Are South African Groundwater Resources Under Threat from Emerging Contaminants and their Transformation Products Leached from Biosolids and Commercial Inorganic Fertiliser Amended Soils?

Report to the

WATER RESEARCH COMMISSION

by

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July 2024

WRC report no. 3215/1/25

ISBN 978-0-6392-0725-4

WATER RESEARCH COMMISSION

This is the final report of WRC project no. C2022/2023/00880.

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EXECUTIVE SUMMARY

The application of biosolids in agricultural lands is a widely adopted approach for biosolids management, thanks to its cost-effectiveness and the agricultural and environmental benefits it offers in the circular economy. However, the use of biosolids and wastewater in agriculture for fertilization and irrigation is now under scrutiny as a possible source of pharmaceuticals and PPCPs in the food system and groundwater. Nevertheless, the impact of using sludge in agricultural lands on contaminating groundwater with pharmaceuticals and PPCPs is not fully understood. South Africa is grappling with water scarcity, as it ranks among the 30 driest countries globally and experiences an average annual rainfall of less than 500mm, around 40% lower than the world average of 850mm. This makes water security crucial for the country's economic, health, social, political, and food security. According to Grey and Sadoff (2007), water security involves ensuring the reliable availability of an acceptable quantity and quality of water for health, livelihood, and production, while effectively managing water-related risks. Given that water security encompasses both quantity and quality, compromised water quality due to contaminants poses a threat to water security. Therefore, it is important to evaluate the current water quality to ascertain the country's water security status and develop appropriate adaptation and mitigation measures. Nonetheless, there is currently a lack of quantitative data on the baseline concentration of pharmaceuticals and PPCPs in groundwater, even though over 50% of the country's rural population depends on groundwater for drinking water (WRC, 2007). This makes it vital to establish effective protection measures.

The main objectives of this study were: a) to assess the emerging contaminant status of representative agricultural lands and the underlying groundwater in Gauteng, b) to quantify the concentration of selected emerging contaminants and their transformation products on sludges, and other biowastes, c) to quantify the concentration range of selected emerging contaminants and their transformation product transfer to the human food chain through crop uptake from sludge amended agricultural lands, d) to quantify the prospect of selected emerging contaminants and their transformation products transfer to groundwater through leaching from sludge and commercial inorganic fertilizer amended agricultural lands, and e) to model the potential transport of emerging contaminants from agricultural lands to the groundwater under varying climatic and agro-ecological zones, employing the Hydrus model.

In order to achieve the stated objectives, a comprehensive three-tier study was undertaken. The initial phase of the study involved conducting a soil and groundwater sampling campaign in farmers' fields across three districts of Gauteng, namely Tshwane, Ekurhuleni, and the West Rand. The second phase consisted of a controlled lysimeter study, both large (1.2m deep, 2m wide) and small (0.45m^2 area, 1m deep) lysimeters at the University of Pretoria experimental farm. Sludge was applied based on the crop's nitrogen requirement before planting the crop. Soil samples (before sludge application and after crop harvest), plant samples (at harvest), and leachate samples (throughout the growing season) were collected and analysed for potential contaminants following prescribed procedures. The third phase of the study involved computer modelling using HYDRUS-2D to extrapolate the findings to the four main South African agro-ecological zones (semi-arid, sub-humid, humid, and super-humid) where the main agricultural production takes place. After calibrating and validating the HYDRUS-2D model with data from the lysimeter study, scenario simulations were carried out to quantify the leaching of carbamazepine and its metabolites from two soil types within the selected four agro-ecological zones. These compounds were found to be prevalent in leachates from the lysimeter study and in groundwater samples from farms across Gauteng.

The presence of pharmaceuticals and PPCPs in the soil-water-plant system of agricultural lands is a reality, although the type and quantity may vary by location. These compounds can be introduced into agricultural systems through atmospheric deposition and the application of commercial fertilizers such as potassium chloride superphosphate, limestone ammonium nitrate, compost, manure, and anaerobically or aerobically digested sludge. The study found pharmaceuticals such as carbamazepine 10,11-epoxide in commercial inorganic fertilisers like potassium chloride, superphosphate, and limestone ammonium nitrate, with the highest concentration reported in superphosphate fertilizer. Furthermore, caffeine, carbamazepine, carbamazepine-10,11-epoxide, and cis-10,11-dihydroxy-10,11-dihydrocarbamazepine were found in both anaerobically and aerobically digested sludge samples, with carbamazepine 10,11-epoxide having the highest concentration. Caffeine and carbamazepine 10,11-epoxide were also detected in compost and cattle manure, while cis-10,11-dihydroxy-10,11-dihydrocarbamazepine was detected in cattle manure. Notably, carbamazepine 10,11-epoxide was the highest detected in both compost and cattle manure.

