largely due to the direct absorption which occurs on the surface of the membrane. High pressure membranes, due to their smaller pore sizes, are much more successful in removing ECPs and EDCs. These membranes have been commonly reported to be more than 90% effective at removing ECPs and EDCs from drinking water (Haarhoff et al. 2015).

2.17 Risk Assessment

The procedure for the assessment of the human health risk of a substance normally consists of comparing the exposure level(s) to which the population(s) are exposed or are likely to be exposed with the exposure level(s) at which no toxic effects are expected to occur (Joint Research Centre 2003). If all the required data is available, a risk assessment is conducted by comparing the exposure level, the outcome of the exposure assessment, with the No Observed Adverse Effect Level (NOAEL), the outcome of the dose-response assessment. If sufficient data is not available to establish a NOAEL, a comparison between the exposure level and the Lowest Observed Adverse Effect Level (LOAEL) can be used to gauge risk (Joint Research Centre 2003).

The precise way in which many ECPs react and change in the environment as well as the concentration at which they will start eliciting effects in the environment remain largely unknown. Modelling programmes and predictive software that can estimate these values do exist although they are often lacking and cannot provide data on the estrogenic effects of these chemicals. The environmental risk or hazard posed by some ECPs will thus be characterized with high uncertainty (Diamond et al. 2011).

A thorough risk assessment process, in relation to both human health and the environment, typically entails three main actions namely: (1) an assessment of the effects, (2) an assessment of potential exposure and (3) finally a risk characterisation (Joint Research Centre 2003). (1) Assessing the effects of a chemical can be subdivided into two stages namely hazard identification (identification of the adverse effects which a substance has an inherent capacity to cause) and response or effects assessment (estimation of the relationship between dose, or level of exposure to a substance and the incidence and severity of an effect). (2) Potential exposure assessments are an estimation of the concentrations/doses to which human populations or fauna and flora and ecosystems in general are or may be exposed. (3) The final part of the process namely risk characterisation is an estimation of the incidence and severity of the adverse effects likely to occur in a human population or any part of an ecosystem due to actual or predicted exposure to a substance (Joint Research Centre 2003).

Exposure can be understood as external exposure which can be defined in a variety of ways which is dependent upon the type of exposure. Types of exposure can include the amount of substance ingested, the total amount in contact with the skin (which can be calculated from exposure estimates expressed as $mg.cm^{-2}$ or $mg.cm^{-3}$) or either the amount inhaled or the concentration of the substance in the atmosphere (Joint Research Centre 2003). Anthropogenic exposure to substances can occur in a variety of ways including from their workplace to indirectly via the environment. Indirect exposure of humans via the environment may occur by consumption of food (fish, crops, meat and milk) and drinking water, inhalation of air and ingestion of soil.

Exposure can be considered as single events, or a series of repeated events, or as continuous exposure. The duration and frequency of exposure, the routes of exposure, human habits and practices as well as the technological processes need to be considered when determining the risk that a chemical poses (Joint Research Centre 2003). Additionally, the spatial scale of the exposure (e.g. personal/local/regional level) can also greatly influence how hazardous a chemical is thus it has to be taken into account (Joint Research Centre 2003). It is worth noting that when assessing the levels of chemicals in the environment, previous releases of the chemical to the environment need to be taken into account. These releases can give rise to a pre-existing background concentration due to their cumulative effect in the environment, which can cause inaccuracies during *in situ* data gathering.

The environment may be exposed to chemical substances during all stages of the chemical's life-cycle from production to disposal or recovery (Joint Research Centre 2003). For each environmental compartment (air, soil, water, sediment) potentially exposed, the risk assessment procedure should account for the following stages of the life-cycle of a substance: production; transport and storage; formulation (blending and mixing of substances in preparations); industrial/professional use (especially large scale use); private or consumer use; service life of articles; waste disposal (including waste treatment, landfill and recovery) (Joint Research Centre 2003).

2.18. Widespread approaches to prioritisation

Expert opinion as well as project specific parameters can often heavily influence scientific inquiries into ECPs. This is due to the fact that both expert opinion and project specifics commonly dictate which chemicals will be investigated and may form the basis or starting point of these studies. Occurrence information, toxicity, endocrine disruption capability, biological persistence (half lives in the environment) and information surrounding the popularity and widespread utilisation of these chemicals formed the backbone of the parameters used to target and monitor ECPs in a recent study by the U.S. Geological Surveys (USGS) (Diamond et al. 2011). Expert opinion along with traditional analysis methods formed the basis of a similar study to that of the USGS that was conducted by the US EPA and was concerned with personal care products (PPCPs) and their effect in and on the environment (Ramirez et al. 2009). These examples clearly illustrate that even a developed nation like the USA which is at the forefront of science and technology still mainly relies on expert opinion when targeting and monitoring ECPs and has not developed an unbiased prioritisation methodology for evaluating these chemicals.

The concentration of multiple pharmaceuticals as well as chemicals that are known to have endocrine disrupting capabilities were analysed in a recent study on the water bodies of America (Benotti et al. 2009). The authors considered different criteria during the selection of the chemicals that were analysed. Pharmaceuticals that have greater toxicity as well as a higher general potency

were emphasised and as such medication that could only be obtained by means of a prescription were central to their study. Anthropogenic toxicity scores, measured occurrence data and interest in the chemical from the general populace formed part of the factors that were taken into account by the researches alongside the popularity of the chemicals (that was measured by occurrence data and volume of use).

The study implemented a similar screening process for EDCs and parameters seen as important included: the reported magnitude of endocrine effect, occurrence, toxicity, biological persistence, accumulative potential, how the chemical changes and functions, and concern towards the chemical expressed by the general populace. The availability of analytical methods was a consideration for both pharmaceuticals and EDCs. Expert opinion did however still form the basis for this research which detracts slightly from the concise and thorough nature of the rest of the methodology.

Environment Canada (EC) have developed a framework for classifying and ordering chemicals and the potential hazards posed by them that constitute the Domestic Substances List (DSL). The accumulative potential, half-life and toxicity as it pertains to non-target animals are the factors that inform the assessment procedure (Arnot and Mackay 2008). It is thus a hazard based approach seeing as actual occurrence information surrounding the chemicals from the Canadian environment is not taken into consideration. Persistence of the chemicals are assessed based on their half-lives in water, where an aquatic half-life of 182 days or more is seen as a concern. The partition coefficient is utilised to ascertain whether a chemical will accumulate in the environment, where chemicals are included that have a minimum partition coefficient value of 5 (log P_{ow}) (Arnot and Mackay 2008). Bioaccumulation and bio-concentration factors can also aid in informing this process where a value of 5000 is seen as the cut-off value to assess persistence (Arnot and Mackay 2008). Toxicity of the chemicals are analysed according to acute toxicity (LC_{50}) as well as chronic toxicity when data is available. As previously mentioned, chronic toxicity is the far more useful measurement for ECPs due to the high acute toxicity values possessed by the majority of these compounds.

Before the commercial production of a novel chemical can commence, the substance must go through stringent analysis and assessment according to the EPA and in accordance with the Toxic Substances Control Act. The environmental fate and consequences must be diligently analysed and reported on during this mandatory analysis. Toxicity analysis is only conducted when a chemical has a biological persistence that is seen as significant, which is often the case when it can remain present in the environment for a time period of more than two months (Diamond et al. 2011). A chemical's capacity for accumulation in the environment can also lead to extended analysis of its toxicity if the accumulation or bio-concentration factors are in excess of 1000 (Diamond et al. 2011). Substances that feature a persistence period in excess of half a year or that feature a

bioaccumulation factor in excess of 5000 will not be allowed to be produced until a thorough analysis of their toxicity data has taken place (Diamond et al. 2011).

Once again this approach (as with the Canadian one) does not calculate risk but is focussed on the hazard that is posed by these chemicals. This is due to the fact that this approach does not rely on measured environmental occurrence data. Other research has focussed on analysing the whole spectrum of environmentally relevant constraints such as persistence, bioaccumulation and toxicity which in known as the PBT approach. Major environmental agencies and governing bodies that follow this approach includes the Oregon Department of Environmental Quality, certain divisions with the EPA an even the United Nations (refer to the Stockholm Convention on Persistent Organic Pollutants (www.pops.int/).

The PBT approach is utilised by the Canadian Domestic Substance List as well as the Toxic Substance Control Act of the United States of America (Diamond et al. 2011). This approach allows for the construction of regulatory framework for these chemicals. Objections surrounding the use of the PBT methodology for the purpose of analysis of ECPs have not been uncommon for all interested and affected parties that rely or utilise water bodies. Substances that feature relatively low production numbers, such as many pharmaceuticals, are often overlooked for analysis. It should, however, be mentioned that the risk that is posed by an ECP often times does not share a direct relationship with its production volume or frequency of its usage. ECPs that are more toxic and generally more potent in their effect towards aquatic ecosystems are often of greater concern (Ankley et al. 2007). Looking purely at a chemical's environmental persistence can provide a skewed interpretation of the amount of exposure that is occurring in the environment especially if these chemicals are constantly being released into the environment, as is the case with the discharge of effluent water. The constant supply of these chemicals into the environment will thus serve to override their inherently short persistence times and half-lives. Traditionally applied toxicity analysis, especially as it pertains to the endpoints of chemicals, has been reported to be inadequate for accurately analysing the potential consequences of both EDCs and certain ECPs (Ankley et al. 2007). Flexibility during the process of accurate risk and hazard orientated prioritisation methodologies are essential when it comes to EDCs and ECPs. The flexibility referred to alludes to the incorporation of both *in situ* and predicted exposure concentrations.

The EC commissioned a study with the purpose of compiling a priority list of EDCs during 1999 (Haarhoff et al. 2015). The study was started by compiling a list of suspected EDCs from a multitude of databases and experts. A total of 564 compounds were identified during this first step for further consideration. These initial compounds were then subjected to three successive screening steps:

The first step of this study was concerned with the production volume (more than 1000 tonnes per year) and persistence of the chemicals with the goal of identifying the chemicals that had a greater

possibility of human exposure (Haarhoff et al. 2015). The persistence of the chemicals was determined by their biodegradability (attained from quantitative structure–activity relationship models (QSAR)) or from the ultimate degradation (complete mineralisation) time (Haarhoff et al. 2015). After this initial step 146 chemicals remained.

The second step in this study focussed on analysing the endocrine disrupting potential of the remaining chemicals (Haarhoff et al. 2015). They were divided into three categories based on their endocrine disrupting potential as determined by a panel of experts (Haarhoff et al. 2015). Category 1 consisted of chemicals that had at least one study providing evidence of endocrine disruption. Category 2 consisted of chemicals that had potential for endocrine disruption. Category 3 compounds were proven not to cause endocrine disruption or suffered from a lack of available data, thus could not be categorised.

The final step in this study was focussed on the concern for exposure and was also based on expert knowledge and was conducted by a panel of experts (Haarhoff et al. 2015). The remainder of the chemicals were classed as high (denoting chemicals which were expected to incur exposure to humans and wildlife and were considered to be persistent and bioaccumulative), medium (denoting chemicals that could incur exposure to humans and wildlife but are biodegradable and thus cannot bioaccumulate) and low (denoting chemicals that feature no human or wildlife exposure).

Evaluating some of the chemical prioritization schemes which are currently in use raises important points with regards to the development of a more inclusive and useful prioritization framework for the analysis of water resources. Prioritising chemicals that are commonly used and that enjoy widespread application according to their toxicity and environmental considerations has limited usefulness. This is due to two primary reasons; the first of which is that there are many important and potentially hazardous chemicals that will be excluded from the initial list due to the fact that they are used less frequently. The second reason that limits the usefulness of this approach centres on the fact that there exists uncertainty around the likelihood that many of these chemicals have of actually entering the environment and water bodies. The European Union has acknowledged these shortcomings and they have also stated that chemicals that are manufactured in lower quantities need to be included with specific focus on chemicals that are known or suspected to possess endocrine disrupting capabilities (Petersen et al. 2007).

More than 40,000 organic chemicals have been identified as ECPs (Diamond et al. 2011). ECPs are often poorly characterized in terms of their presence in aquatic environments and their potential effects on aquatic wildlife and humans, although some have been proven to be harmful to fish, other animals, and even humans (Diamond et al. 2011). Clarity needs to be found over which of these chemicals pose the highest risk. The creation of a comprehensive list of potentially harmful ECPs would result in an unmanageable list of more than 40,000 substances (Diamond et al. 2011), thus

some type of prioritisation of these chemicals is needed to identify the chemicals that are of greatest concern to provide focus to monitoring campaigns. Studies focussing on ECPs and their prioritisation typically follow one of three approaches namely: hazard-based, hazard-based combined with persistence and bioaccumulation potential, or persistence, bioaccumulation and toxicity (PBT)(Diamond et al. 2011).

2.18.1 Approach #1

The risk-based approach is usually based on the proportion of the maximum observed concentration of a specific ECP to its predicted endpoint, based on either chronic toxicity or estrogenicity effect (Diamond et al. 2011). Estrogenic activity has become a routine consideration and a standard indication of sub-lethal effects as many chemicals are not highly toxic. These chemicals can, however, still have sub-lethal effects that may not be detected using standard toxicity tests (Diamond et al. 2011). This approach is easy to implement and communicate and it gives an idea of what is happening in reality as it relies on *in situ* data measurements. Although this approach is relevant to predicting ecological risk, it only makes provision for ECPs that have been found in water bodies and does not consider the production data of chemicals (Diamond et al. 2011).

A risk-based approach can see widespread application in organisations and studies that seek to evaluate the environmental risk posed by ECPs that are based on *in situ* measurements that have been gathered from multiple monitoring exercises and research inquiries. Due to the dependence of this approach on measured occurrence data, it can prove an invaluable starting point for sustained monitoring studies. Site specific research can also benefit from this approach as measurements obtained from that specific site can be included in the calculations and can thus become more relevant and accurate.

In the study by Diamond et al. (2011) the authors used three calculations to determine risk and they are as follows:

Calculation 1:

Risk Value = Highest Measured Concentration/ Minimum Chronic Toxicity Limit

Calculation 2:

No Effect Endocrine Activity Risk Value=Highest Measured Concentration/ Predicted No Effect Concentration

Calculation 3:

Endocrine Activity Risk Value=Highest Measured Concentration/Predicted Effect Concentration

ECPs for which the No Effect Endocrine Activity Risk Value calculations equated to less than 1 were described as unlikely to be present in water bodies at quantities that were sufficient enough to cause significant disturbance to the endocrine systems and reproductive capacities of organisms in the environment. These ECPs will then be considered as unimportant in terms of the risk they pose for endocrine disruption. Chemicals that score higher than 1 (seen as important chemicals with regards to endocrine disruption capabilities) for the Endocrine Activity Risk Value can thus be considered to occur at sufficient environmental concentrations to cause harm to the reproductive systems of organisms. Chemicals that score more than 1 for calculation number two as well as less than 1 for calculation number three are seen as rather ambiguous and as such are treated with a great degree of uncertainty. This is due to the fact that the possibility for these chemicals to cause reproductive harm and to disrupt the endocrine systems of organisms cannot be accurately gauged.

2.18.2 Approach #2

Approach number two assigns scores to a chemical's characteristics in terms of its bioaccumulation potential and half-life in water (persistence in the environment) which is then used to calculate a risk based quotient (Diamond et al. 2011). As this approach depends largely on environmental occurrence information it relies on samples obtained from the environment. These scores which range from 1 to 3 are assigned based upon whether the chemical has scored relatively low, medium or high in that category and thus how much of a threat it poses. This approach sees widespread application and its scoring system is also commonly used by agencies including the US EPA and the Canadian Domestic Substance List (Diamond et al. 2011). The scores that were assigned to the various relevant factors for every ECP are then added together to create an estimation of how great a risk all the chemicals pose. The maximum score that can be achieved is a nine (3+3+3) and can only occur if a chemical has a high score assigned to it for each individual factor under consideration. A score of seven or more will mean that the chemical is considered of high importance as it poses a significant potential threat and as such it will be seen as a priority ECP. Any chemical that has achieved the maximum score of three for any single factor will also be flagged as a potential priority ECP. More substances are commonly analysed using this approach due to the less stringent initial requirements that a chemical has to meet to be included in the target analyte list. Analyses can also been seen as more thorough due to the fact that biological accumulation and environmental persistence are taken into consideration in addition to the risk based quotient. A total score of nine will lead to a chemical being considered to be a priority due to three predominant reasons. The first reason is that they have been found in water bodies at quantities that surpass the lower limits of either their toxic or endocrine disrupting thresholds. Secondly they can potentially undergo bio-magnification and thus have devastating consequences for organisms that are found in higher trophic levels. The third reason is that they can remain prevalent and present in the environment for extended periods of time owing to their long half-lives

in water and thus inferred persistence. Environmentally concerned companies or individuals can find this approach useful particularly those who feel that the incorporation of occurrence data is absolutely essential to the prioritisation of ECPs. This is due to the thorough estimation of risk that is applied with this approach. It can also prove valuable to site-specific analysis as *in situ* data that has been acquired from the site itself can be incorporated into the approach leading to the results becoming more specific and relevant to that site.

2.18.3 Approach #3

The PBT prioritization approach is similar to the hazard, persistence and bioaccumulation approach, except that it relies on predicted toxicity values obtained from software and does not require *in situ* data measurements (Diamond et al. 2011). Mathematical models are then used to estimate or predict ecotoxicological effects. ECOSAR is the most popular quantitative structure–activity relationship (QSAR) model that was developed for this purpose (Sanderson et al. 2004). Despite the models often having serious drawbacks such as an inadequate coverage of the various structures of pharmaceuticals, these programs are utilised to estimate pharmaceutical baseline toxicities (Sanderson et al. 2004). Although models are helpful in estimating potential toxicity or the behaviour of a compound in the environment, they cannot replace *in situ* measurements or controlled tests. The PBT approach can lead to an undesired scenario where an ECP is scored as a high priority but may actually never occur at concentrations that would cause chronic toxicity or endocrine disruption in the environment.

ECPs prioritised by approach number three cannot be considered to be risk based due to the fact that no occurrence information is taken into account. This means that it focuses primarily on the estimation of the potential hazard that these substances can pose. It is also not reliant on *in situ* data measurements as it can use software that estimates the toxicity, persistence and bio-accumulation of chemicals based on their chemical structures. A total score of seven is still seen as a priority chemical when the three categories are summed. People who are concerned with the theoretical hazard that ECPs can pose will find this approach very useful. This includes studies that seek to determine whether chemicals that are not currently monitored as part of ECP monitoring programmes (due to lower manufacturing or occurrence data) should perhaps start being analysed and monitored due to the theoretical risk that they pose.

The advantages and constraints of each approach must be understood if ECPs are to be prioritised using one of them and to this end a summary of these approaches has been included as Table 1 which originated from the study by Diamond et al (2011).

Table 1 Prioritisation approaches for ECPs based on Diamond et al., 2011.

Approach	Summary	Advantages	Constraints
1	Risk-based calculation that utilises occurrence data and effect concentrations. Focusses on ECPs having the most frequent use and those that have the highest occurrence in water bodies.	Straight forward application and ease of data interpretation. Analysis of results does not require specialist knowledge. Accuracy can be substantiated by using data obtained by scientific inquiry. Can determine actual risk and not just theoretical risk.	Occurrence information can be hard to come by and as such accumulating all the required information for this approach can be time consuming. ECPs lacking occurrence data (which is common) cannot be analysed by this approach.
2	Similar to approach 1 in that it also relies on occurrence data. Also concerns itself with bioaccumulation and persistence and strives to combine this with occurrence information to predict possible risk	Accuracy can be substantiated by using data obtained by scientific inquiry. Can determine actual risk to an even greater extent than approach number 1 as ECPs with lower occurrences can still become a priority. Numerous applications from an environmental health perspective.	Occurrence information can be hard to come by and as such accumulating all the required information for this approach can be time consuming. ECPs lacking occurrence data (which is common) cannot be analysed by this approach.
3	Typically uses predictive software to calculate toxicity, bioaccumulation and persistence. These predicted values are assigned a weight and are combined to calculate potential hazard. Largely theoretical.	Uses a traditional approach and can give great insight into the theoretical hazard that a substance can pose. Data collection can also be done more rapidly.	Substance seen as a priority may never occur at environmentally relevant concentrations and might thus not be reflective of actual risk. Accuracy of software used to make calculations might also be a concern.

Environmental programs in the U.S., Canada, and Europe tend to focus on the production data of chemicals when determining the risk that they pose (Diamond et al. 2011). The reasoning is that chemicals that are produced in larger quantities are more likely to reach surface waters, thus they present a greater risk than chemicals produced in smaller quantities. This approach fails to take into account that some chemicals are unlikely to enter surface waters. The most threatening ECPs from a health impact perspective are not necessarily produced in high volume and are therefore not on their lists.

There are four main issues that hamper the development of more effective monitoring efforts (Diamond et al. 2011):

1. Lack of understanding how *in situ* measurements of ECPs translate into ecological risks.

2. Different definitions for ECPs leading to studies that focus on varying sets of chemicals which they identify as ECPs.

3. The trace amounts at which ECPs typically occur in the environment means that detecting them is often difficult if traditional analytical methods are used.

4. Lack of toxicity data and when available it is limited to species specific data.

A thorough prioritization process should include at least some form of risk assessment so that ECPs that pose the greatest possible threat to the environment can be located and can thus be monitored as high priority chemicals. An accurately integrated evaluation of the risk assessment information is required to accurately reflect on the existing condition as it relates to the occurrence of ECPs in order to ensure that an accurate, meaningful and representative prioritisation process is established (Diamond et al. 2011).

ECPs can be similar to “traditional” pollutants for example heavy metals or ammonia, when considering the risk they pose to the environment, as they occur with more obvious stressors that could mask subtle sub-lethal effects (Diamond et al. 2011);

- The anatomical and physiological impacts on separate organisms within a freely breeding population can possibly be undetectable at the community or even at the population level.
- Short environmental and specifically aquatic half-lives do not necessarily mean that the chemical does not possess pseudo persistent characteristics. These characteristics and their associated effect can be the direct result of the uninterrupted release of the chemical into water resources.

ECPs do nevertheless vary from “traditional” pollutants in that:

- The precise modes of action that are characteristic of various ECPs can cause tremendously diverse impacts on dissimilar organisms and/or life stages.
- The effect of ECPs on future generations might be more severe than on the current generation due to the strong propensity for endocrine disruption that many of them possess. Many ECPs are also not extremely toxic and may thus not kill organisms they come into contact with directly.
- Many ECPs feature unidentified modes of action and the relationships between the concentrations they are present at and the effect they illicit are not well understood. This is particularly true when they occur at low concentrations.

These differences mean that the conventional and widely applied risk-based method for prioritising pollutants might require certain modifications in order to assess ECPs in a more representative and applicable manner (Diamond et al. 2011). It appears that basing an ECP prioritization framework on reasonably representative occurrence information will likely be the most useful approach (Diamond et al. 2011).

It should, however, be noted that the use of *in situ* measurements of occurrence data and manufacturing volumes only are not adequate for the prioritisation of ECPs as this data must be combined and analysed in conjunction with pertinent information surrounding possible environmental effects and their propensity for accumulation and persistence within the environment and all the organisms that live within it. The combination of these characteristics is required to thoroughly prioritize ECPs in terms of potential ecological risk. Analysing toxicity and potential for endocrine disruption can been seen as the most pertinent of environmental or effect endpoints during the screening for or prioritising of ECPs (Diamond et al. 2011). The difficulty in determining and quantifying the synergistic effects for mixtures of compounds is also worth noting.

2.18.4 A previous South African approach

In a South African prioritisation study completed in 2009 (Ncube, 2009), the following steps were followed to first form a comprehensive list of ECPs and secondly to prioritise these chemicals so that a decision could be made surrounding their removal from South African water bodies. The initial step of this study was to select a preliminary list of chemicals that would be refined and then later analysed more intensely (Ncube, 2009). Various databases were consulted and all ECPs that are either restricted or banned in specific areas were also included. Stakeholder consultation also took place and experts were also given the opportunity to provide insight and opinions which validated the chemicals that were considered. This resulted in the elimination of unnecessary chemicals and overall refinement of the group of chemicals that were analysed in more detail (Ncube, 2009).

The next step was the further verification of the list by considering occurrence information as well as the potential of the chemicals to cause negative health effects (Ncube, 2009). A literature review was utilized to accomplish this. Information surrounding the physico-chemical properties of the various ECPs was also gathered for use in the prioritization process once a final analyte list of chemicals was decided upon, as these characteristics can be used to predict the fate of an ECP once it enters the environment (Ncube, 2009). A PBT approach also formed part of the prioritization process (Ncube, 2009). This step was centered around gathering supplementary data on ECPs to assist with analysis. Water quality monographs were used to present the data and illustrate it in a clear way (Ncube, 2009).

The next step in this study was the taking of fish tissue, sediment and water samples for analysis to determine if and where ECPs occurred in water bodies (Ncube, 2009). Analytes present in the samples were included in the final list of compounds that were prioritized and analysed further. This list was also subjected to the approval of stakeholders, experts and industry leaders (Ncube, 2009).

Once a final list of ECPs was decided upon, the actual prioritization took place that divided the chemicals into the following groups: short term, medium term and long term, based on the need for

further priority analysis within South African water bodies (Ncube, 2009). The ECPs that were placed onto the short term list were viewed as chemicals that warranted the highest concern and required further continued monitoring.

For an ECP to be placed in the short term category it had to possess the ability to cause negative health impacts to humans (Ncube, 2009). Chemicals that cause water quality problems including problems surrounding the taste and smell of the water were also placed on the short term list, as were chemicals that cause an increase in risk perception amongst the general population. If an ECP had poor removal rates using traditional water treatment processes or if the regulation of the chemical was enabled due to pre-determined drinking water standards, it was included in the short term list. The short term list was rounded out by the inclusion of ECPs that were known to occur within South African water bodies and especially those that were found in drinking water (Ncube, 2009). Finally, stakeholder consultation was completed again before the final list was decided on (Ncube, 2009).

Chapter 3: Methodology

The methodology for this project consisted of two components. The first was concerned with obtaining a relevant and inclusive list of ECPs that were to be prioritised after relevant data had been collected for them. These ECPs were prioritised in order to gain a ranked list of priority ECPs that are relevant to South African conditions and around which future research efforts within South Africa should be focussed. The resultant list will also be a suitable starting point for any agencies wishing to start monitoring ECPs and for scientific studies that focus on ECPs within a South African context. The second part of the methodology was centred on using geographic information system (GIS) to locate areas that are likely to be the most vulnerable to ECPs and areas that might be potential ECP hotspots. These identified areas can be used to assist with the identification of suitable sampling sites for monitoring agencies wishing to monitor ECP concentrations in vulnerable areas and for future studies surrounding ECPs.

3.1 Prioritisation Methodology

The list of compounds that was subjected to the process of prioritisation and ranking was obtained after a thorough literature review of multiple sources. The literature included both local and international studies, to ensure the list was as comprehensive and inclusive as possible. Specific focus was given to other prioritisation studies regarding ECPs and all the substances that were concluded to be priority substances from these studies were included in the initial list of compounds. Thus this study can be seen as a second tier prioritisation and ranking study as the initial list of compounds were already found to be priority substances based on other scientific studies. This study thus seeks to refine a list of ECPs that have already been found to be priority pollutants as well as being known to be potentially hazardous in certain regions and it also strives to make this refined list specifically applicable to South African circumstances and conditions.

The method followed for this project was partway between approach number 2 and approach number 3 (as detailed in Chapter 2). The initial list of compounds was first split into two groups namely: those with occurrence or usage data available and those where neither usage nor occurrence data was available. If there was some form of usage or occurrence data available for a compound a risk-based approach could be employed and the actual threat posed by the substance could be calculated. This was done in an attempt to ascertain what the actual potential risk was that these compounds posed to both human and ecological health. As previously mentioned in the literature review, accurate information on usage or occurrence of ECPs is not always readily available and this is particularly true in the South African setting.

When data surrounding occurrence or usage was not available for a given compound, it was classed in the list of compounds that lack this data. These compounds were prioritised via a hazard-

based approach as the theoretical threat that they pose could be calculated, but without occurrence or usage data an actual risk-based approach was not possible. This was the case as a compound could hold a large theoretical threat based upon its toxicity, persistence and physico-chemical data, but it could perhaps never occur in high enough concentrations in the environment to have any effect or cause any significant harm. The list of compounds analysed and placed within the group of compounds that lack data can always be moved over to the list of compounds that have occurrence or usage data as this data becomes available in the future. Thus a compound can always be analysed according to the risk-based approach as more usage and occurrence data on the relevant compound becomes available.

For the purpose of prioritisation and analysis, the list of compounds was analysed within three tables, each of which focussed on a different aspect that is pertinent to the potential risk or hazard that is posed by the ECPs. The tables focussed on (1) physico-chemical data, (2) occurrence data and the efficiency of waste water treatment plants at removing the compounds, (3) persistence, bioaccumulation and toxicity, respectively. A secondary analysis on information surrounding the prescription and import of these substances can be added when available and then ordered to sort the substances from the most frequently used to the least frequently used. It also analysed studies that investigated the efficiency of conventional waste water treatment plants at removing ECPs to determine how effectively these substances are being removed from water resources. The third table was centred on determining the toxicity of the ECPs as well as their affinity to bioaccumulate within organisms as well as analysing their ability to persist within the environment.

The attributes and factors of the ECPs that were considered to be important within the persistence, bioaccumulation and toxicity (PBT) table and the physico-chemical data table were as follows: octanol-water coefficient, biological half-life, toxicity (LD_{50} and EC_{50}) within a standardised endpoint (rats or algae), endocrine disruption capability, volatility and vapour pressure. These were the factors that were considered of vital importance when determining what hazard the various ECPs posed and, thus these factors played a major role in determining the priority that would be assigned to a compound.

Physico-chemical data was obtained from materials safety data sheets (MSDSs) for the compounds concerned (primarily from Sigma Aldrich) and from studies that investigated or contained data on the toxicity, persistence of compounds. However, in instances where such information was unavailable or could not be found, chemical modelling programmes were used to gain the required information. The PBT Profiler programme (www.pbtprofiler.net) was used for this purpose. These programmes predict the physico-chemical, toxicity and persistence data based upon the chemical structure of the compound. The program relies on input in the form of the chemical's name or CAS number. These programmes have been commonly used in various studies regarding ECPs and it

was the most efficient, cost effective and reliable manner in which to acquire the data that was missing after the extensive literature review was completed. A well-known prioritisation study by Diamond et al. (2011) also relied upon modelling programmes to acquire data that was not freely available. Numerous studies prior to this also did so (Diamond et al. 2011).

During the final part of the prioritisation, the data from the various tables were combined to determine what risk/hazard was posed by the various ECPs. The first step towards achieving this was by ranking the ECPs within each table based on the relevant data that was obtained about the ECPs. Thus every table resulted in a ranked list of ECPs for that particular set of factors. The lowest rank was assigned to the highest scoring chemical, thus the chemical that had the highest score for a particular factor, such as toxicity for example, would receive a rank of 1. This was done with the full knowledge that not inverting the ranking would provide the same result. The inverse order was used as it was thought that it made analysis after each step simpler as the most significant chemical for that specific parameter would receive the ranking of 1 instead of 168, which it would have received if the ranks were not assigned inversely.

To gain an all-inclusive rank for a particular ECP, the rank that it held within each table was simply summed together, giving it a score based on all the factors that are relevant to determine its potential risk or hazard. This means that compounds with lower summed rank values are of higher concern and are thus more of a priority than compounds with a higher summed rank value. The end result of this process was a ranked list of priority ECPs.

3.2 GIS Methodology

The methodology was based on locating the river catchment areas within the Gauteng region that would be the most susceptible to contamination. Figure 3.1 below shows an overview of the various phases that were followed in order to locate suitable sampling areas which could possibly contain contaminants in most vulnerable areas within Gauteng with a specific focus on anthropogenic chemicals. This was done by identifying all the protected and vulnerable areas within each of the catchments by looking at the ecosystem status of each catchment as defined by the South African National Biodiversity Institute, identifying the number of medical facilities and waste water treatment plants as well as determining the population density of the areas.

From this information an analysis was done to determine the catchment(s) which have the highest vulnerability and could have the most detrimental effects if high levels of contaminates were found. This analysis was completed by combining the variables listed above within the catchments using an overlay approach. Here each of the factors most likely to contribute to contamination within the catchment was analysed according to a criterion and further ranked based on risk. The combinations of variables were then overlaid to extract the catchment(s) that would be the most

susceptible to contaminants. The water features within these vulnerable catchments were further extracted and maps depicting the areas which are most vulnerable as well as having a high probability of containing contaminants were created. Further detail is provided in Figure 3.1.

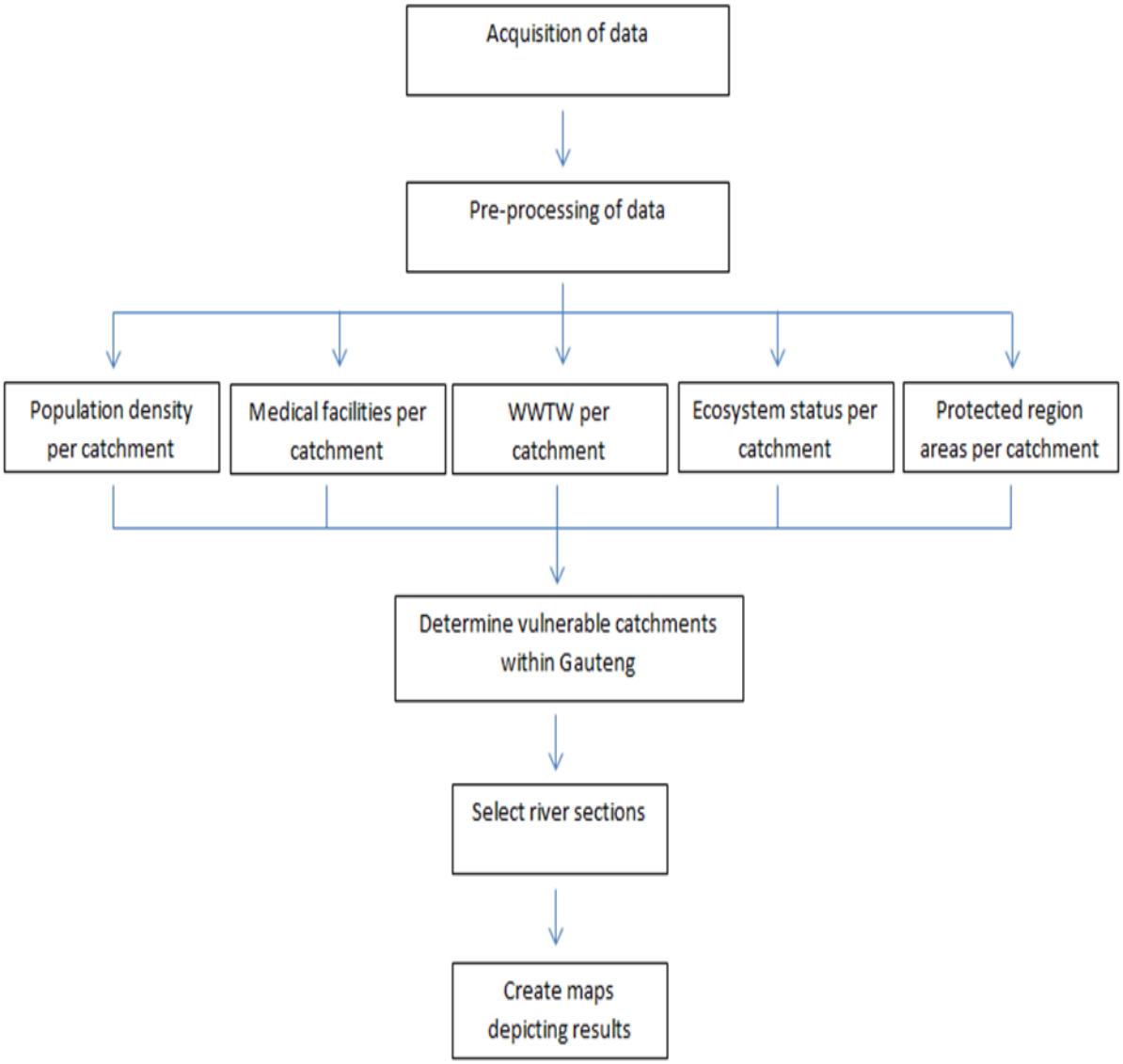

Figure 3.1: Overview of GIS methodology for anthropogenic substances

A similar diagram depicting the process followed for the agricultural chemicals is shown in Figure 3.2. The overall process was very similar. It is worth noting that population density was retained as a parameter, but for different reasons compared to its role for the anthropogenic chemicals. For the both types of chemicals population density meant there was a greater risk of those chemicals finding their way into the water resources of the region. In the case of the agricultural chemicals

population density had a direct influence on the potential for an agricultural chemical to cause harm as regions where more people live can mean that a chemical has the potential to cause more harm than in sparsely populated areas.

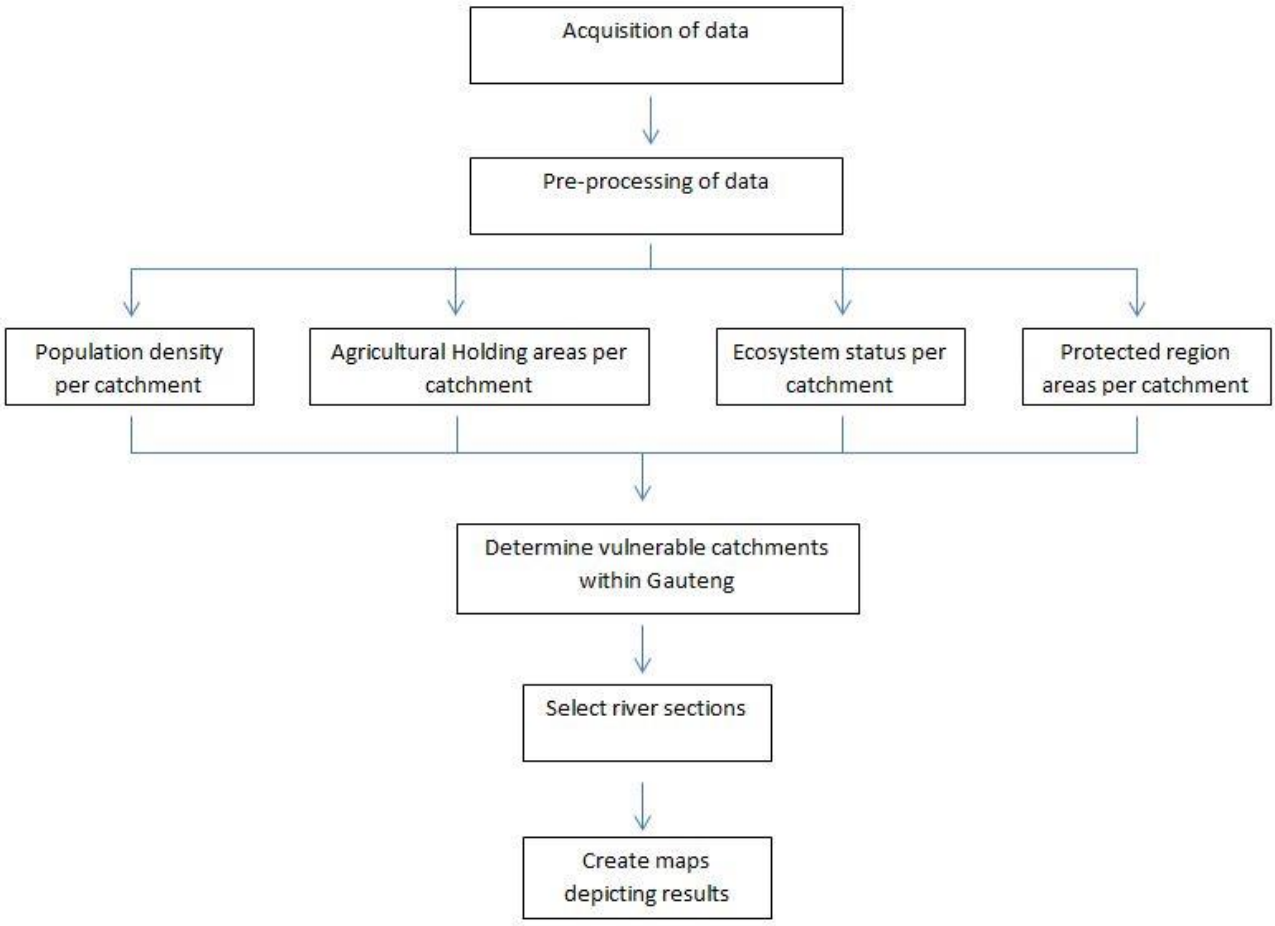

Figure 3.2: Overview of GIS methodology for agricultural substances

3.2.1 Acquisition of relevant data

For this research study a number of datasets were required. A detailed summary of the required spatial and non-spatial datasets are summarised in Table 2 below.

Table 2 Required spatial and non-spatial datasets for GIS modelling.