The study found the presence of four out of ten candidate pharmaceuticals and PPCPs in the groundwater of three districts in the Gauteng province. The detected compounds include N4-

acetyl sulfamethoxazole, carbamazepine-10,11-epoxide, caffeine, and 10,11-dihydroxy carbamazepine. Among these, N4-acetyl sulfamethoxazole and carbamazepine-10,11-epoxide had the highest detection frequency of 77.8% and 72.2%, respectively. While caffeine had the least (33.3%). Additionally, three out of the nine were detected in soils of agricultural lands overlying the groundwater. The detected compounds include carbamazepine-10,11-epoxide, 10,11-dihydroxy carbamazepine, and N4-acetyl sulfamethoxazole.

In a controlled lysimeter study, caffeine, N4 acetyl sulfamethoxazole, and carbamazepine-10,11-epoxide were found in drainage water below the root zone, while caffeine, carbamazepine-10,11 epoxide, and cis-10,11-dihydro-10,11-dihydrocarbamazepine were detected in maize crop organs in the micro lysimeters. This indicates the mobile nature of the compounds and their potential in compromising food and water security if not controlled.

Model simulation results indicated that carbamazepine and its metabolite carbamazepine-10,11 epoxide could leach below the root zone of 1.2 m depth, regardless of the agro-ecological zone and soil types. The annual leaching losses of both compounds increased with higher total annual rainfall at the sites (Super-humid > humid > sub-humid > semi-arid). Notably, the leaching losses of the metabolite carbamazepine-10,11 epoxide below the root zone were significantly higher than the parent carbamazepine compound due to its higher water solubility and lower absorbability.

The recent study underscores the importance of establishing the baseline levels of emerging contaminants in South African groundwater and soils. It is imperative that fertilizer guidelines, encompassing commercial inorganic fertilizer, compost, and biosolids, integrate requirements for emerging contaminant levels in order to ensure fertilizer quality registration. This process should begin with determining the concentrations that could potentially lead to groundwater contamination through leaching and uptake by plants, posing risks to human health.

ACKNOWLEDGEMENTS

This report publication stems from a project titled: Are South African Groundwater Resources Under Threat from Emerging Contaminants and Their Transformation Products Leached from Biosolids and Commercial Inorganic Fertilizer-Amended *Soils?*
(WRC Project No. C2022/2023 – 00880).

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The project team is grateful to the following institutions for their various assistance:

- Water Research Commission
- Gauteng Department of Agriculture and Rural Development (GDARD
- Ekurhuleni Water Care Company (ERWAT)
- Farmers and Extension Officers in Tshwane, Ekurhuleni, and West Rand

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INTRODUCTION

Concerns regarding potential human and environmental health risks associated with emerging contaminants in food and water systems have raised a great alarm, calling for an investigation into their entry points in food and water systems. To date, several practices and human activities have been investigated and identified as potential entry points for emerging contaminants into food and water systems. Among these access points are landfill practices, septic systems, sewer leakage, livestock breeding facilities, wastewater discharge, and contaminated surface water. The use of fertilizers (organic and inorganic) and pesticides in agricultural lands also forms a suspected entry point for emerging contaminants in food systems (through uptake) and groundwater (through leaching). However, few studies have investigated the potential of groundwater pollution by emerging contaminants from the later entry points. Although these studies mentioned that agricultural lands could be a source of emerging contaminants in groundwater, their studies reflect only the transport of certain PPCPs and hormones under the Northern Hemisphere European and Northern American climate (rainfall and temperatures) and soils. These studies have also monitored the transport of these compounds, mostly in light-textured soils. Previous studies have reported that climatic conditions (temperature and rainfall) and soil properties (OM, texture, porosity, and pH) play crucial roles in the transport of emerging contaminants within the soil profile.

Considering that South Africa is a dry country and that water security is one of its biggest challenges, protecting its groundwater resources is crucial for sustainable growth to achieve the UN2030 developmental goals. Despite this, little (if any) information exists regarding the emerging contaminant status of South African agricultural soils. No information could be extracted from the literature reporting the potential risk or safety of food and groundwater concerning the fate of emerging contaminants from agricultural lands under South African agroclimatic conditions. Therefore, it is important to establish the emerging contaminant baseline status of South African agricultural soils and investigate the effect of fertilization practices on groundwater pollution by emerging contaminants. Such information is crucial for establishing local information-based restrictions and guidelines to safeguard dwindling water resources and food safety from lands planted in such environments. The aims of this study were: a) to assess the emerging contaminant status of representative agricultural lands and the underlying groundwater in Gauteng, b) to quantify the concentration of selected emerging

contaminants and their transformation products on sludges, and other biowastes, c) to quantify the concentration range of selected emerging contaminants and their transformation product transfer to the human food chain through crop uptake from sludge amended agricultural lands, d) to quantify the prospect of selected emerging contaminants and their transformation products transfer to groundwater through leaching from sludge and commercial inorganic fertilizer amended agricultural lands, and e) to model the potential transport of emerging contaminants from agricultural lands to the groundwater under varying climatic and agro-ecological zones, employing the Hydrus model.