Required Dataset	**Format**	**Main Purpose**	**Source** (all the data was directly requested and as such was obtained via personal communication)

Population Density	Shapefile per ward	Used to determine which catchment would be most vulnerable.	Statistics South Africa
Waste water treatment plants	Excel sheet	Locate containment points and create risk weighting	Department of Water Affairs
Medical facilities	Shapefile (points)	Locate containment points and create risk weighting	Department of Health
Protected Areas	Shapefile (polygons)	Determine areas of vulnerability and contribute to the selection of catchments	South African National Biodiversity Institute
Water Catchments	Shapefile (polygons)	Used as base data	Department of Water Affairs
Water features	Shapefile (lines and polygons)	Used as base data and obtain sampling areas	MapIT and AfriGIS
Landuse data	Raster data	Ecosystem status	National Geo-spatial Information
Agricultural data	Shapefile (polygons)	To determine areas of vulnerability	National Department of Agriculture
Orientation data	Various formats	Orientation, visualisation and planning	South African National Biodiversity Institute, AfriGIS, Department of Rural Development and Land reform

3.2.2 Pre-processing of data

To successfully analyse the data and select suitable sampling sites the first step was to ascertain data interoperability between the required datasets. This means that the data formats needed to be compatible with each other as well as the GIS software package that was used. For the purpose of this research project Environmental Systems Research Institute (ESRI's) ArcGIS software package (version 10.1) was utilised. The ArcGIS data interoperability function is known as Spatial ETL tool and this tool allows the user to do conversions between formats as well create a platform where the data can be analysed and visualised regardless of the format. All the datasets acquired for this study were also clipped to the Gauteng Province for faster analysis and processing with the exception of the catchments as the full catchment boundary was needed for accurate selection,

here an intersect tool was used to create a selection of the catchments that overlapped the Gauteng Province boundary.

3.2.3 Selecting Vulnerable Catchment(s) (Anthropogenic Chemicals)

The term ‘anthropogenic compounds’ will be used to describe all the chemicals that are not used during agricultural practises such as antibiotics or personal care products. Selecting the most vulnerable catchments in Gauteng would give an indication of where contaminants would most likely have the greatest impact if found. The first step was to determine the population density per catchment. The current population density data was populated per ward and not per catchment. To reallocate data from one set of polygon (area) data to another set of polygons a geostatistical analysis tool had to be used. Here areal interpolation was implemented in a two-step process, first a smooth prediction surface was created from the source polygon in this case the population per ward and then this surface was reallocated to each of the target polygons which was the catchment areas within Gauteng. This gave an accurately estimated population per catchment.

Medical facilities and waste water treatment plants are most likely to be the sources of contaminants due to the high concentration of ECPs used and processed by them respectively, therefore the second step in selecting the vulnerable catchments was to locate the number of medical facilities and waste water treatment works per catchment. This was done using a spatial join which joins attributes and calculates statistics based on spatial relationships. For both medical facilities and the waste water treatment works, the count statistic indicates the number of features that were joined in the matching target area (catchments). This layer was then joined with the population density layer calculated in the previous step.

The next objective in selecting the vulnerable catchments was to locate all the protected areas and areas of concern per catchment. This was completed by importing all the protected and high priority areas into ArcGIS then using the model builder tool to clip all the features within each catchment. The summed area of these protected areas per catchment were then calculated by exporting the attribute table to excel and summing the various areas for each catchment and further creating a field in the layer with the population density attribute table and manually updating the summed area of protected areas per catchment. The area of protected areas per catchment would give a good indication of the extent that the vulnerable areas cover within each catchment. The smaller the difference between the catchment area and protected areas the higher the vulnerability status of the catchment became.

Lastly the ecosystem status of each catchment was extracted using the South African National Biodiversity Institute (SANBI) dataset which classifies areas according to whether an ecosystem is critically threatened, threatened, vulnerable or least threatened. This was also done using a spatial join, however here the attribute containing the status was joined to the catchments dataset. These

were the variables needed to identify the catchments that would potentially be most vulnerable if contaminants were found. With the information created in the catchment database and using the "select by" attribute function it was now possible to select the catchment areas with high population density, high number of potential containment outlets as well as a larger vulnerable areas that can be affected.

Using Structured Query Language (SQL) within ArcGIS software using the "select by" attribute tool the most vulnerable catchments were extracted. This was done in phases within one SQL query, the first phase was to identify the population density within Gauteng per catchment and if the population density was more than a third of the total population it was added to the query. Phase two was to identify the summed number of medical facilities within Gauteng. If a catchment had more than a third of all the medical facilities it was added to the query. More than a third was considered as it was the average mode per catchment. If a catchment had more than two waste water treatment works it was also added to the query. This parameter was based on the average amount of waste water treatment plants that were located within each catchment. This formed part of the third phase. The fourth phase extracted catchments that had a critically threated ecosystem status from the attribute table within the database and lastly if the area of protected areas for a catchment was more than 1000 ha it was added to the query for selection. The catchment(s) had to fulfil all the above requirements for it to be selected as a vulnerable catchment. Furthermore, the river dataset was overlayed with Gauteng and the river sections that overlapped the vulnerable areas were extracted using a select by location tool.

3.2.4 Selecting Vulnerable Catchment(s) (Agricultural Chemicals)

To determine the catchments which are vulnerable due to ECPs from agricultural holdings (areas where the land use was indicated as agricultural) the first step was to locate all the agricultural holdings within Gauteng bases from the Department of Agriculture Forestry and Fisheries data. This was completed by importing the shapefile into ArcGIS, adding new fields to the attribute table and using a calculate geometry tool within the attribute table to calculate the areas of the individual holdings. The summed area of the agricultural holdings per catchment were then calculated by first joining the agricultural holding layer with the Gauteng catchment by location and then by applying a join via attribute to the original dataset where all the information of the variables were stored. Furthermore, making use of Structured Query Language (SQL) as with the first selection done above, the select by attribute tool was used to compute the most vulnerable catchments with regards to agricultural holdings instead of medical facilities and waste water treatment works. This once more was done in phases within one SQL query, the first phase was to identify the population density within Gauteng per catchment that fell in the highest category within the natural break selection and it was added to the query. The second phase in this regard was to extract all the

catchments that had an endangered ecosystem status from the attribute table within the database and then for the third phase to select protected areas where the area for each catchment was more than 1 000 ha and was added to the query for selection. Lastly the agricultural holdings which fell into the largest category with their summed area being 7 000 ha or more per catchment were added to the query. The size limits were obtained based on a visual inspection of the data, based on what was perceived to be a significantly large area compared to the total for the province. The SQL query was based on “AND” functions and only the catchment(s) that fulfilled all the above conditions were selected and stated as vulnerable catchment(s). Furthermore, the river dataset was again overlayed with Gauteng and the river sections that overlapped the vulnerable areas were extracted using a select by location tool.

3.2.5 Displaying Results

To display the outputs, the layers were scaled, categorised and symbolised. Each of the variables together with some orientation data was employed to create maps to depict each stage of the methodology together with the final results displaying the vulnerable catchments and river sections for both the anthropogenic and agricultural holdings.

Chapter 4: Results and Discussion

4.1Results

4.1.1 Results obtained by the prioritisation approach

Table 3 contains the results from the hazard based prioritisation of the 168 ECPs that were analysed in this study. The rank that each ECP attained for each analysed category (partition coefficient, toxicity and half-life in water) is included within the table. The total score for each respective ECP was calculated by summing together the aforementioned ranks. These scores were then used to give each individual ECP its final ranking. The values in the final ranking column of the table is thus representative of the final rank of each individual ECP in terms of the potential hazard it poses following a PBT approach.

Table 3 Results of preliminary prioritisation of ECPs arranged alphabetically per compound class. The source of data was Sigma Aldrich MSDSs unless otherwise indicated.

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Pharmaceuticals: Analgesics and anti-inflammatory drugs									
Acetaminophen	103-90-2	log P: 0.31 (Hansch et al., 1995)	86	1944	91	15	5	182	88
Acetylsalicylic acid	50-78-2	log Pow: 1.19	75	1500	81	15	5	161	77
Antipyrine	60-80-0	log Pow: 0.538	83	1705	86	15	5	174	83
Benzocaine	94-09-7	XLogP3 1.9 (Pubchem)	63	3042	103	15	5	171	82
Codeine	76-57-3	XLogP3 1.1 (Pubchem)	77	427	44	60	3	124	55

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Dextropropoxyphene	1639-60-7	log Kow: 4.18	31	84	17	38	4	52	13
Diclofenac	15307-86-5	XLogP3 4.4 (Pubchem)	28	62.5	15	38	4	47	11
Fenoprofen	34597-40-5	XLogP3 3.3 (Pubchem)	42	> 200	28	15	5	75	20
Ibuprofen	15687-27-1	log Kow 2.48 (Scheytt et al. 2005)	56	636	50	15	5	111	43
Indomethacine	53-86-1	XLogP3 4.3 (Pubchem)	29	12	5	38	4	38	7
Ketoprofen	22071-15-4	log Pow 0.97 (Drugs.com)	78	62.4	14	15	5	97	34
Ketorolac	66635-83-4	XLogP3 1.9 (Pubchem)	63	189	27	38	4	94	31
Mefenamic acid	61-68-7	log Pow 5.33 (chemspider.com)	15	740	57	38	4	76	21
Naproxen	22204-53-1	XLogP3 3.3 (Pubchem)	42	248	32	15	5	79	23
Propyphenazone	479-92-5	XLogP3 1.7 (Pubchem)	65	860	63	38	4	132	59
Salicylic acid	69-72-7	log Pow: 2.21	58	891	65	15	5	128	57
Pharmaceuticals: Antibiotics									
4-aminoantipyrine [4-AA]	83-07-8	XLogP3 0.1 (Pubchem)	90	1700	85	15	5	180	87
Amoxicillin	26787-78-0	XLogP3 -2 (Pubchem)	106	> 15 000	127	38	4	237	111
Azythromycin	83905-01-5	XLogP3 4 (Pubchem)	33	> 2,000	93	180	1	127	56

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Cefazolin	25953-19-9	XLogP3 -0.4 (Pubchem)	95	> 11,000	123	38	4	222	107
Cefotaxime	63527-52-6	XLogP3 -1.4 (Pubchem)	103	> 20,000	130	38	4	237	111
Chlortetracycline	57-62-5	log Pow: -0,62	98	3000	102	180	1	201	99
Ciprofloxacin	85721-33-1	XLogP3 -1.1 (Pubchem)	102	> 2,000	93	60	3	198	96
Clarithromycin	81103-11-9	XLogP3 3.2 (Pubchem)	43	1,270	76	180	1	120	51
Doxycyclin	564-25-0	XLogP3 -0.7 (Pubchem)	99	262	35	60	3	137	62
Enrofloxacin	93106-60-6	XLogP3 -0.2 (Pubchem)	94	5000	113	180	1	208	103
Erythromycin	114-07-8	XLogP3 2.7 (Pubchem)	52	4600	111	180	1	164	79
Fluconazole	86386-73-4	log Pow: 1,473	70	1271	77	180	1	148	70
Lincomycin	154-21-2	XLogP3 0.2 (Pubchem)	88	262	35	38	4	127	56
Metronidazole	443-48-1	XLogP3 0 (Pubchem)	91	3000	102	38	4	197	95
Nalidixic acid	389-08-2	log Pow: 1,41	72	1160	74	38	4	150	72
Norflaxin	70458-96-7	XLogP3 -1 (Pubchem)	101	> 4,000	109	60	3	213	105
Ofloxacin	82419-36-1	XLogP3 -0.4 (Pubchem)	96	3590	107	180	1	204	102
Oxytetracycline	79-57-2	XLogP3 -1.6 (Pubchem)	104	3000	102	60	3	209	104
Roxithromycin	80214-83-1	XLogP3 3.1 (Pubchem)	45	830	62	180	1	108	41

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Sulfamethazine	57-68-1	XLogP3 0.3 (Pubchem)	87	50000	133	38	4	224	109
Sulfapyridine	144-83-2	XLogP3 0 (Pubchem)	91	15800	128	38	4	223	108
Sulfisomidine	208-204-3	XLogP3 1.2 (Pubchem)	74	3000	102	38	4	180	87
Sulfamethoxazole	723-46-6	XLogP3 0.9 (Pubchem)	80	6,200	116	38	4	200	98
Tetracyclin	60-54-8	XLogP3 -2 (Pubchem)	106	807	60	60	3	169	80
Trimethoprin	738-70-5	XLogP3 0.9 (Pubchem)	80	> 5,300	114	60	3	197	95
Pharmaceuticals: Beta-blockers									
Acebutolol	34381-68-5	XLogP3 1.7 (Pubchem)	65	3000	102	38	4	171	82
Atenolol	29122-68-7	XLogP3 0.2 (Pubchem)	88	> 2,000	93	38	4	185	91
Celiprolol	260-497-7	XLogP3 1.9 (Pubchem)	93	> 2157	94	38	4	161	77
Metoprolol	37350-58-6	XLogP3 1.9 (Pubchem)	63	5,500	115	38	4	182	88
Pindolol	13523-86-9	XLogP3 1.8 (Pubchem)	64	263	36	15	5	105	39
Propranolol	525-66-6	XLogP3 3 (Pubchem)	46	660	53	15	5	104	38
Sotalol	3930-20-9	XLogP3 0.2 (Pubchem)	88	3450	106	15	5	199	97
Pharmaceuticals: Blood lipid lowering agents									
Bezafibrate	41859-67-0	XLogP3 3.8 (Pubchem)	37	1082	72	60	3	112	44

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Fenofibric acid	42017-89-0	log Pow: 3.895	35	1242	75	38	4	114	46
Gemfibrozil	25812-30-0	XLogP3 3.8 (Pubchem)	37	1414	80	38	4	121	52
Mevastatin	73573-88-3	XLogP3 3.9 (Pubchem)	34	> 2,000	93	15	5	132	59
Pravastatin	81093-37-0	XLogP3 1.6 (Pubchem)	67	12000	124	15	5	196	94
Pharmaceuticals: Neuroactive compounds									
Carbamazepine	298-46-4	log Kow 1.51 (Scheytt et al. 2005)	68	1957	92	38	4	164	79
Citalopram	59729-33-8	XLogP3 3.2 (Pubchem)	43	825	61	180	1	105	39
Diazepam	439-14-5	XLogP3 3 (Pubchem)	48	249	33	38	4	83	26
Fluoxetine	54910-89-3	XLogP3 4 (Pubchem)	33	825	61	60	3	97	34
Imipramine	50-49-7	XLogP3 4.8 (Pubchem)	23	355	39	60	3	65	16
Paroxetine	61869-08-7	XLogP3 3.5 (Pubchem)	40	> 500	46	60	3	89	28
Temazepam	846-50-4	XLogP3 2.2 (Pubchem)	59	2000	93	38	4	156	74

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Venlafaxine	93413-69-5	XLogP3 2.9 (Pubchem)	47	9000	120	60	3	170	81
Contrast media									
Diatrizoic acid	117-96-4	XLogP3 1.8 (Pubchem)	64	12300	125	180	1	190	92
Iohexol	66108-95-0	XLogP3 -3 (Pubchem)	109	20000	130	60	3	242	113
Iomeprol		XLogP3 -2.3 (Pubchem)	108	14300	126	60	3	237	111
Iopromide	73334-07-3	XLogP3 -2.1 (Pubchem)	107	21403	131	60	3	241	112
Personal care products: Cosmetics									
Galaxolide	1222-05-5	XLogP3 4.8 (Pubchem)	23	>5000	113	60	3	139	64
Tonalid	21145-77-7	XLogP3 5.3 (Pubchem)	16	570	47	60	3	66	17
Pharmaceuticals: Diuretics									
Furosemide	54-31-9	XLogP3 2 (Pubchem)	61	2600	98	60	3	162	78
Hydrochlorothiazide	58-93-5	XLogP3 -0.1 (Pubchem)	93	> 10000	121	60	3	217	106
Pharmaceuticals: Psycho-stimulants									
Caffeine	58-08-2	log Pow: -0.091 at 23 °C	92	367.7	40	15	5	137	62
Personal care products: Disinfectants									
Chloroform	67-66-3	log Pow: 1,97	62	908	68	38	4	134	60
Bromoacetic acid	79-08-3	log Pow: 0,41	85	50	11	8.7	6	102	37

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Bromodichloromethane	75-27-4	XLogP3 2.4 (Pubchem)	57	1388	79	75	2	138	63
Chloroacetonitrile	107-14-2	log Pow: 0,45	84	220	29	15	5	118	50
Dibromoacetic acid	631-64-1	XLogP3 1.5 (Pubchem)	69	1737	87	15	5	161	77
Dibromoacetonitrile	3252-43-5	XLogP3 1.7 (Pubchem)	65	245	31	38	4	100	36
Dibromochloromethane	124-48-1	XLogP3 2.6 (Pubchem)	53	370	41	38	4	98	35
Dichloroacetic acid	79-43-6	log Pow: 0,942	79	2820	100	15	5	184	90
Dichloroacetonitrile	3018-12-0	XLogP3 1.3 (Pubchem)	73	330	38	38	4	115	47
Formaldehyde	50-00-0	XLogP3 1.2 (Pubchem)	74	800	59	15	5	138	63
Monochloroacetic acid	79-11-8	log Pow: 0,2	88	90.4	20	15	5	113	45
Nitrosodimethylamine	62-75-9	XLogP3 -0.6 (Pubchem)	97	37	8	38	4	109	42
Nonylphenol	84852-15-3	log Pow: 5,4 at 23 °C	14	580	48	38	4	66	17
Trichloroacetic acid	76-03-9	log Pow: 1,645	66	3320	105	38	4	175	84
Trichloroacetonitrile	545-06-2	XLogP3 2.1 (Pubchem)	60	250	34	60	3	97	34
Triclosan	3380-34-5	log Pow: 4.7	24	3700	108	60	3	135	61
Phthalates									
Benzyl butyl phthalate	85-68-7	log Pow: 4.91 at 20 °C	20	2330	97	15	5	122	53
Bis[2-ethylhexyl] phthalate	117-81-7	XLogP3 7.4 (Pubchem)	3	30000	132	15	5	140	65

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Bisphenol A	80-05-7	log Pow: 3.4 at 21.5 °C	41	2000	93	38	4	138	63
Dibutyl phthalate	84-74-2	XLogP3 4.7 (Pubchem)	24	8000	117	8.7	6	147	69
Diethyl phthalate	84-66-2	log Pow: 2.2 at 41 °C	59	8600	119	15	5	183	89
Diisobutyl phthalate	84-69-5	log Pow: 4.11 at 20 °C	32	10392	122	15	5	159	76
Dimethyl phthalate	131-11-3	log Pow: 1.47	71	8200	118	15	5	194	93
Pesticides									
2,4-Dichlorophenoxyacetic acid [2,4-D]	94-75-7	log Pow: 2.81	50	375	42	38	4	96	33
2-methyl-4-chlorophenoxyacetic acid	94-74-6	XLogP3 2.6 (Pubchem)	53	700	55	15	5	113	45
Acetochlor	34256-82-1	log Pow: 2,719	51	763	58	60	3	112	44
Aldicarb	116-06-3	XLogP3 1.1 (Pubchem)	77	0.5	1	38	4	82	25
Aldrin	309-00-2	log Pow: 6,50	9	39	9	180	1	19	2
Atrazine	1912-24-9	log Pow: 2,61log Pow: 5	19	672	54	60	3	76	21
Chlorpyrifos	2921-88-2	log Pow: 5,27	17	82	16	180	1	34	6
Clofibrin acid / Clofibric acid	882-09-7	log Kow 2.88 (Scheytt et al. 2005)	48	897	66	38	4	118	50
Cyanazine	21725-46-2	XLogP3 2.2 (Pubchem)	59	149	24	180	1	84	27
Cypermethrin	52315-07-8	log Pow: 5	19	57.5	13	180	1	33	5

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
DDD	72-54-8	log Pow: 6,02	11	113	21	180	1	33	5
DDE	72-55-9	log Pow: 6,51	8	880	64	180	1	73	19
DDT	50-29-3	log Pow: 6,91	5	87	18	180	1	24	4
Deltamethrin	52918-63-5	XLogP3 6.2 (Pubchem)	10	9.36	4	60	3	17	1
Dieldrin	60-57-1	XLogP3 3.7 (Pubchem)	38	37	8	180	1	47	11
Diquatdibromide	85-00-7	log Kow: 4.60	25	120	22	38	4	51	12
Endosulphan	115-29-7	log Pow: 3,83	36	18	7	180	1	44	10
Endosulphan sulphate	1031-07-8	log Pow: 3,66	39	8	3	180	1	43	9
Endrin	72-20-8	log Pow: 5,20	18	3	2	180	1	21	3
Enilconazole	35554-44-0	XLogP3 3.8 (Pubchem)	37	227	30	60	3	70	18
Fenoprop	93-72-1	XLogP3 3.8 (Pubchem)	37	650	52	38	4	93	30
Glyphosphate	1071-83-6	XLogP3 -4.6 (Pubchem)	110	4873	112	15	5	227	110
Heptachlor epoxide	1024-57-3	log Pow: 5,40	14	15	6	180	1	21	3
Heptachlor	76-44-8	XLogP3 4.3 (Pubchem)	29	40	10	180	1	40	8
Hexachlorobenzene [HCB]	118-74-1	XLogP3 5.7 (Pubchem)	13	10000	121	180	1	135	61
Hexachlorocyclohexane isomers	319-84-6	log Pow: 3,80	37	177	26	180	1	64	15
Hexazinone	51235-04-2	XLogP3 1.3 (Pubchem)	73	1690	84	38	4	161	77
Imidacloprid	138261-41-3	XLogP3 0.8 (Pubchem)	81	410	43	60	3	127	56
Lindane	58-89-9	Pow: 3,5 at	40	88	19	180	1	60	14

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
		22 °C							
Metazachlor	67129-08-2	log Pow: 2,49	55	1000	70	60	3	128	57
Methoxychlor	67129-08-2	log Pow: 2,49	55	1855	90	60	3	148	71
Metolachlor	51218-45-2	XLogP3 3.1 (Pubchem)	45	2200	95	60	3	143	68
Paraquat	1910-42-5	XLogP3 1.7 (Pubchem)	65	57	12	38	4	81	24
Simazine	122-34-9	XLogP3 2.2 (Pubchem)	59	971	69	60	3	121	58
Tebuthiuron	34014-18-1	XLogP3 1.6 (Pubchem)	67	644	51	38	4	122	53
Vinclozolin	50471-44-8	XLogP3 3.1 (Pubchem)	45	10000	121	60	3	169	80
PAHs									
Acenaphthene	83-32-9	log Pow: 3,9	34	1700	85	38	4	123	54
Acenaphthylene	208-96-8	XLogP3 3.7 (Pubchem)	38	1760	88	15	5	131	58
Benzo[a]pyrene	50-32-8	log Pow: 5,97	12	1600	82	60	3	97	34
Fluoranthene	206-44-0	log Kow 4.90 (4.58) Ministry of Environment, Lands and Parks Province of British Columbia	21	2000	93	60	3	117	49
Fluorene	86-73-7	XLogP3 4.2 (Pubchem)	30	>2000	93	15	5	128	57
Naphthalene	91-20-3	log Pow: 3,30	42	490	45	38	4	91	29
Phenanthrene	85-01-8	log Pow: 4,57	26	1800	89	60	3	118	50

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Pyrene	129-00-0	log Pow: 4,88	22	2700	99	60	3	124	55
Pharmaceuticals: Antiretrovirals									
Abacavir	136470-78-5	XLogP3 0.9 (Pubchem)	80	2000	93	38	4	177	85
Lamivudine	134678-17-4	log Pow: -0,93	100	2000	93	15	5	198	96
Stavudine	3056-17-5	log Kow: 0.144	89	4000	109	15	5	203	101
Zidovudine	30516-87-1	XLogP3 0 (Pubchem)	91	3084	104	15	5	200	98
Pharmaceuticals: Antivirals									
Famciclovir	104227-87-4	log Pow: 0,739	82	2000	93	38	4	179	86
Penciclovir	39809-25-1	XLogP3 -1.6 (Pubchem)	104	2000	93	15	5	202	100
Ribavirin	36791-04-5	XLogP3 -1.8 (Pubchem)	105	2700	99	15	5	209	104
Additional Substances									
Benzophenone	119-61-9	log Pow: 3.18	44	> 10,000	121	15	5	170	81
Cinchonidine	485-71-2	XLogP3 2.7 (Pubchem)	52	316	37	38	4	93	30
Cinchonine	118-10-5	XLogP3 2.7 (Pubchem)	52	152	25	38	4	81	24
Clofibric acid	882-09-7	XLogP3 2.6 (Pubchem)	53	897	67	38	4	124	55
Clotrimazole	23593-75-1	XLogP3 5 (Pubchem)	19	708	56	60	3	78	22
Diphenylamine	122-39-	log Pow: 3,5	40	1120	73	38	4	117	49

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
	4								
Diuron	330-54-1	log Pow: 2.84 at 20 °C	49	1017	71	38	4	124	55
Ephedrin	299-42-3	XLogP3 0.9 (Pubchem)	80	600	49	15	5	134	60
Ethinylestradiol	57-63-6	XLogP3 3.7 (Pubchem)	38	2952	101	60	3	142	67
Ifosfamine	3778-73-2	XLogP3 0.9 (Pubchem)	80	143	23	38	4	107	40
Minoxidil	38304-91-5	XLogP3 1.2 (Pubchem)	74	1321	78	60	3	155	73
Nicotine	54-11-5	log Pow: 1.17	76	50	11	38	4	91	29
Omeprazole	73590-58-6	XLogP3 2.2 (Pubchem)	59	2210	96	60	3	158	75
Phenytoin	57-41-0	XLogP3 2.5 (Pubchem)	54	1635	83	38	4	141	66
Ranitidine	66357-35-5	XLogP3 0.3 (Pubchem)	87	>5 000	113	38	4	204	102
Tamoxifen	10540-29-1	XLogP3 7.1 (Pubchem)	4	4100	110	60	3	117	49
Telmisartan	144701-48-4	XLogP3 6.9 (Pubchem)	6	> 2000	93	60	3	102	37
Brominated Flame Retardants									
Decabromodiphenyl ether	1163-19-5	XLogP3 10.4 (Pubchem)	1	2000	93	180	1	95	32
Hexabromocyclododecane	3194-55-6	XLogP3 7.1 (Pubchem)	4	10000	121	60	3	128	57
Octabromodiphenyl ether	32536-52-0	XLogP3 9 (Pubchem)	2	5000	113	180	1	116	48

Substance	CAS-No	Partition Coefficient		Toxicity		Degradation rates		Total Score	Final Ranking
		Value	Partition Coefficient Rank	Acute Toxicity Rat (LD50 Oral in mg/kg)	Toxicity Rank	Half-life in Water (days) (www.pbtprofiler.net)	Half-life Rank		
Pentabromodiphenyl ether	32534-81-9	XLogP3 6.9 (Pubchem)	6	5000	113	180	1	120	51
Tetrabromobisphenol A	79-94-7	XLogP3 6.8 (Pubchem)	7	5000	113	180	1	121	52

4.1.2 Results obtained by the GIS (potential sampling site selection process)

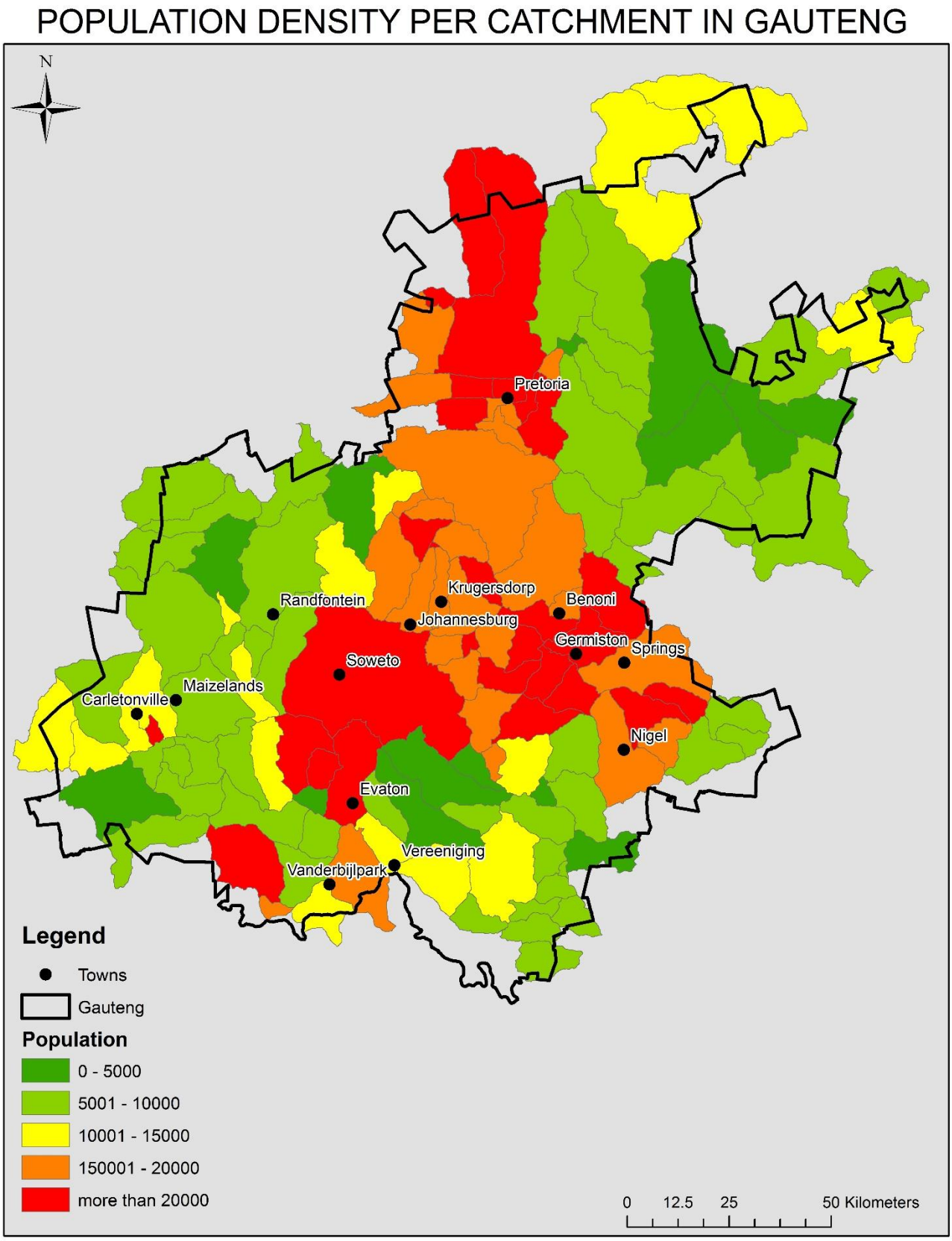

Figure 4.1: Population density per catchment in Gauteng

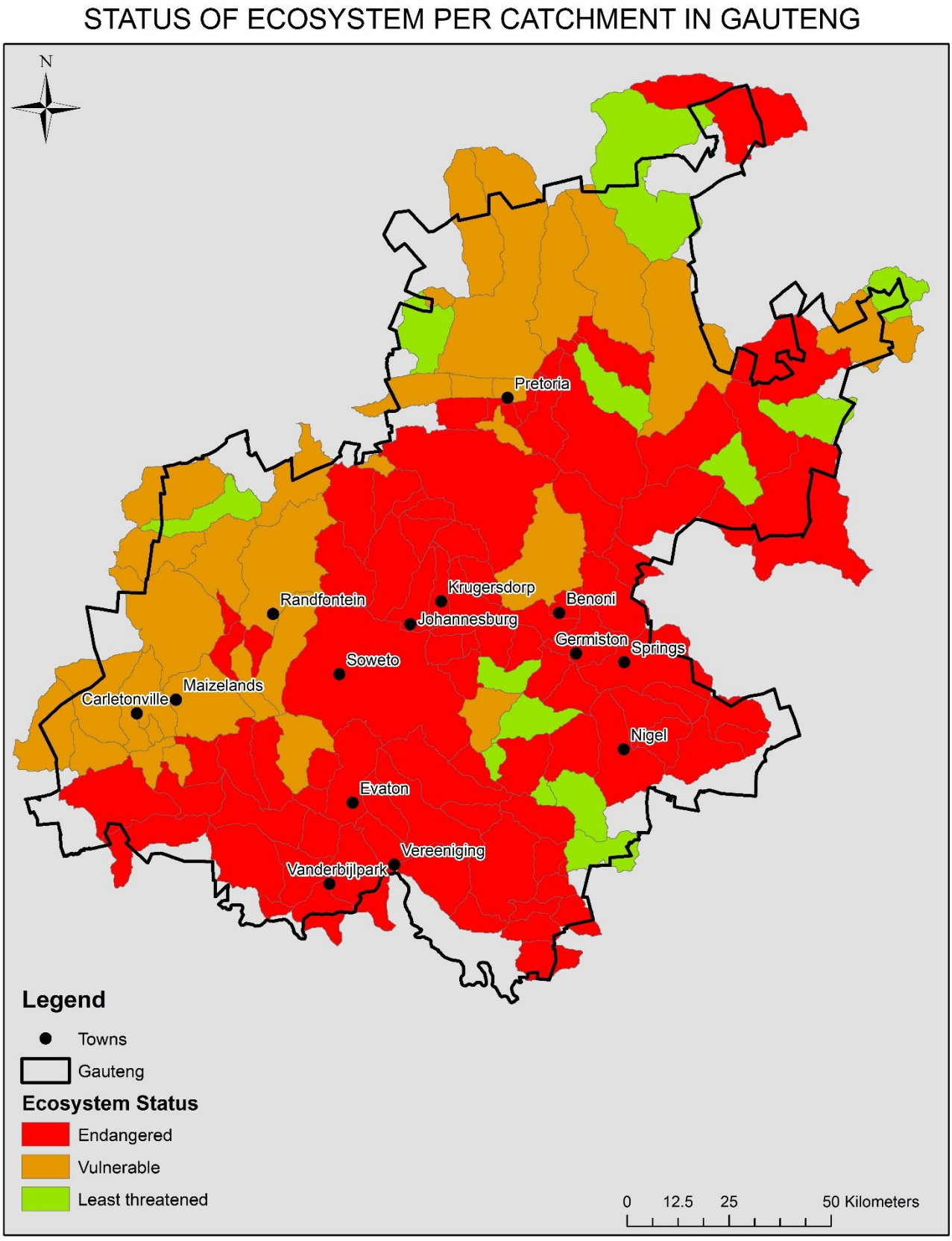

Figure 4.2: Status of ecosystem per catchment in Gauteng

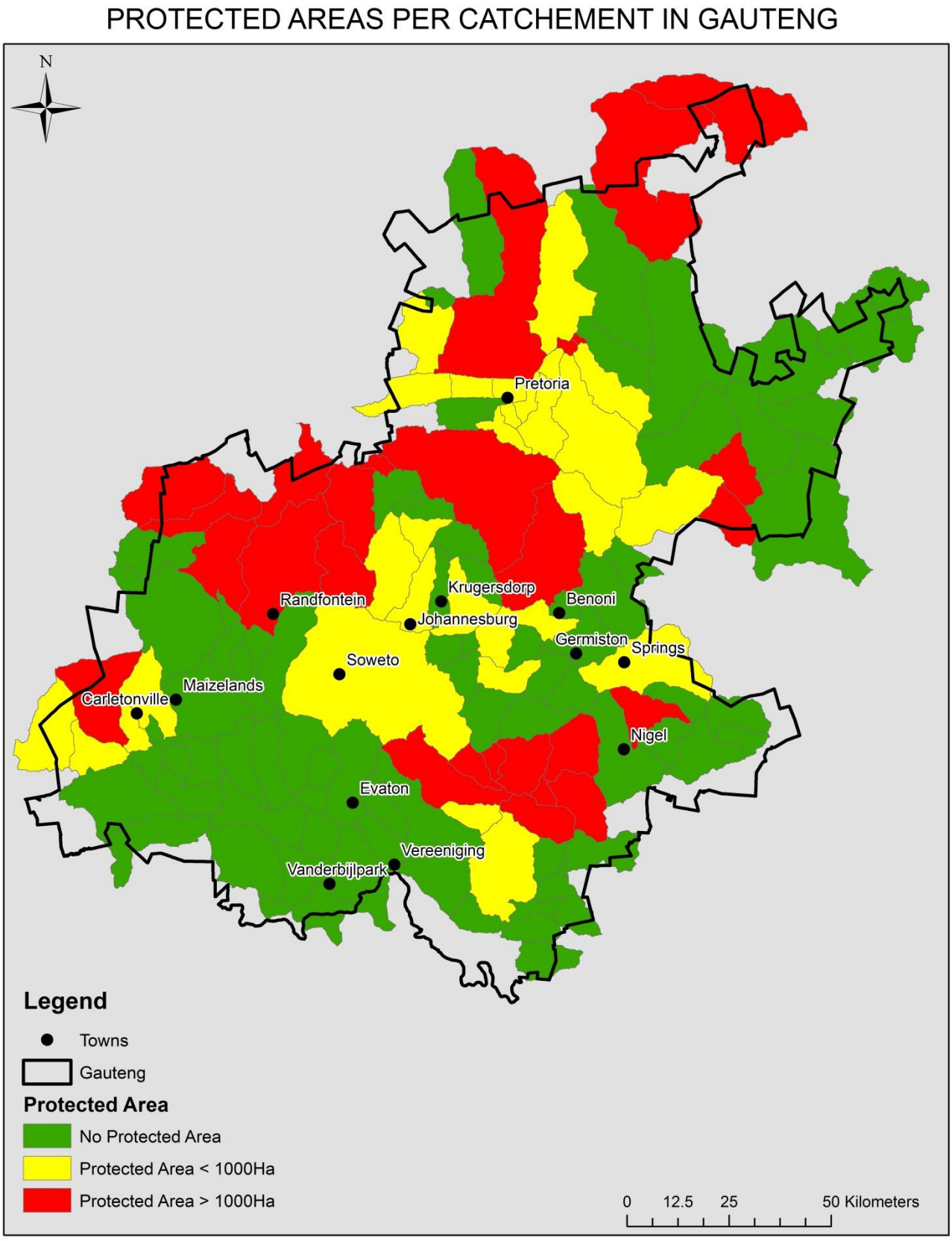

Figure 4.3: Protected areas per catchment in Gauteng.

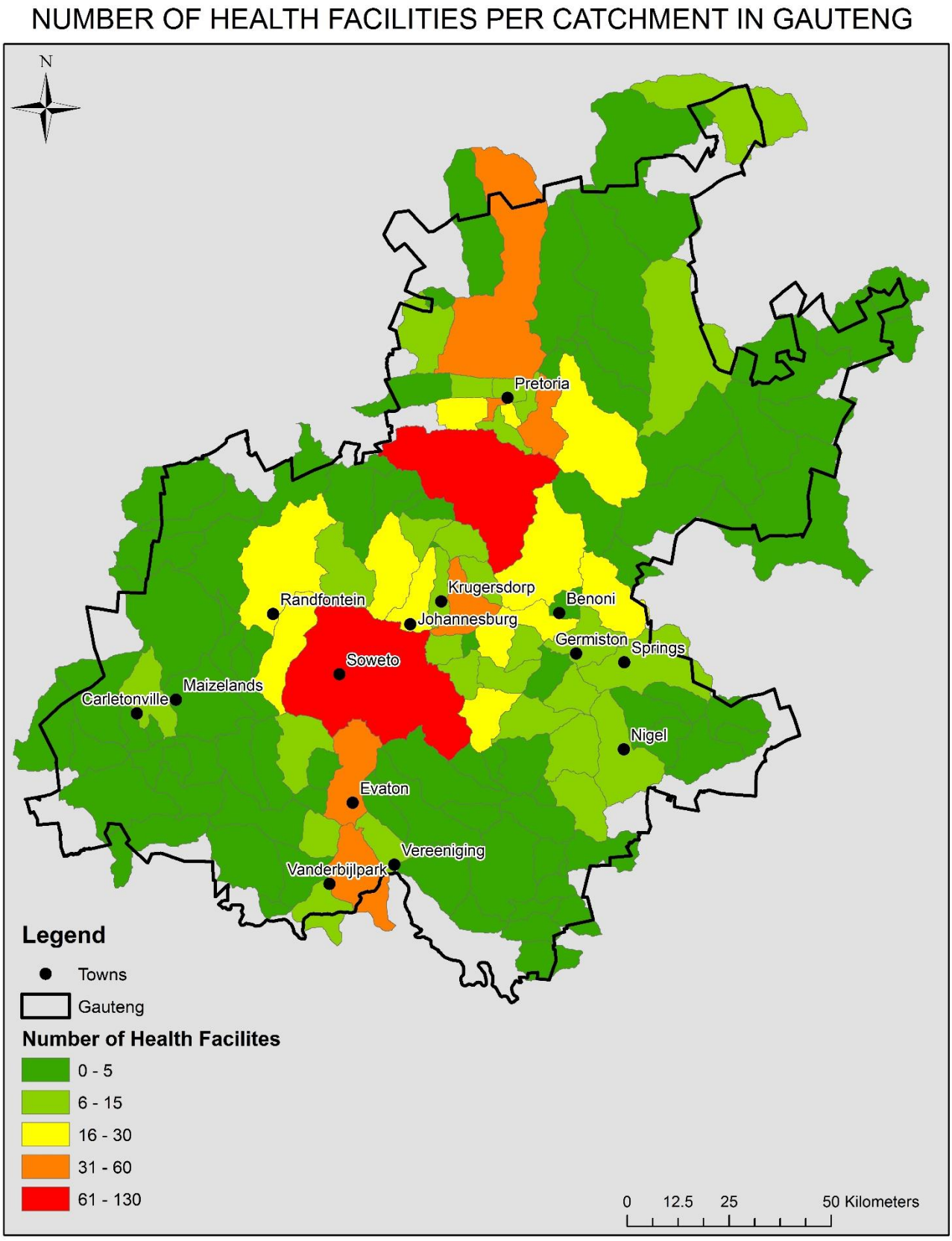

Figure 4.4: Number of health facilities per catchment in Gauteng.

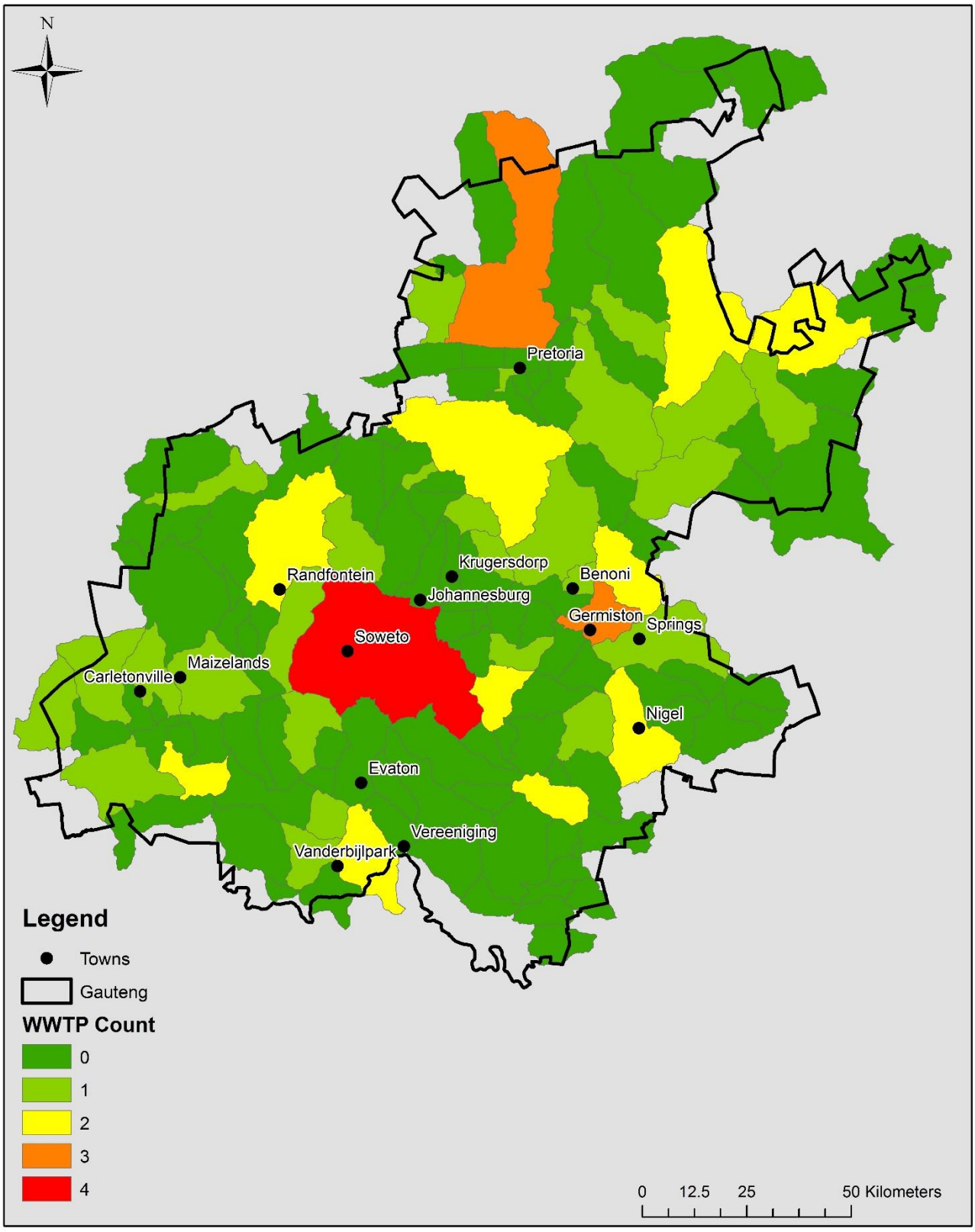

Figure 4.5: Number of waste water treatment plants per catchment in Gauteng.

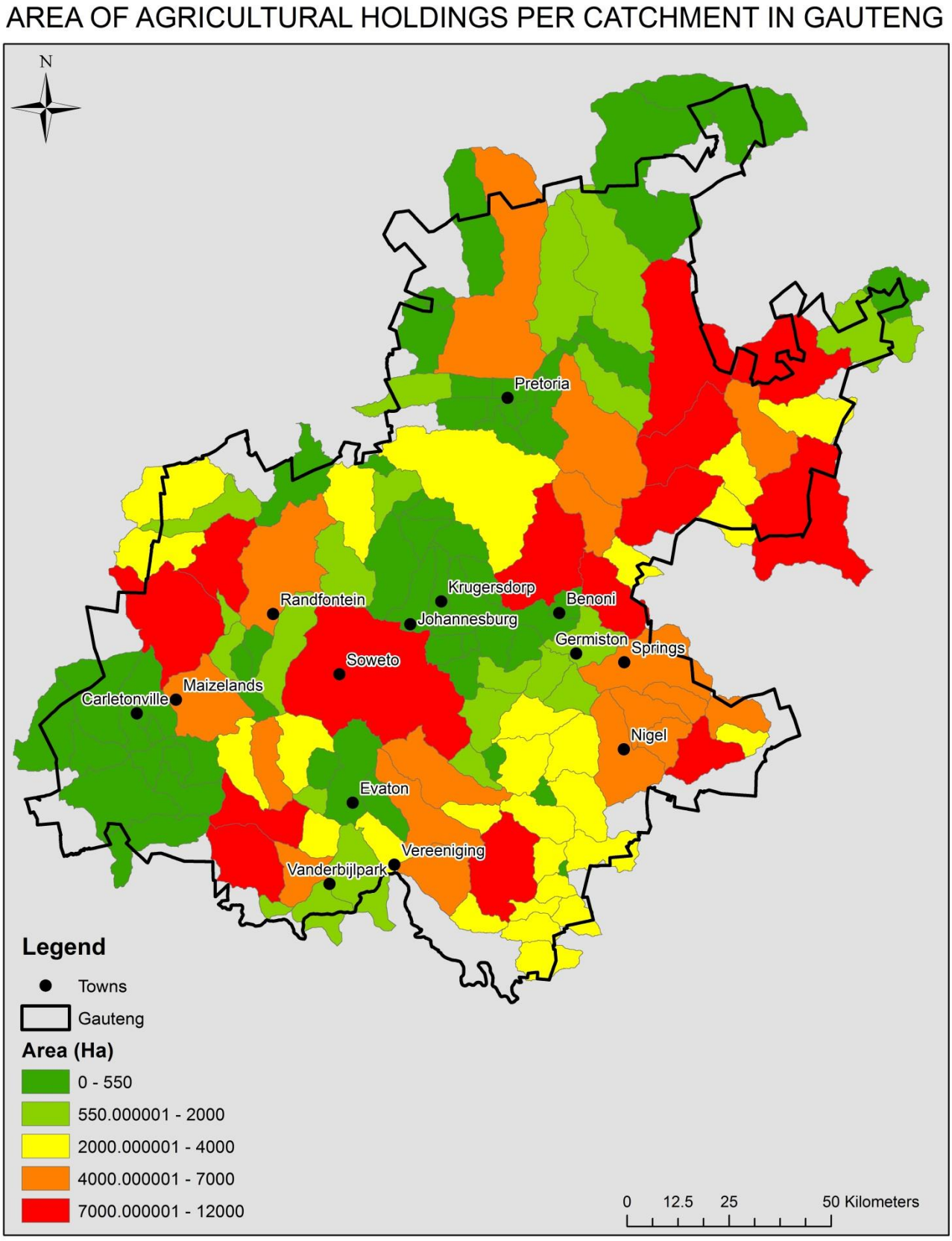

Figure 4.6: Area of agriculture per catchment in Gauteng

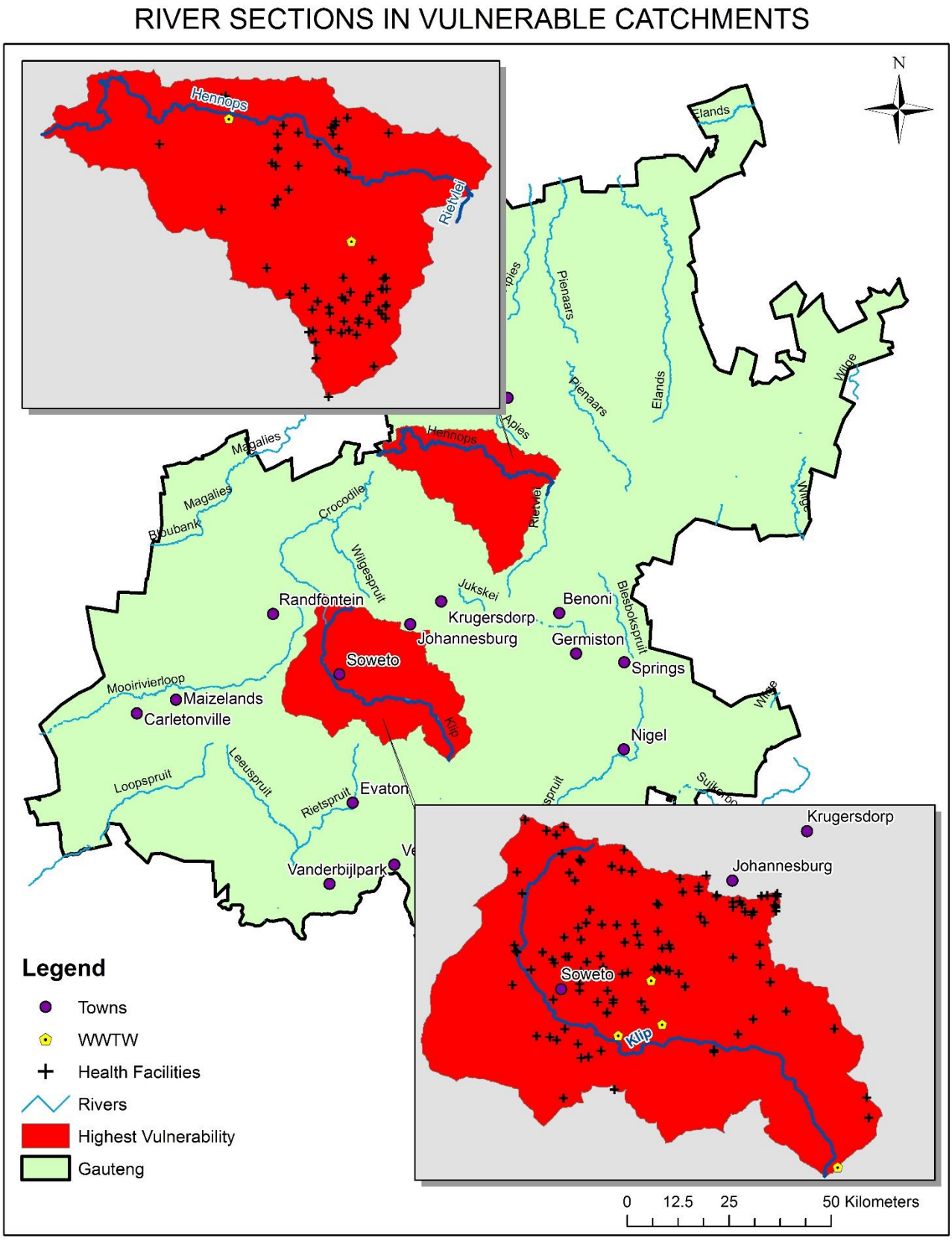

Figure 4.7: River sections in most vulnerable catchments for anthropogenic substances.

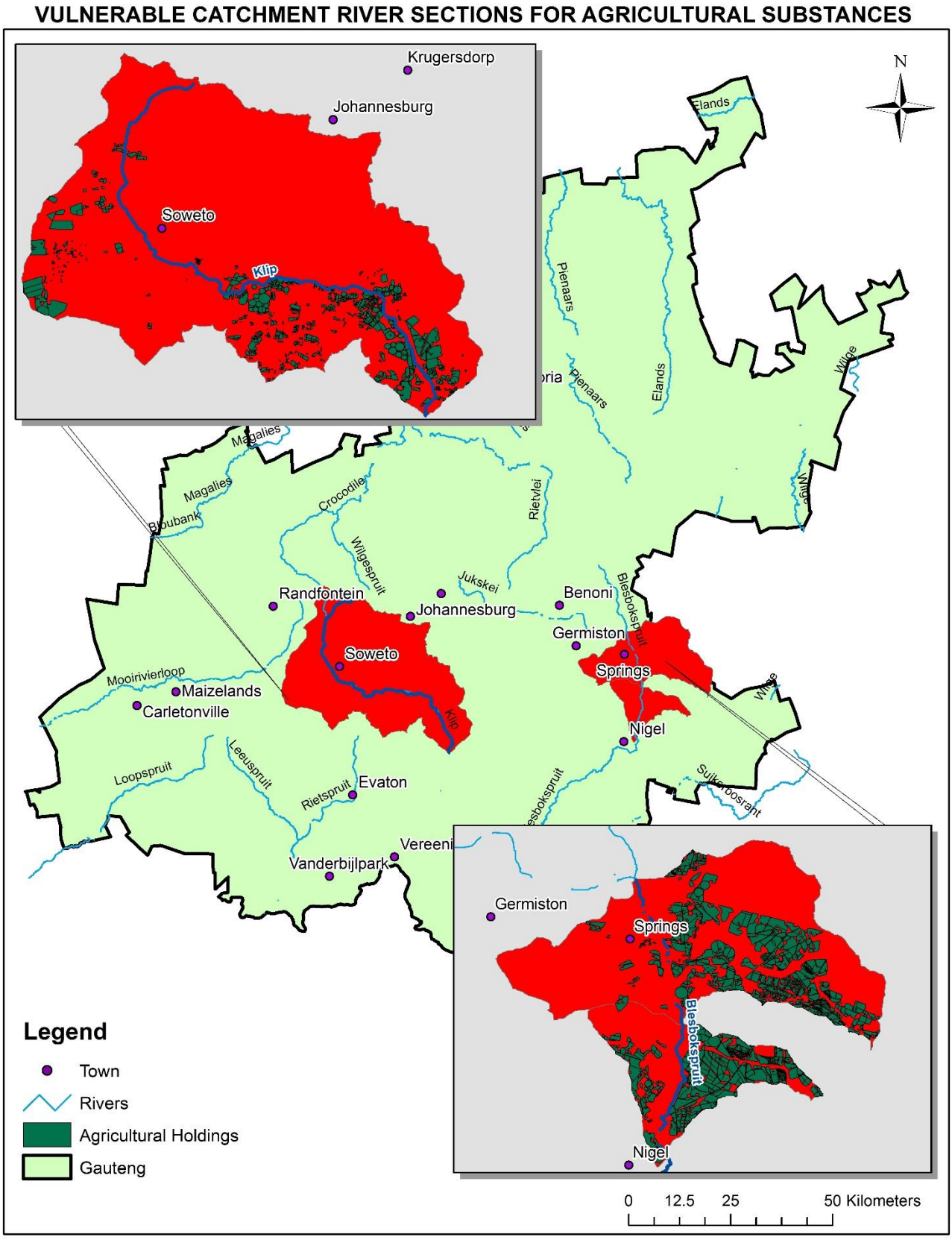

Figure 4.8: Vulnerable catchment river sections for agricultural substances

4.2 Discussion

4.2.1 Discussion of the results obtained by the prioritisation approach

Gauteng is a highly urbanized province and one of the most densely populated areas in South Africa. Considering this, the population density distribution per catchment in Gauteng will be higher in more urbanized areas, this is illustrated by the map in Figure 4.1 where catchments close to major towns have higher population density than those on the outskirts of Gauteng. The number of health facilities were proportional to the population density: the more populated the catchment the more health facilities were found. Furthermore, looking at the overall ecosystem status in Gauteng it can be noted that more than 80% of all the catchments within Gauteng have an endangered status which means that more than 60% of the ecosystem has been significantly degraded and has 60 or more threatened red data list plant species as well as irreversible loss of natural habitat. This status is based on criteria developed by the Department of Environmental Affairs in the National Environmental Management: Biodiversity Act number 10 of 2004 (DEA, 2004).

From Table 3 it appears that the hazard posed by pharmaceuticals varies between subdivisions, with analgesics and anti-inflammatory drugs generally posing a greater hazard than the antibiotics. This statement is supported by the fact that 9 of the 16 chemicals (56.25%) that fall into the category of analgesics and anti-inflammatory drugs had a final hazard ranking of under 50 (lower ranks indicating the higher priority and potential hazard). Based on the total number of compounds considered, this puts these chemicals well into the upper 50% of the total ECPs analysed in terms of the potential hazard that they pose. As a class of ECPs, analgesics and anti-inflammatory drugs definitely warrant further investigation and monitoring to determine occurrence data based on the findings of the hazard based analysis conducted in this study. Of the antibiotics, only one namely Roxithromycin of the 25 that were considered had a final hazard ranking that was lower than 50. This would initially lead to the conclusion that this group of chemicals pose relatively inconsequential harm to the environment, however the capacity of antibiotics to increase the drug resistance of naturally occurring and potentially disease causing microbes in the environment mean that this class of ECPs might well pose significant potential harm to both the environment and human health. It is worth noting that the lack of published log K_{ow} values could also contribute to the erroneous conclusion of inconsequential risk. The hazard that antibiotics pose might just be less direct as well as less obvious upon initial observation and analysis.

From an international perspective it would seem that the research focus surrounding the threat that antibiotics pose has shifted from looking for a direct threat for example toxicity to looking for secondary problems they could cause such as the increased resistance of pathogens in water resources (Kummerer 2009). This was likely the result of numerous studies reporting the small

potential for direct risk to human health that is posed by antibiotics in water bodies (Kummerer 2009).

Two of the seven beta-blockers that were analysed ranked in the upper 50% of the total chemicals. The remaining beta-blockers had ranks of 77 and higher which means that the hazards they pose would be largely insignificant when compared to the majority of the other analysed ECPs. This means that apart from Pindolol and Propranolol (ranked 39 and 38 respectively) beta-blockers are not expected to cause major ecological damage when compared to other ECP classes. The majority of the blood lipid lowering class of ECPs had final ranks between 40 and 60 with Pravastatin being the only exception as it had a rank of 94. Based on the rankings obtained by this class further investigation into the risk that they pose should be conducted, especially into their ability to bioaccumulate as it is their partition coefficients that result in their intermediate ranks.

Neuroactive compounds were an ECP class that was found to be quite hazardous based on the final hazard based ranking that these chemicals attained. 5 of the 8 neuroactive compounds that formed part of the analysis had final rankings of less than 50 and were thus ranked well within the upper 50% of the ECPs that were analysed. Only Carbamazepine, Temazepam and Venlafaxine ranked high enough to be considered non-threatening when compared to other ECPs based on this approach. Mention should be made of the capacity to elicit behavioural changes in organisms that came into contact with neuroactive compounds. This capacity did not form part of the analysis in the applied hazard based prioritisation and the full hazard posed by neuroactive compounds might have been underestimated, especially from an environmental and ecological point of view. This statement is further supported by the fact that the chemicals can have impacts on the behaviour of aquatic organisms even at low concentrations (Rivetti et al. 2015). For a better understanding into the hazard that is posed by neuroactive compounds when they enter the environment further investigations into their behavioural altering capabilities and the consequences thereof should be conducted. These results should then be incorporated into future hazard or risk based analysis of both ECPs and neuroactive compounds specifically.

From the class of cosmetics, Tonalid obtained a final ranking of 17 meaning it could pose harm to the environment and human health when compared to other ECPs. The other cosmetic that was analysed namely Galaxolide possessed moderate potential as a hazard to the environment and human health based on its final rank of 64. The moderate risk rankings that were obtained by cosmetics in this study correlates well with other studies that focus on cosmetics in water resources such as the study by Diamond et al. (2011). Within the review of emerging contaminants by Thomaidis et al. (2012) certain cosmetic products such as synthetic musks were mentioned due to their tendency to accumulate in sediment and certain organic matter, however the low toxicity scores for this class of chemicals makes them less harmful and thus of lower priority.

Similarly the hazard and final rank that was obtained for caffeine was also moderate. Caffeine's ability to cause harm could potentially be amplified by its widespread and frequent use. This could potentially also be the case with brominated flame retardants as these substances are used in numerous manufactured goods and their addition to many of these goods is required by law such as for example in building materials. Brominated flame retardants that were analysed obtained quite similar final rankings of between 32 and 57. This is the case largely due to the persistence and log K_{ow} scores of these compounds. As such this class of compounds warrants further investigation and should be considered as a priority ECPs due to the nearly unanimous elevated potential hazard that is posed by all of the chemicals in this class. Brominated flame retardants have in recent years become the focus of numerous scientific inquiries, especially relating to their potential to cause harm to the environment both internationally (Segev et al. 2009) and locally (Olukunle et al. 2012). The motivation behind the analysis of these compounds correlates with the reasons for the ranks they obtained in this study as their persistence and log K_{ow} scores have been stated as the reasons why they pose a potential threat to the environment and need to be further investigated (Alaee et al. 2003).

Pesticides were the largest class of ECPs that were analysed in terms of sheer numbers (36 of a total of 168). As previously mentioned, the risk posed by pesticides is likely to be elevated in South Africa due to the size of the agricultural sector and consequently the high usage of pesticides. This class of ECPs featured some of the chemicals that obtained the lowest total hazard ranking and has thus the highest potential to cause harm to the environment and human health. This class contained chemicals that obtained total hazard rankings from 1 through to 6 and thus contained the most hazardous chemicals of all the ECPs that were considered. 27 out of the 36 (75%) chemicals that constituted the ECP class of pesticides had final hazard rankings of 50 or lower, meaning that they are ranked well within the top 45% of ECPs with regards to their potential to cause harm. The high ranks that pesticides achieved are caused by their long half lives in conjunction with their high toxicity scores. These facts in conjunction with the aforementioned widespread and frequent use of pesticides in South Africa means that this class of ECP will likely pose the greatest hazard to the environment and human health in South Africa out of all the existing classes of ECPs.

Pesticides are included in numerous international studies on ECPs most notably from a study by Diamond et al. (2011). This study found that the pesticides are one of the ECP classes of the highest concern in a European setting and that this is largely caused by the physical and chemical characteristics of pesticides as well as their widespread use and the sheer number of them that are produced and used. The diversity of this compound class was also reported to be noteworthy. An article by Thomaidis et al. (2012) supported these findings in their review of emerging contaminants. Other studies that included pesticides in their studies and reported similar findings include: Haarhoff et al. (2015), Gavrilescu et al. (2014), Deblonde et al. (2011) and Bueno et al. (2012).

Due the lack of data in the categories of toxicity and aquatic half-life, not all the PAHs could be prioritised and compared with the other ECPs. The only PAHs for which a full set of the required data could be obtained and which could then be compared with the other classes of ECPs were acenaphthene, acenaphthylene, benzo[a]pyrene, fluoranthene, fluorene, naphthalene, phenanthrene and finally pyrene. All of these aforementioned chemicals were ranked within the upper 50% of ECPs in terms of their potential to be hazardous. Full data will be required before the other PAHs can be compared with other classes of ECPs as their toxicity equivalency scores only allows for them to be compared with each other and not with the rest of the ECPs. Based on the chemicals that could be analysed this class should definitely be considered a high priority class of ECPs. As such the continued monitoring and studies to make full data available are required in order to make more accurate assessments of the potential risk that they pose.

Disinfectants are a class of ECP that generally pose a great variety of hazard to both human health and the environment when compared with other ECPs. The hazard posed by this class can vary from substantial to essentially inconsequential. This is due to the fact that the chemicals that constitute this class of ECP had final hazard rankings that fell between 17 (nonylphenol) and 90 (dichloroacetic acid). As such there is no universal statement that can be made with regards to the hazard that is posed by this class in general and the chemicals of this class should be analysed individually to assess the potential harm that they could cause. It is worth noting that these compounds typically have relatively short half-lives in the environment and as such if they are not continuously released into the environment it is quite likely that they will not pose any harm. This is due to the fact that they will be rendered harmless and will be eliminated from the environment long before they will be able to cause any noticeable, detectable or significant damage. The toxicity of the breakdown products should be considered, however.

The ECP classes of contrast media and diuretics pose a relatively insignificant hazard to both human health and the environment based on the ranking of the chemicals that constitute these classes. The same can be said for antiretroviral and antivirals as these classes also feature chemicals that had rankings indicative of little or no harm. It is also worth noting that compared to the other ECP classes, relatively few international studies reported on these chemicals and the studies that did focussed on these chemicals individually and did not consider other ECP classes. None of the chemicals found in the aforementioned classes had a rank lower than 78. This means that these chemicals are well outside the upper 50% of the analysed ECPs in terms of their final hazard based rankings. Phthalates also did not have any chemicals with a final ranking of less than 50, as their lowest ranking is the chemical benzyl butyl phthalate which has a total final ranking of 53. It is worth noting that 3 of the remaining 6 phthalates that were analysed had total rankings between 60 and 70, which means that they can be considered borderline cases as they are located right on the edge of the upper 50% of the analysed ECPs. This means that further analysis of the

potential hazard posed by phthalates to both human and environmental health should be done if possible especially seeing as they are known carcinogens, although carcinogenicity was not part of the analysis process in this study. Carcinogenicity was not considered, as this study aimed to focus solely on the toxicity of the chemicals it analysed. It should also be mentioned that inclusion of carcinogenicity would have conflicted with the ranked list this study aimed to provide, as there are no varying levels of carcinogenicity that would allow for appropriate differentiation between substances.

The chemicals that constitute the “additional substances” class of ECPs were comprised of a wide array of chemicals with different functions and purposes. The chemicals cannot be divided into the other classes of ECPs and as such they were grouped together. They were indicated to be priority substances based on various literature reports and that is the primary reason behind their inclusion. As such these chemicals need to be analysed individually to determine the potential for harm that they each possess. Nine of the chemicals that were included in this class ranked within the top 50% of chemicals that were analysed. These chemicals were as follows: Cinchonidine (30), Cinchonine (24), Clotrimazole (22), Diphenylamine (49), Diuron (55), Ifosfamine (40), Nicotine (29), Tamoxifen (49) and Telmisartan (37). These chemicals will thus be treated as high priority ECPs based on the rankings they obtained and as such their continued study and monitoring is highly recommended.

Limitations to the hazard based analysis included the limitations of the PBT profiler programme that was used to predict the aquatic half-life of the ECPs. This programme is unable to predict these half-lives with an optimal amount of accuracy and as such it assigns pre-set values to the chemicals and the chemicals cannot obtain unique values as they would likely have. The programme assigns values that are akin to intervals. These intervals were at 8.7, 15, 30, 60, 75 and 180 days respectively and all the ECPs were assigned one of these values that was the most representative of what the actual degradation time would likely be based on its chemical structure. As these values were used to obtain ranks for the ECPs it created a scenario where numerous ECPs all achieved the same rank despite the possibility that they might not have an identical aquatic half-life when they occur in the environment. This can lead to the data obtained from the PBT profiler being unrepresentative of the actual *in situ* data and this can lead to an overall skewing of the data and it can make the process of accurate analysis and interpretation difficult. It should be noted, however, that these limitations are very unlikely to have a large impact on the overall ranking of the compounds. This is due to the fact that compounds that have a long half-life will still fall into the interval that is given the highest priority and chemicals that were divided into the 15 day interval for example will still remain in the environment for a much shorter amount of time than chemicals that fall within the 60 day interval. This holds true even if the actual chemicals were to have real half-lives of 13 days and 65 days respectively, for example.

The accuracy of the other data (partition coefficients and toxicity) can also be a concern due to the fact that different sources can report different results. As the values directly influence the final ranking that is obtained by a specific chemical, data inaccuracies can negatively influence the results of the hazard based analysis. Using acute toxicity data is also not optimal as the majority of these chemicals tend to occur in the environment at concentrations far below the levels required for acute toxicity to become a real concern. Many are also continuously being released into the environment and as such they gain pseudo-persistent effects. This means that chronic toxicity values and studies would be far more useful to assess the actual hazard that is posed by ECPs however there is a severe lack of chronic toxicity data available which makes its usage near impossible. It should also be mentioned that the toxicity data that is available has not been universally conducted on the same test species which makes a comparison of these results challenging. To avoid this problem, only oral toxicities to rats were utilised in this prioritisation study. Some of the ECPs (predominantly those of the PAHs) lacked the required toxicity data that was used to compare the other chemicals. Toxicity equivalency scores can be used to compare these chemicals amongst themselves but some of them could not be analysed during the main hazard based prioritisation approach due to their aforementioned lack of data. Many PAHs also lacked data in terms of their half-lives in water, as the PBT profiler was unable to analyse them and could thus not predict their half-lives. This made their analysis via the hazard based prioritisation approach completely impossible. It must be mentioned that as the hazard was calculated based on toxicity alone, other pertinent factors that can greatly increase the potential risk and hazard posed by a substance such as carcinogenicity and potential for endocrine disruption were not analysed. The omission of endocrine disruption as a factor was due mainly to a lack of data as the endocrine disrupting capability of all the chemicals analysed in this study was not known at the time when the study was conducted.

ECPs in South African Water Bodies

Table 4 provides an overview of studies that have found ECPs in South African water bodies. From the table it becomes apparent that although research on ECPs in South African water systems is lacking, some research on these chemicals has been conducted and they have been found to be present in numerous water sources, including drinking water in certain cases. From Table 4 it also becomes apparent that the majority of the research has been conducted relatively recently as historic water pollution monitoring in South Africa was centered on more conventional and well-known sources and forms of water pollution.

Table 4 also shows that pesticides are the group of compounds whose presence in water resources has been most frequently reported in a South African context. This conclusion was based on the extensive list of pesticides that formed part of the prioritisation process that were also found in

South African water resources by other studies. The large number of pesticides whose presence has been determined in South African water bodies is likely a direct result of the large size of the agricultural sector in South Africa. The size of this sector leads to the frequent widespread use of pesticides in order to assume high crop production. This increases the chances of these pesticides ending up in water resources thus it follows logically that such an extensive list of pesticides have been found to be present in South African water bodies. The high toxicity scores that are typical of this compound class also leads to numerous studies being conducted on them.

Antibiotics were the second most frequent class of compounds that has been found in South African water bodies. It can safely be assumed that the use and thus presence of antibiotics in South African water bodies will vary seasonally. Thus studies to locate antibiotics will likely be more successful in the colder winter months than in the warmer summer months, as the general population uses more antibiotics during the winter months due to colds and flu. The increased occurrence of antibiotics in the environment during the colder winter months has been reported in numerous studies, which includes a review study conducted by Kummerer (2009). Due to the fact that this project was a second tier prioritization approach it can be assumed that many compounds including antibiotics would have already been excluded within the initial prioritization approaches and as such all the substances found in South African water bodies could not be included or indicated in Table 4. This could potentially skew some of the deductions made from it with regards to the substances or ECPs in general, however the statements that were made are of value when it comes to the substances that were prioritized in this study in general. As such it is of value to note that although research surrounding ECPs are lacking the studies that were looking for ECPs in South African water bodies seemed to focus their attention on the correct substances as studies on pesticides in South African water bodies are numerous when compared with other compound classes.

Table 4 ECPs in South African Water Systems

Substance	**South African Reference(s)**	**Sampling medium**	**Rank obtained in this study**
Analgesics and anti-inflammatory drugs			
Acetaminophen	(Odendaal et al. 2015) (Agunbiade and Moodley 2014)	Drinking Water, Fresh Water Systems	88

	(Matongo et al. 2015)		
Benzocaine	(Odendaal et al. 2015)	Drinking Water	82
Diclofenac	(Agunbiade and Moodley 2014)	Fresh Water Systems	11
Ibuprofen	(Amdany, Chimuka and Cukrowska 2014) (Agunbiade and Moodley 2014) (Matongo et al. 2015)	Waste Water Treatment Plants, Fresh Water Systems	43
Ketoprofen	(Agunbiade and Moodley 2014)	Fresh Water Systems	34
Naproxen	(Amdany, Chimuka and Cukrowska 2014)	Waste Water Treatment Plants	23
Antibiotics			
Ciprofloxacin	(Agunbiade and Moodley 2014)	Fresh water Systems	96
Erythromycin	(Agunbiade and Moodley 2014) (Matongo et al. 2015)	Fresh Water Systems	79
Fluconazole	(Odendaal et al. 2015)	Drinking Water	70
Metronidazole	(Matongo et al. 2015)	Fresh Water Systems	95
Nalidixic acid	(Odendaal et al. 2015) (Agunbiade and Moodley 2014)	Drinking Water, Fresh Water Systems	72
Sulfamethazine	(Matongo et al. 2015)	Fresh Water Systems	109

Sulfisomidine	(Odendaal et al. 2015)	Drinking Water	87
Sulfamethoxazole	(Agunbiade and Moodley 2014) (Matongo et al. 2015)	Fresh Water Systems	98
Tetracyclin	(Agunbiade and Moodley 2014)	Fresh Water Systems	80
Trimethoprin	(Matongo et al. 2015)	Fresh Water Systems	95
Beta-blockers			
Atenolol	(Agunbiade and Moodley 2014)	Fresh Water Systems	91
Neuroactive compounds			
Carbamazepine	(Odendaal et al. 2015) (Burger and Nel 2008) (Matongo et al. 2015)	Drinking Water, Freshwater Systems	79
Temazepam	(Odendaal et al. 2015)	Drinking Water	74
Psycho-stimulants			
Caffeine	(Naude et al. 2015) (Agunbiade and Moodley 2014) (Matongo et al. 2015)	Freshwater Systems	62
Disinfectants			
Chloroform	(Amdany, Chimuka and Cukrowska 2014)	Waste Water Treatment Plants	60
Triclosan	(Amdany, Chimuka and Cukrowska 2014)	Waste Water Treatment Plants	61

Phthalates			
Bis[2-ethylhexyl] phthalate	(Fatoki et al. 2010)	Freshwater Systems (Venda)	65
Dibutyl phthalate	(Fatoki et al. 2010)	Freshwater Systems (Venda)	69
Diethyl phthalate	(Fatoki et al. 2010) (Naude et al. 2015)	Freshwater Systems	89
Dimethyl phthalate	(Fatoki et al. 2010) (Naude et al. 2015)	Freshwater Systems	93
Pesticides			
2,4-Dichlorophenoxyacetic acid [2,4-D]	(Burger and Nel 2008)	Freshwater Systems	33
Acetochlor	(Burger and Nel 2008)	Freshwater Systems	44
Aldicarb	(Burger and Nel 2008)	Freshwater Systems	25
Aldrin	(Burger and Nel 2008)	Freshwater Systems	2
Atrazine	(Odendaal et al. 2015) (Burger and Nel 2008)	Drinking Water, Freshwater Systems	21
Chlorpyrifos	(Burger and Nel 2008) Bennet et al. (2003) Dabrowski et al. (2003) London et al. (1995a) (Naude et al. 2015)	Freshwater Systems	6

Cypermethrin	(Burger and Nel 2008)	Freshwater Systems	5
DDD	Heath et al. (1999) Sereda and Meinardt (2003)	Freshwater Systems	5
DDE	Heath et al. (1999) Sereda and Meinardt (2003)	Freshwater Systems	19
DDT	Heath et al. (1999) Sereda and Meinardt (2003)	Freshwater Systems	4
Deltamethrin	(Burger and Nel 2008) Sereda et al. (2003) Dalvie et al. (2003) Dabowski et al. (2003)	Freshwater Systems	1
Dieldrin	Bouwman et al. (2003) Heath et al. (1999)	Freshwater Systems	11
Endosulphan	(Burger and Nel 2008) Bennet et al. (2003) Dalvie et al. (2003a) London et al. (2000)	Freshwater Systems	10
Enilconazole	(Odendaal et al. 2015)	Drinking Water	18
Heptachlor	Heath et al. (1999)	Freshwater Systems	8
Hexazinone	(Odendaal et al. 2015)	Drinking Water	77
Imidacloprid	(Odendaal et al. 2015)	Drinking Water	56

Lindane	(Burger and Nel 2008) Heath et al. (1999) Fatoki et al. (2010)	Freshwater Systems	14
Metazachlor	(Odendaal et al. 2015)	Drinking Water	57
Metolachlor	(Odendaal et al. 2015)	Drinking Water	68
Simazine	(Odendaal et al. 2015) (Burger and Nel 2008)	Drinking Water, Freshwater Systems	58
Tebuthiuron	(Odendaal et al. 2015)	Drinking Water	53
Vinclozolin	(Burger and Nel 2008)	Freshwater Systems	80
PAHs			
Acenaphthene	(Naude et al. 2015)	Freshwater Systems	54
Acenaphthylene	(Naude et al. 2015)	Freshwater Systems	58
Fluoranthene	(Naude et al. 2015)	Freshwater Systems	49
Fluorene	(Naude et al. 2015)	Freshwater Systems	57
Naphthalene	(Naude et al. 2015)	Freshwater Systems	29
Phenanthrene	(Naude et al. 2015)	Freshwater Systems	50
Pyrene	(Naude et al. 2015)	Freshwater Systems	55
Additional Substances			
Cinchonidine	(Odendaal et al. 2015)	Drinking Water	30

Cinchonine	(Odendaal et al. 2015)	Drinking Water	24
Diphenylamine	(Odendaal et al. 2015)	Drinking Water	49
Ephedrin	(Odendaal et al. 2015)	Drinking Water	60
Minoxidil	(Odendaal et al. 2015)	Drinking Water	73
Phenytoin	(Odendaal et al. 2015)	Drinking Water	66
Telmisartan	(Odendaal et al. 2015)	Drinking Water	37
Brominated Flame Retardants			
Decabromodiphenyl ether	(Naude et al. 2015)	Freshwater Systems	32
Hexabromocyclododecane	(Naude et al. 2015)	Freshwater Systems	57
Octabromodiphenyl ether	(Naude et al. 2015)	Freshwater Systems	48
Pentabromodiphenyl ether	(Naude et al. 2015)	Freshwater Systems	51

A study completed in 2012 (Olukunle et al. 2012) confirmed the presence of BFRs in South African water bodies by finding these ECPs in the sediment of the Jukskei River in Gauteng. The highest concentration of BFRs within the Jukskei River was found at Eastgate in Alexandra (Olukunle et al. 2012). The elevated reading in this region was attributed to the high amount of run-off within this area in conjunction with poorly managed refuse dumps associated with the informal settlements along the banks of the river (Olukunle et al. 2012). It is worth noting that all the BFR concentrations in the water samples were below the detection limits of the equipment utilised in this study. (Olukunle et al. 2012).

Table 5 contains information on the majority of the prioritised PAHs toxic equivalency scores. This was necessitated so that PAHs could be compared with each other in terms of toxicity. The PAHs that lack a toxic equivalency score all feature more than 2 fused rings and have a low partition coefficient which means that they are unlikely to remain in the water for extended periods of time.

This means that even if they are toxic it is unlikely that they will be found in the water and are thus more likely to accumulate in the sediment.

From the table it becomes apparent that benzo[a]pyrene is the most toxic PAH by a significant margin. However it should be noted that it is the carcinogenicity of PAHs that are more cause for concern than their toxicity. However as the prioritisation approach within this study relied upon toxicity it is of value to analyse the toxic equivalency of PAHs as they lack toxicity information. This enables the comparison of PAHs amongst each other, however they still cannot be compared to other substance in terms of toxicity. This does place limitations on the amount of comparison, ranking and prioritisation that is possible for the PAH class of compounds within the larger group of ECPs due to current toxicity data limitations.

Table 5 Toxic Equivalency of Prioritised PAHs

PAH	Toxic Equivalency	Reference	Number of Fused Rings
Benzo[a]pyrene	1	Nisbet Lagoy 1992	5
Acenaphthene	0.001	Nisbet Lagoy 1992	2
Acenaphthylene	0.001	Nisbet Lagoy 1992	2
Anthracene	0.01	Nisbet Lagoy 1992	3
Benz[a]anthracene	0.1	Nisbet Lagoy 1992	4
Benzo[b]fluoranthene	0.1	Nisbet Lagoy 1992	4
Benzo[c]fluorene			3
Benzo[ghi]perylene	0.01	Nisbet Lagoy 1992	6
Benzo[j]fluoranthene			4
Benzo[k]fluoranthene	0.1	Nisbet Lagoy 1992	4
Chrysene	0.01	Nisbet Lagoy	4

		1992	
Cyclopenta[cd]pyrene			4
Dibenz[a,h]anthracene	0.1	Nisbet Lagoy 1992	5
Dibenzo[a,e]pyrene			5
Dibenzo[a,h]pyrene			4
Dibenzo[a,i]pyrene			6
Dibenzo[a,l]pyrene			5
Fluoranthene	0.001	Nisbet Lagoy 1992	3
Fluorene	0.001	Nisbet Lagoy 1992	2
Indeno[1,2,3-cd]pyrene	0.1	Nisbet Lagoy 1992	5
Naphthalene	0.001	Nisbet Lagoy 1992	2
Phenanthrene	0.001	Nisbet Lagoy 1992	3
Pyrene	0.001	Nisbet Lagoy 1992	4

4.2.2 Discussion of the GIS results (potential sampling site selection)

The GIS results obtained from this study provides a clear indication of where the biggest potential problem areas with regards to ECPs (both anthropogenic and agricultural) lie within the province of Gauteng. ECPs are likely to be found within the indicated river sections and as such the GIS results obtained by this study can serve as a valuable starting point for any sampling driven research that might be conducted in the future. The municipal wards that fall within the indicated high risk areas are listed in Appendix 1. These wards can use the results of this study in attempts to mitigate or avoid potential harm to both ecosystems and the public that are exposed to these ECPs. Educating the public and garnering their support in attempts to minimise the amount of ECPs that end up in water resources could have positive effects in the future.

It is worth noting that the identified areas are by no means the only areas that are potentially exposed to ECPs. The identified areas are simply a representation of the areas that are most likely exposed to the highest amount of potential harm based on the parameters that were deemed important in this study (see GIS methodology). It is expected that other areas within the province are also at risk and that a thorough ECP sampling study will have to be conducted throughout Gauteng in order to more accurately determine which areas are most susceptible to harm and where mitigation efforts should be focused.

Chapter 5: Conclusion

ECPs in general pose a novel and potentially significant challenge to not only water resources but to other environmental compartments such as the air, soil, ecosystems and even human health as well (Gavrilescu et al. 2014). The development and mass production of novel chemicals has been reported to often exceed the ambit of existing safety monitoring and risk assessment methods. The unexpected negative effects of these chemicals can also show the inadequacy of current preventative and remediation technologies and can have consequences such as irreversible environmental damage (Gavrilescu et al. 2014).

Continued advances in technology coupled with increases in the global population are likely to cause a decrease in water availability, increased water reuse and importantly an increase in the concentrations of ECPs found in water bodies (Cizmas et al. 2015). This leads to the conclusion that further research regarding ECPs and the potential risk they pose to humans and the environment is imperative. Research into improving the technology of WWTPs and increasing their efficiency at removing all classes of ECPs from waste water is also required (Cizmas et al. 2015). Lastly standardizing risk assessment methodologies as well as monitoring methodologies will also make data more universally comparable and will greatly aid research as well as help to inform decision makers (Cizmas et al. 2015).

When assessing the threat that a specific ECP can pose after a sample has been obtained, certain considerations must be taken into account for an accurate assessment to be completed. These considerations are: contaminant concentration; contaminant characteristics and category or compound class under which the chemical falls (for example whether the chemical is an antibiotic or a pesticide); scale and level of contamination; the risk intensity generated for health or the environment; the opportunity for the threat assessment to be applied *in situ* or *ex situ*; the later use of the site; and available resources (Gavrilescu et al. 2014). A holistic, multi-disciplinary approach is recommended for to evaluate the potential threats posed by ECPs and also with respect to the removal of these pollutants from a specific environment (Gavrilescu et al. 2014).

Garica et al (2011) reported that both acute and chronic eco-toxicity tests surrounding ECPs needs improvement. The study further stated that more *in situ* data measurement of ECPs is also required in an attempt to create more accurate predicted environmental concentrations. Within this study it was found that 53.8% of the personal care products they examined (14 of a total of 26 chemicals) were found to be harmful to aquatic life based on ecotoxicity testing. This confirms that certain ECPs possess the potential to cause harm in the environment. Thus this study serves to illustrate the need for further testing and the refinement of methodologies for determining the risk and hazard posed by ECPs in the environment (García et al. 2011).

Species specific toxicity testing for ECPs are required as different species might react differently to the various chemicals (Cizmas et al. 2015). A certain species might be more sensitive to one chemical whilst a different species might be more sensitive to a different chemical. This clearly illustrates the need for increased species specific research (Cizmas et al. 2015). Additionally the effect that the mixing of compounds has on the toxicity must also be examined as these chemicals never occur alone in the environment and the combination of chemicals could potentially have worse effects than the effect of a single chemical (Cizmas et al. 2015). If this is the case, the risk these chemicals pose could potentially be underestimated. A study completed in 2015 (Herrmann et al. 2015) recommended that further research is required in terms of the risk posed by neurological drugs on the environment as there does not exist any conclusive evidence that neurological drugs are harmless once they enter natural water bodies.

From the results and discussion sections of this report, it becomes apparent that of the ECPs considered, pesticides pose the greatest potential hazard based on the approach used in this study. Pesticides are of particular concern in South Africa due to the frequent and widespread usage thereof owing to the scale of the agricultural sector within the country. Pesticides as a class of ECPs pose substantial potential harm to ecosystems and the environment throughout the country. Provinces that feature higher use of pesticides, such as the Free State (Dabrowski et al. 2014), will potentially be exposed to greater harm. As such it is imperative that future research regarding the potential detriment that pesticide usage can entail for both humans and the environment should be conducted in order to improve the understanding of the potential hazards and to gain insight into possible mitigation measures and solutions.

The creation of a universally accepted standard definition surrounding what exactly an ECP is and what compounds form part of this definition will greatly aid in the science of analysing and studying ECPs. Currently there is disparity regarding what exactly constitutes an ECP and initial analyte lists of studies concerning ECPs are largely determined by the specifics of the project or by the researchers. This creates problems in terms of the comparison and universal validity of these studies. This would mean that future studies would not need to rely on calculated data but could utilise actual measured data, which would reduce the limitations of the studies. Including full data on material safety datasheets would also prove useful to all the industries that work with these chemicals frequently.

The literature review with regards to occurrence information surrounding ECPs in South African water bodies has found that there is a lack of data available in this country. As such the creation of a database that contains pertinent information surrounding the occurrence, toxicity (especially chronic toxicity), persistence and bio-accumulative potential of all ECPs would provide an invaluable

resource from both a scientific and environmental point of view. This database should be in the public domain and scientists from across the country should be granted easy access it.

The hazard based prioritisation method used in this study is not without its shortcomings and limitations, however it provides useful insight into which ECPs may pose a greater threat than others. From this study, the scientific reasoning behind which ECPs warrant further investigation as a consequence of their final priority ranking can be acquired. As such this study can prove to be a valuable stepping stone for other studies wishing to investigate ECPs and the potential harm that these substances could entail for human health as well as for the environment.

References

Agunbiade, F.O. and Moodley, B., 2014. Pharmaceuticals as Emerging Organic Contaminants in Umgeni River Water System, Kwazulu-Natal, South Africa., *Environmental Monitoring and Assessment 186*(11), pp.7273–7291.

Alaee, M., Arias, P., Sjodin, A., Bergman, A., 2003. An Overview of Commercially Used Brominated Flame Retardants, Their Applications, Their Use Patterns in Different Countries/Regions and Possible Modes of Release. *Environment International*, 29(6), pp.683–689.

Ambrósio, A.F., Soares-Da-Silva, P., Carvalho, C.M., Carvalho, A.P., 2002. Mechanisms of Action of Carbamazepine and Its Derivatives, Oxcarbazepine, BIA 2-093, and BIA 2-024. *Neurochemical research*, 27(1-2), pp.121–130.

Amdany, R., Chimuka, L., Cukrowska, E., Kukucka P., Kohoutek J.,Vrana B., 2014. Investigating The Temporal Trends in PAH, PCB and OCP Concentrations in Hartbeespoort Dam, South Africa, Using Semipermeable Membrane Devices (SPMDs). *Water SA*, 40(3), pp.425–436.

Amdany, R., Chimuka, L., Cukrowska, E., 2014. Determination of Naproxen, Ibuprofen and Triclosan in Wastewater Using the Polar Organic Chemical Integrative Sampler (POCIS): A Laboratory Calibration and Field Application. *Water SA*, 40(3), pp.407–414.

Aneck-Hahn, N.H., Schulenburg, G.W., Bornman, M.S., Farais, P., De Jager, C., 2007. Impaired Semen Quality Associated With Environmental DDT Exposure in Young Men Living in a Malaria Area in the Limpopo Province, South Africa, *Journal of Andrology*, Vol. 28(3)

Aneck-Hahn, N.H., Bornman, M.S., De Jager, C., 2009. Oestrogenic Activity in Drinking Waters from a Rural Area in the Waterberg District, Limpopo Province, South Africa, *Water SA,* Vol. 35(3)

Ankley, A.,Gerald T., Bryan W. Brooks, D.B.H. and Sumpter, J.P., 2007. Repeating History: Pharmaceuticals in the Environment. *Environmental Science and Technology*, 41(24), pp.211–217.

Arnot, J. A. and Mackay, D., 2008. Policies for Chemical Hazard and Risk Priority Setting: Can Persistence, Bioaccumulation, Toxicity, and Quantity Information Be Combined? *Environmental Science and Technology*, 42(13), pp.4648–4654.

Barnhoorn, I.E.J., Bornman, M.S., van Dyk, J.C., G.B. and P.G., 2011. Edibility of Selected Freshwater Fish from the Rietvlei Dam, Report to the Water Research Commission

Benotti, M.J., Trenholm, R.A., Vanderord, B.J., Holady, J.C., Stanford, B.D., Snyder, S.A., 2009. Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water. *Environmental Science and Technology*, 43(3), pp.597–603.

Bergman, A., Heindel, J.J., Jobling, S., Kidd, K.A., Zoeller, R.T. 2013 State of Science Endocrine Disrupting Chemicals – 2012, *World Health Organization Press* pp. 1-289

Birnbaum, L.S. and Staskal, D.F., 2004. Brominated Flame Retardants: Cause for Concern? *Environmental Health Perspectives*, 112(1), pp.9–17.

Bornman, M.S., Barnoorn, I.E.J., Genthe, B., 2010. DDT for Malaria Control: Effects in Indicators and Health Risk, *Report to the Water Research Commission,* WRC Report No. 1674/1/09, ISBN 978-1-77005-915-3

Bornman, M.S., Barnoorn, I.E.J., Aneck-Hahn, N.H., 2009. A Pilot Study on the Occurrence of Endocrine Disruptive Chemicals in a DDT-Sprayed Area, *Report to the Water Research Commission,* WRC Report No KV 220/09, ISBN 978-1-77005-825-5

Boxall, A.B.A., Rudd, M.A., Brooks, B.W., Caldwell, D.J., Choi, K., Hickmann, S., Innes, E., Ostapyk, K., Staveley, J.P., Verslycke, T., Ankley, G.T., Beazley KF, Belanger S.E.,Berninger, J.P., Carriquiriborde, P., Coors, A., Deleo, P.C., Dyer, S.D., Ericson, J.F., Gagné, F., Giesy. J.P., Gouin, T., Hallstrom, L., Karlsson, M.V., Larsson, D.G., Lazorchak, J.M., Mastrocco, F., McLaughlin, A., McMaster, M.E., Meyerhoff, R.D., Moore, R., Parrott, J.L., Snape, J.R., Murray-Smith, R., Servos, M.R., Sibley, P.K., Straub, J.O., Szabo, N.D., Topp, E., Tetreault, G.R., Trudeau, V.L., van der Kraak, G. 2012. Review Pharmaceuticals and Personal Care Products in the Environment : What Are the Big Questions? *Environmental Health Perspectives*, 120(9), pp.1221–1229.

Boxall Alistair BA, Sinclair Chris J, Fenner Kathrin, Kolpin Dana, M.S.J., 2004. When Synthetics Chemicals Degrade in the Environment. *Environmental Science and Technology*, 38(19), p.368A–375A.

Brausch, J.M. and Rand, G.M., 2011. A Review of Personal Care Products in the Aquatic Environment: Environmental Concentrations and Toxicity. *Chemosphere*, 82(11), pp.1518–1532.

Bueno, M.J.M. Gomez MJ, Herrera S, Hernando MD, Agüera A, Fernández-Alba AR., 2012. Occurrence and Persistence of Organic Emerging Contaminants and Priority Pollutants in Five Sewage Treatment Plants of Spain : Two Years Pilot Survey Monitoring. *Environmental Pollution*, 164, pp.267–273.

Burger, A.E.C., Nel, A., 2008. Scoping Study to Determine the Potential Impact of Agricultural Chemical Substances (Pesticides) with Endocrine Disruptor Properties on the Water Resources of South Africa, *Report to the Water Research Commission,* Report Number 1774/1/08.

Burger, A.E.C., Nel, A., 2005. Scoping Study to Determine the Potential Impact of Agricultural Chemical Substances (Pesticides) with Endocrine Disruptor Properties on the Water Resources of South Africa, *Environmental Chemistry Letters* 14(1), pp27-49

Cajaraville, M.P. Cancio I, Ibabe A, Orbea A. 2003. Peroxisome Proliferation as a Biomarker in Environmental Pollution Assessment. *Microscopy Research and Technique*, 61(2), pp.191–202.

Cheek, A.O., Vonier, P.M, Oberdorster, E., Burow, B.C., McLahlan, J.A., 1998. Environmental Signalling: A Biological Context for Endocrine Disruption. *Environmental Health Perspectives*, 106(SUPPL. 1), pp.5–10.

Cizmas, L., Sharma, V.K., Gray, C.M., McDonald, T.J., 2015. Pharmaceuticals and Personal Care Products in Waters : Occurrence, Toxicity, and Risk. *Environmental Chemistry Letters*, 13(4), pp.381–394.

Costanzo, S.D. Watkinsona, A.J. Murbyb, E.J. Kolpinc, D.W. Sandstromd M.W., 2007. Is There a Risk Associated with the Insect Repellent DEET (N,N-Diethyl-M-Toluamide) Commonly Found in Aquatic Environments? *Science of The Total Environment*, 384(1-3), pp.214–220.

Crane, M., Watts, C. and Boucard, T., 2006. Chronic Aquatic Environmental Risks from Exposure to Human Pharmaceuticals. *Science of the Total Environment*, 367(1), pp.23–41.

Crook, J., 2010. NWRI White Paper Regulatory Aspects of Direct Potable Reuse in California. National Water Research Institute (U.S.), p.38.

Dabrowski, J.M., Peall, S.K.C., Reinecke, A.J., Liess, M., Schultz, R., 2002. Runoff-Related Pesticide Input into the Lourens River, South Africa: Basic Data for Exposure Assessment and Risk Mitigation at the Catchment Scale. *Water, Air, and Soil Pollution*, 135(1-4), pp.265–283.

Dabrowski, J.M., Shadung, J.M. and Wepener, V., 2014. Prioritizing Agricultural Pesticides used in South Africa Based on Their Environmental Mobility and Potential Human Health Effects. *Environment International*, 62, pp.31–40.

Dalvie, M., Africa, A., London, L., 2009. Change in the Quantity and Acute Toxicity of Pesticides Sold in South African Crop Sectors, 1994-1999. *Environment International*, 35(4), pp.683–687.

Dalvie, M., Cairncross, E., Solomon, A., London, L. 2003. Contamination of rural surface and ground water by endosulfan in farming areas of the Western Cape, South Africa. *Environmental Health,* 2(1).

Daughton, C.G. and Ternes, T. A., 1999. Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? *Environmental Health Perspectives*, 107(SUPPL. 6), pp.907–938.

De Jager, C., Aneck-Hahn, N.H., Bornman, M.S., Farias, P., Leter, G., Eleuteri, P., Rescia, M. Spanò, M., 2009. Sperm chromatin integrity in DDT exposed young men living in a malaria area in the Limpopo Province, South Africa*. Human Reproduction, 24(10):2429-38*

Deblonde, T., Cossu-Leguille, C. and Hartemann, P., 2011. Emerging Pollutants in Wastewater: A Review of the Literature. *International Journal of Hygiene and Environmental Health*, 214(6), pp.442–448.

Delgado, L.F. 2012. The Removal of Endocrine Disrupting Compounds, Pharmaceutically Activated Compounds and Cyanobacterial Toxins during Drinking Water Preparation Using Activated Carbon-A Review. *Science of the Total Environment*, 435-436, pp.509–525.

Department of Environmental Affairs. 2004. National Environmental Management: Biodiversity Act *Government Gazette,* Act no10 of 2004

Department of Water Affairs. 1998. National Water Act. *Government Gazette,* Act no36 of 1998

Diamond, J.M., Latimer HA, Munkittrick KR, Thornton KW, Bartell SM, Kidd KA. 2011. Prioritizing Contaminants of Emerging Concern for Ecological Screening Assessments. *Environmental Toxicology and Chemistry*, 30(11), pp.2385–94.

Dobbins, L. Usenko S, Brain RA, Brooks BW. 2009. Pharmaceuticals and Personal Care Products in the Environment Probabilistic Ecological Hazard Assessment of Parabens Using Daphnia Magna and Pimephales Promelas. *Environmental Toxicology and Chemistry*, 28(12), pp.2744–2753.

Doggrell, S. A, 1990. The Membrane Stabilizing and Beta 1-Adrenoceptor Blocking Activity Of (+)-And (-)-Propranolol on the Rat Left Atria. *General Pharmacology*, 21(5), pp.677–680.

Dzialowski, E.M., Turner, P.K., Brooks, B.W., 2006. Physiological and Reproductive Effects of Beta Adrenergic Receptor Antagonists in Daphnia magna. *Archives of Environmental Contamination and Toxicology*, 50(4), pp.503–510.

Farkas, Michael H, Berry, James O, Aga, D.S., 2007. Chlortetracycline Detoxification in Maize via Induction of Glutathione S -Transferases after Antibiotic Exposure. *Journal of Mass Spectrometry*, 41(4), pp.1450–1456.

Farré, M., 2008. Fate and Toxicity of Emerging Pollutants, Their Metabolites and Transformation Products in the Aquatic Environment. *TrAC - Trends in Analytical Chemistry*, 27(11), pp.991–1007.

Fatoki, O.S., Bornman M.S., Ravandhalala, L.,Chimuka, L., Genthe, B., Adeniyi, A., 2010. Phthalate Ester Plasticizers in Freshwater Systems of Venda, South Africa and Potential Health Effects. *Water SA*, 36(1), pp.117–126.

Fent, K., 2010. A Tentative Environmental Risk Assessment of the UV-Filters 3-(4-Methylbenzylidene-Camphor), 2-Ethyl-Hexyl-4-Trimethoxycinnamate, Benzophenone-3, Benzophenone-4 and 3-Benzylidene Camphor. *Marine Environmental Research*, 69, pp.S4–S6.

Fent, K., Weston, A. A. and Caminada, D., 2006. Ecotoxicology of human pharmaceuticals. *Aquatic Toxicology*, 76(2), pp.122–159.

Ferguson, J. Baxter, A., Young, P., Kennedy, G., Elliott, C., Weigel,S., Gatermann, R., Ashwin, H., Stead, S., Sharman, M., 2005. Detection of Chloramphenicol and Chloramphenicol Glucuronide Residues in Poultry Muscle, Honey, Prawn and Milk Using a Surface Plasmon Resonance Biosensor and Qflex Kit Chloramphenicol. *Analytica Chimica Acta*, 529(1-2 SPEC. ISS.), pp.109–113.

Fong, P.P. and Ford, A.T., 2013. The Biological Effects of Antidepressants on the Molluscs and Crustaceans: A Review. *Aquatic Toxicology*, 151, pp.4–13.

García, S., García-Encina, P. and Irusta-Mata, R., 2011. Environmental Risk Assessment (ERA) of Pharmaceuticals and Personal Care Products (PPCPs) Using Ecotoxicity Tests. *Ecotoxicology* 23(8), pp.1–8.

García-Galán, M.J., Silvia Díaz-Cruz, M. and Barceló, D., 2008. Identification and Determination of Metabolites and Degradation Products of Sulfonamide Antibiotics. *TrAC - Trends in Analytical Chemistry*, 27(11), pp.1008–1022.

Gavrilescu, M. Demnerová, K., Aamand, J., Agathos, S., Fava, F., 2014. Emerging Pollutants in the Environment: Present And Future Challenges in Biomonitoring, Ecological Risks and Bioremediation. *New Biotechnology*, 32(1), pp.147–156.

Gunnarsson, B., 2006. Environmental Risk Assessment and Environmental Classification of Drugs. Chapter 8. *Environment and Pharmaceuticals*. Available at: http://www.janusinfo.se/Global/Miljo_och_lakemedel/lakemed_miljo_eng2007.pdf.

Haarhoff, J. Coetzee, L.Z Ceronio, A D Msagati, T.A.M Mamba, B.B., Gumbi, N. Nkambule, T.W.E., 2015. Status Quo Report on the State of Knowledge on Persistent Organic Pollutants and Contaminants of Emerging Concern, Report to the Water Research Commission

Hansen, L.K. Frost, C.P., Larson, J.H., Metcalfe, C.D., 2008. Poor Elemental Food Quality Reduces the Toxicity of Fluoxetine on Daphnia Magna. *Aquatic Toxicology*, 86(1), pp.99–103.

Hayes, T.B., Case, P., Chui, S., Chung, D., Haefele, C., Haston, K., Lee, M., Mai, V.P., Marjuoa, Y., Parker, J., Tsui, M. 2006. Pesticide mixtures, Endocrine disruption, and amphibian declines: Are we underestimating the impact? *Environmental Health Perspcectives,* (114) pp. 40-50.

Heath, R.G.M., Claassen, M. 1999. An overview of the pesticide and metal levels present in populations of the larger indigenous fish species of selected South African rivers. *Report to the Water Research Commission*, Report Number 428/1/99.

Herrmann, M. Olsson, O., Fiehn, R.,Herrel, M.,Kummerer, K., 2015. The Significance of Different Health Institutions and their Respective Contributions of Active Pharmaceutical Ingredients to Wastewater. *Environment International*, 85, pp.61–76.

Hu, Z., 2013. Adsorption Removal of Tetracycline from Aqueous Solution by Anaerobic Granular Sludge: Equilibrium and Kinetic Studies. , *Water Pollution Research,* 67(7): 1490-1496

Huntington, T.G., 2006. Evidence for Intensification of the Global Water Cycle: Review and Synthesis. *Journal of Hydrology*, 319(1-4), pp.83–95.

Ishibashi, H., Matsumura, N., Hirano, M., Matsuoka, M., Shiratsuchi, H., Ishibashi,Y., Takao, Y.,Arizono, K, 2004. Effects of Triclosan on the Early Life Stages and Reproduction of Medaka Oryzias Latipes and Induction of Hepatic Vitellogenin. *Aquatic Toxicology*, 67(2), pp.167–179

Isidori, M. , Lavorgna M , Nardelli A , Parrella A , Previtera L , Rubino M, 2005. Ecotoxicity of Naproxen and its Phototransformation Products. *Science of the Total Environment*, 348(1-3), pp.93–101.

Jackson, Robert B, Carpenter, Stephen R, Dahm, Clifford N, McKnight, Diane M, Naiman, Robert J, Postel, Sandra L, Running, S.W., 2005. Water in a Changing World. *Ecological Applications*, 86(4), pp.249–250.

Joint Research Centre, 2003. Technical Guidance Document on Risk Assessment. *European Chemicals Bureau*, Part II, pp.7–179.

Jorgensen, S.E. and Halling-Sorensen, B., 2000. Editorial: Drugs in the Environment. *Chemosphere*, 40(7), pp.691–699.

Kavlock, R.J. Daston, G.P., DeRosa, C., Fenner-Crisp, P., Gray, L.E., Kaattari, S., Lucier, G., Luster, M., Mac, M.J., Maczka, C., Miller, R., Moore, J., Rolland, R., Scott, G., Sheehan, D.M., Sinks, T., Tilson, H.A., 1996. Research Needs for the Risk Assessment of Health and Environmental Effects of Endocrine Disruptors: A Report of the U.S. EPA-Sponsored Workshop. *Environmental Health Perspectives*, 104 Suppl , pp.715–740.

Keller, B.J., Yamanaka, H., Thurman, R.G., 1992. Inhibition of Mitochondrial Respiration and Oxygen-Dependent Hepatotoxicity by Six Structurally Dissimilar Peroxisomal Proliferating Agents. *Toxicology*, 71(1-2), pp.49–61.

Kümmerer, K., 2009. Antibiotics in the aquatic environment - A review - Part I. *Chemosphere*, 75(4), pp.417–434.

Kümmerer, K. Erbe, T., Gartiser, S., Brinker, L., 1998. AOX-Emissions from Hospitals into Municipal Waste Water. *Chemosphere*, 36(11), pp.2437–2445.

Larsson, J.D.G., 2014. Antibiotics in the Environment. *Upsala Journal of Medical Sciences*, 119(15 SPEC. ISS.), pp.108–112.

Laufs, U. and Liao, J.K., 1998. Post-Transcriptional Regulation of Endothelial Nitric Oxide Synthase mRNA Stability by Rho Gtpase. *The Journal of Biological Chemistry*, 273(37), pp.24266–24271.

Liang, D.W., Zhang, T., Fang, H., He., J., 2008. Phthalates Biodegradation in the Environment. *Applied Microbiology and Biotechnology*, 80(2), pp.183–198.

Liu, Q., Zhou, Q., Jiang, G., 2014. Nanomaterials for Analysis and Monitoring of Emerging Chemical Pollutants. *TrAC - Trends in Analytical Chemistry*, 58, pp.10–22.

London, Dalvie, M.A., Nowicki, A., Cairncross, E. 2000. Approaches for regulating water in South Africa for the presence of pesticides. *Water SA,* 31 (1), pp.53-60.

Lopez, J., 2010. Endocrine-disrupting Chemical Pollution: Why the EPA Should Regulate These Chemicals under the Clean Water Act., *Sustainable Development Law and Policy*, 10(3), pp.19–22.

Maliszewska-Kordybach, B., 1999. Sources, Concentrations, Fate and Effects of Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment. Part A: PAHs in Air. *Polish Journal of Environmental Studies*, 8(3), pp.131–136.

Manzetti, S. and Ghisi, R., 2014. The Environmental Release and Fate of Antibiotics. *Marine Pollution Bulletin*, 79(1-2), pp.7–15.

Matongo, S., Birungi, G., Moodley, B., 2015. Occurrence of Selected Pharmaceuticals in Water and Sediment of Umgeni River, KwaZulu-Natal, South Africa. *Environmental Science and Pollution Research Internationa*l, pp.10298–10308.

Matsumoto, M., Hirata-Koizumi, M., Ema, M., 2008. Potential Adverse Effects of Phthalic Acid Esters on Human Health: A Review of Recent Studies on Reproduction. *Regulatory Toxicology and Pharmacology : RTP*, 50(1), pp.37–49.

McAvoy, D.C. Schatowitz, B., Jacob, M., Hauk, A., Eckhoff, W., 2002. Measurement of Triclosan in Wastewater Treatment Systems. *Environmental Toxicology and Chemistry / SETAC*, 21(7), pp.1323–1329.

Meteyer, C.U., Rideout,B.A., Gilbert, M., Shivaprasad, H. L., Oaks, J.L., 2005. Pathology and Proposed Pathophysiology of Diclofenac Poisoning in Free-Living and Experimentally Exposed Oriental White-Backed Vultures (Gyps bengalensis). *Journal of Wildlife Diseases*, 41(4), pp.707–716.

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

Mofenson, L.M., 2010. Prevention in Neglected Subpopulations: Prevention of Mother-To-Child Transmission of HIV Infection. *Clinical infectious diseases : an official publication of the Infectious Diseases Society of America*, 50 Suppl 3(Suppl 3), pp.S130–S148.

Muñoz, I. López-Doval, J.C., Ricart, M., Villagrasa, M., Brix, R., Geiszinger, A., Ginebreda, A., Guasch, H., de Alda, M.J., Romaní, A.M., Sabater, S., Barceló, D., 2009. Bridging Levels of Pharmaceuticals in River Water with Biological Community Structure in the Llobregat River Basin (Northeast Spain). *Environmental Toxicology and Chemistry*, 28(12), pp.2706–2714.

Naude, Y., Gorst-Allman, P. and Rohwer, E., 2015. A Cheap and Simple Passive Sampler Using Silicone Rubber for the Analysis of Surface Water By Gas Chromatography-Time Of Flight Mass Spectrometry. *Water SA*, 41(2, SI), pp.182–188.

Ncube, E., Voyi, K., Preez, H., 2012. Implementing a Protocol for Selection and Prioritisation of Organic Contaminants in the Drinking Water Value Chain : Case study of Rand Water, South Africa. , 38(4), pp.487–504.

Ncube, E., 2009. Selection and Prioritization of Organic Contaminants for Monitoring in the Drinking Water Value Chain, Thesis, University of Pretoria, Chapter 3

Nieuwenhuijsen, M.J., Toledano, M., Eaton, B., Naomi, E., Fawell, J., Elliott, P., 2000. Chlorination Disinfection Byproducts in Water and Their Association with Adverse Reproductive Outcomes : A Review. *Occupational and Environmental Medicine*, 57, pp.73–85.

Nisbet, I.C., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology,* 16, pp.290–300.

Odendaal, C. Seaman, M.T., Kemp, G., Patterton, H.E., Patterton, H.G., 2015. An LC-MS / MS Based Survey of Contaminants of Emerging Concern in Drinking Water in South Africa. *South African Journal of Science*, 111(9/10), pp.1–6.

Oki, Taikan, Kanae, S., 2006. Global Hydrological Cycles and World Water Resources. *SCIENCE*, 313, pp.1068–1072.

Olukunle, O.I., Okonkwo, O.J., Kefeni, K.K. and Lupankwa, M., 2012. Determination of Brominated Flame Retardants in Jukskei River Catchment Area in Gauteng, South Africa. *Water Science and Technology*, 65(4), pp.743–750.

Orvos, D.R., Versteeg, J.D., Inauen, J., 2002. Aquatic toxicity of triclosan. *Environmental Toxicology and Chemistry,* 21(7), pp.1338–1349.

Osunmakinde, C.S., Thsabalala, O., Dube, S., Nindi, M.M., 2013. Verification and Validation of Analytical Methods for Testing the Levels of PPHCPs (Pharmaceutical and Personal Health Care Products) in Treated Drinking Water and Sewage*, Report to the Water Resource Commission,* Report Number 2094/1/13

Parrott, J.L. and Blunt, B.R., 2005. Life-Cycle Exposure of Fathead Minnows (Pimephales Promelas) to an Ethinylestradiol Concentration below 1 Ng/L Reduces Egg Fertilization Success and Demasculinizes Males. *Environmental Toxicology*, 20(2), pp.131–141.

Patterton, H.G., 2013. Scoping Study and Research Strategy Development on Currently Known and Emerging Contaminants Influencing Drinking Water Quality, *Report to the Water Resource Commission,* Report Number 2093/1/13

Peck, A.M., 2006. Analytical Methods for the Determination of Persistent Ingredients of Personal Care Products in Environmental Matrices. *Analytical and Bioanalytical Chemistry*, 386(4), pp.907–939.

Peng, X. Wang C, Zhang K, Wang Z, Huang Q, Yu Y, Ou W. 2014. Profile and Behaviour of Antiviral Drugs in Aquatic Environments of the Pearl River Delta, China. *The Science of the Total Environment*, 466-467, pp.755–761.

Pérez, S. and Barceló, D., 2007a. Application of Advanced Ms Techniques to Analysis and Identification of Human and Microbial Metabolites of Pharmaceuticals in the Aquatic Environment. *TrAC - Trends in Analytical Chemistry*, 26(6), pp.494–514.

Pérez, S. and Barceló, D., 2007b. Fate and Occurrence of X-Ray Contrast Media in the Environment. *Analytical and Bioanalytical Chemistry*, 387(4), pp.1235–1246.

Petersen, 2007. DG Environment Study on Enhancing the Endocrine Disrupter Priority List with a Focus on Low Production Volume Chemicals, *Water and Environment, Report to the European Commission*

Qu Bin, Li Qiu-Tian, Wong Kim Ping, Tan Theresa M. C., H.B., 2001. Mechanism of Clofibrate Hepatotoxicity: Mitochondrial Damage and Oxidative Stress in Hepatocytes., 31(5), pp.659–669.

Renew, J.E. and Huang, C.H., 2004. Simultaneous Determination of Fluoroquinolone, Sulfonamide and Trimethoprim Antibiotics in Wastewater Using Tandem Solid Phase Extraction And Liquid Chromatography-Electrospray Mass Spectrometry. *Journal of Chromatography A*, 1042(1-2), pp.113–121.

Rivetti, C., Campos, B. and Barata, C., 2015. Low Environmental Levels of Neuro-Active Pharmaceuticals Alter Phototactic Behaviour and Reproduction in Daphnia Magna. *Aquatic Toxicology*, 170, pp 289-296

Rogers, C.J., Twyman, R.E. and Macdonald, R.L., 1994. Benzodiazepine and B-Carboline Regulation of Single Receptor Channels of Mouse Spinal Neurones in Culture. *The Journal of Physiology*, pp.69–82.

Sanderson, H., Johnson, D.J., Reitsma, T., Brain, R.A., Wilson, C.J., Solomon, K.R., 2004. Ranking and Prioritization of Environmental Risks of Pharmaceuticals in Surface Waters. *Regulatory Toxicology and Pharmacology*, 39(2), pp.158–183.

Sarmah, A.K., Meyer, M.T. and Boxall, A.B. a, 2006. A Global Perspective on the Use, Sales, Exposure Pathways, Occurrence, Fate and Effects of Veterinary Antibiotics (Vas) in the Environment. *Chemosphere*, 65(5), pp.725–759.

Schaider, L. A. Rudel, R.A., Ackerman, J.M., Dunagan, S.C., Brody, J.G., 2014. Pharmaceuticals, Perfluorosurfactants, and Other Organic Wastewater Compounds in Public Drinking Water Wells in a Shallow Sand And Gravel Aquifer. *Science of the Total Environment*, 468-469, pp.384–393.

Scheytt, T., Mersmann, P., Lindstadt, R., Heberer, T. 2005. Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. *Chemosphere,* 60 (2), pp. 245-253.

Schramm, K.W., Kaune, A., Beck, B., Thumm, W., Becheti, A., Kettrup, A., Nickolova, P., 1996. Acute Toxicities of Five Nitromusk Compounds in Daphnia, Algae and Photoluminescent Bacteria. *Water Research*, 30(10), pp.2247–2250.

Schulz, R., 2001. Comparison of Spray Drift- and Runoff-Related Input of Azinphos-Methyl and Endosulfan from Fruit Orchards into the Lourens River, South Africa. *Chemosphere*, 45(4-5), pp.543–551.

Schwarzbauer, J. Heim, S., Brinker, S., Littke, R., 2002. Occurrence and Alteration of Organic Contaminants in Seepage and Leakage Water from a Waste Deposit Landfill. *Water Research*, 36, pp.2275–2287.

Schwarzenbach, R.P., Egli, T., Hofstetter, T.B., von Gunten, U., Wehrli, B., 2010. Global Water Pollution and Human Health. *Annual Review of Environment and Resources*, 35(1), pp.109–136.

Segev, O., Kushmaro, A. and Brenner, A., 2009. Environmental Impact of Flame Retardants (Persistence and Biodegradability). *International Journal of Environmental Research and Public Health*, 6(2), pp.478–491.

Sereda, B.L. and Meinhardt, H.R. 2003. Insecticide Contamination of the Water Environment in Malaria Endemic Areas of Kwazulu-Natal (South Africa). Report to the Water Research Commission. Report number 1119/1/03.

Sharpless, C.M. and Linden, K.G., 2003. Experimental and Model Comparisons of Low- and Medium-Pressure Hg Lamps for the Direct and H2O2 Assisted UV Photodegradation of N-Nitrosodimethylamine in Simulated Drinking Water. *Environmental Science and Technology*, 37(9), pp.1933–1940.

Sjödin, A., Patterson, D.G. and Bergman, A., 2003. A Review on Human Exposure to Brominated Flame Retardants--Particularly Polybrominated Diphenyl Ethers. *Environment international*, 29(6), pp.829–839.

Snyder, S. A., Vandervoort. B., Drewes, J., Dickenson, E., Snyder, E.M., Bruce, G.M., Pleus, R.C., 2009. State of Knowledge of Endocrine Disruptors and Pharmaceuticals in Drinking Water, *Water Intellegence Online,* Available at: http://stats.lib.pdx.edu/proxy.php?url=http://search.proquest.com/docview/21338004?accountid=13265\nhttp://wq5rp2ll8a.search.serialssolutions.com/?ctx_ver=Z39.88-2004andctx_enc=info:ofi/enc:UTF-8andrfr_id=info:sid/ProQ:pollutionandrft_val_fmt=info:ofi/fmt:kev:m.

Sonnenschein, C. and Soto, A.M., 1998. An Updated Review of Environmental Estrogen and Androgen Mimics and Antagonists. *Journal of Steroid Biochemistry and Molecular Biology*, 65(1-6), pp.143–150.

Staels, B., Dallongeville, J., Auwerx, J., Schoonjans, K., Leitersdorf, E., Fruchart, J.C. 1998. Mechanism of Action of Fibrates on Lipid and Lipoprotein Metabolism, Cardiovascular Drugs, (98) pp. 2088-2093

Stales, C. A Peterson, D.R., Parkerton, T.F., Adams, W.J., 1997. The Environmental Fate of Phthalate Esters: A Literature Review. *Chemosphere*, 35(4), pp.667–749.

Sumpter, J.P., 1998. Xenoendorine Disrupters--Environmental Impacts. *Toxicology letters*, 102-103, pp.337–342.

Terasaki, M., Makino, M. and Tatarazako, N., 2009. Acute Toxicity of Parabens and Their Chlorinated By-Products with *Daphnia Magna* and *Vibrio Fischeri* Bioassays. *Journal of Applied Toxicology*, 29(3), pp.242–247.

Ternes, T. A. and Hansruedi, S., 2004. Scrutinizing Pharmaceuticals and Personal Care Products in Wastewater Treatment. *International Geoscience and Remote Sensing Society 2014*, (1), pp.1–5.

Thomaidis, N.S., Asimakopoulos, A.G. and Bletsou, A.A., 2012. Emerging Contaminants : A Tutorial Mini-Review., *Global NEST Journal* 14(1), pp.72–79.

Thomas, J.H., 2007. Rapid Birth-Death Evolution Specific to Xenobiotic Cytochrome P450 Genes in Vertebrates. *PLoS Genetics*, 3(5), pp.720–728.

Tran, D.Q. Ide, C.F., Mclachlan, J.A., Arnold, S.F., 1996. The Anti-Estrogenic Activity of Selected Polynuclear Aromatic Hydrocarbons in Yeast, *Biochemical and Biophysical Research Communications*, 229, pp.102–108.

Van Jaarsveld, J, Pul, W., Leeuw, F., 1997. Modelling Transport and Deposition of Persistent Organic Pollutants in the European Region. *Atmospheric Environment* 31(7): 1011-1024

Vane, J.R. and Botting, R.M., 1998. Anti-inflammatory Drugs and their Mechanism of Action., Inflammation Research 47(Sup 2), pp.78–87.

Watkinson, A. J. Murby, E.J., Kolpin, D.W., Costanzo, S.D., 2009. The Occurrence of Antibiotics in an Urban Watershed: From Wastewater to Drinking Water. *Science of the Total Environment*, 407(8), pp.2711–2723.

Wensing, M., Uhde, E. and Salthammer, T., 2005. Plastics Additives in the Indoor Environment - Flame Retardants and Plasticizers. *Science of the Total Environment*, 339(1-3), pp.19–40.

Wild, S.R. and Jones, K.C., 1995. Aromatic Hydrocarbons in the United Kingdom Environment : A Preliminary Source Inventory and Budget. *Environmental Pollution* 88, pp.91–108.

Wilson, C. and Tisdell, C., 2001. Why Farmers continue to use Pesticides despite Environmental, Health and Sustainability Costs. *Ecological Economics*, 39(3), pp.449–462.

Wood, T.P., Duvenage, C.S.J. and Rohwer, E., 2015. The Occurrence of Anti-Retroviral Compounds used for HIV Treatment in South African Surface Water. *Environmental Pollution*, 199, pp.235–243. Available at:

World Health Organization, Unicef and Unaids, 2013a. Global Update on Hiv Treatment 2013 : Results, Impact and Opportunities. *Global update on HIV treatment 2013: results, impact and opportunities*, p.7.

World Health Organization and United Nations Environment Programme, 2013b. *State of the Science: Endocrine Disrupting Chemicals - 2012, Summary for Decision Makers*, Available at: http://apps.who.int/iris/bitstream/10665/78102/1/WHO_HSE_PHE_IHE_2013.1_eng.pdf?ua=1.

Appendix 1: Ward Numbers of Wards Located Along Vulnerable Rivers Areas

Below is a list of all the wards located along the rivers inside the vulnerable areas that were identified during the GIS process. The people living in these wards may be at the highest risk of being exposed to ECPs if they use the water from the resource directly. Monitoring should be considered and measures to mitigate water contamination via ECPs should be implemented.

Ward Number	Municipality
79800009	Johannesburg
79800010	Johannesburg
74202012	Meyerton
79700053	East Rand
79800013	Johannesburg
79800014	Johannesburg
79800023	Johannesburg
79800049	Johannesburg
79800050	Johannesburg
79800053	Johannesburg
79800071	Johannesburg
79800084	Johannesburg
79800119	Johannesburg
79800122	Johannesburg
79800127	Johannesburg
79800128	Johannesburg
79800130	Johannesburg
79700089	East Rand
79900007	Pretoria
79900048	Pretoria
79900057	Pretoria
79900061	Pretoria
79900065	Pretoria
79900066	Pretoria
79900069	Pretoria
79900070	Pretoria
79900078	Pretoria
79900091	Pretoria
4594	East Rand
4606	East Rand
4585	East Rand
4590	East Rand
4593	East Rand