In order to achieve the stated objectives, a comprehensive three-tier study was undertaken. The initial phase of the study involved conducting a soil and groundwater sampling campaign in farmers' fields across three districts of Gauteng, namely Tshwane, Ekurhuleni, and West Rand. The second phase consisted of a controlled lysimeter study, which was conducted in lysimeters at the University of Pretoria experimental farm. The third phase of the study involved computer modelling using HYDRUS-2D to extrapolate the findings to the four main South African agro-ecological zones namely, semi-arid, sub-humid, humid, and super humid.

CHAPTER 1: LITERATURE REVIEW

1.1. Environmental pollution

Anthropogenic activities induced environmental pollution as a significant challenge. Terrestrial biosphere systems are contaminated by pollutants through human activities. For example, the air is polluted by harmful gaseous substances emitted by the combustion of fossil fuels, agricultural activities and exhaust gases from factories, industries, and transport (FEC, 2022). According to the World Health Organization (WHO), over 99% of the world's population breathes air with pollutant levels above the upper limits (WHO, 2015). Human (children) mortalities (600 000) were reported in 2012 because of respiratory complications, induced by inhaling polluted air (UNECEP, 2015). Air pollution increases cardiovascular and respiratory diseases and conditions (Khaniabadi et al., 2019).

The most concerning pollutants in the atmosphere include ozone, carbon monoxide, ammonia, nitrous oxide, nitrogen dioxide, particulate matter, sulphur, and volatile organic compounds (WHO, 2015). Aquatic environments are contaminated with pathogens, microplastics, inorganic, and organic compounds. These originate from various sources, such as surface runoff from agricultural lands, and dumping sites (Ahmed et al., 2009; Di & Wang, 2018; Randall & Mulla, 2001). The soil is contaminated with microplastics, heavy metals, inorganic chemicals, and organic chemicals originating from various sources.

These sources include irrigation water, pesticide applications, and fertiliser applications (Gemeda et al., 2021; Jia et al., 2022). Sustainable environmental management practices must, therefore, be adopted to reduce, cease, and manage pollution. This will ensure the current and future protection of the environment and its inhabitants, including humans. This literature review, therefore, focused on emerging contaminants (ECs) in biowastes, agricultural lands, and water bodies (surface and groundwater).

1.1.1 Emerging contaminants

According to Sauvé and Desrosiers (2014), scientists learnt of ECs years following the publication by Rachel Carson in 1962, titled *Silent Spring*. Carson contended that the widespread use of pesticides, specifically dichlorodiphenyltrichloroethane (DDT), to kill pests, such as mosquitoes, leads to the death of voluminous birds (Carson, 1962). Several researchers

did not believe her, and she was criticised because DDT was popularly used and observed as a solution to eliminating pests (Sauvé & Desrosiers, 2014). Subsequently, scientists conducted research, supporting her claims, whereafter DDT was banned (Sauvé & Desrosiers, 2014). To this moment, EC research is one of the most popular in the scientific field.

Several definitions of ECs exist. Sauvé and Desrosiers (2014) define ECs as compounds appearing in the environment recently. Noguera-Oviedo and Aga (2016) define ECs as compounds in the environment for some time; because of innovative technologies, ECs were detected recently, only discovering them at environmentally relevant concentration levels. Some of the ECs are called "emerging contaminants of concern". This either recently appeared or has long been detected in the environment with known and suspected ecotoxicological risks to the ecosystem and human health (Sauvé & Desrosiers, 2014). Several classes of ECs are observed, such as pharmaceuticals, personal care products, industrial chemicals, and lifestyle chemicals. Table 1.1 presents a list of major classes of ECs, their subclasses, and examples from each subclass.

Table 1. 1: Major classes of emerging contaminants, their subclasses, and examples from each subclass (Stefanakis & Becker, 2016)

Emerging contaminants classes	Subclass (es)	Example (s)
Pharmaceuticals	Antibiotics	Chloramphenicol, sulphamethoxazole, lincomycin, amoxicillin, erythromycin, trimethoprim
	Anti-inflammatory drugs and analgesics	Fenoprofen, diclofenac, paracetamol, ibuprofen, codeine, acetaminophen, acetylsalicylic acid
	β-blockers	Sotalol, atenolol, timolol, propranolol, metoprolol
	Psychiatric drugs	Salbutamol, carbamazepine, primidone, diazepam
	X-ray contrasts	Diatrizoate, iopamidol, iopromide
	Lipid regulators	Gemfibrozil, fenofibrate, fenofibric acid, clofibric acid, bezafibrate

Emerging contaminants classes	Subclass (es)	Example (s)
Personal care products	Pesticides, biocides, and herbicides	N, N-diethyltoluamide (DEET), atrazine, terbuthylazine, simazine
	Fragrances	phthalates, musk's
	Sunscreen agents	Methyl benzylidene camphor, benzophenone
	Antimicrobials	Triclosan, triclocarban
	Industrial chemicals	Flame retardants
	Plasticiser	Bisphenol A
Lifestyle chemicals	Stimulants	Caffeine

1.1.2 Suspected sources of emerging contaminants

This section and subsections summarise suspected sources of ECs affecting the environment and human health (Figure 1.1). These sources include using biosolids and animal manures in agricultural lands, landfill practices, and livestock breeding facilities (Figure 1.1).

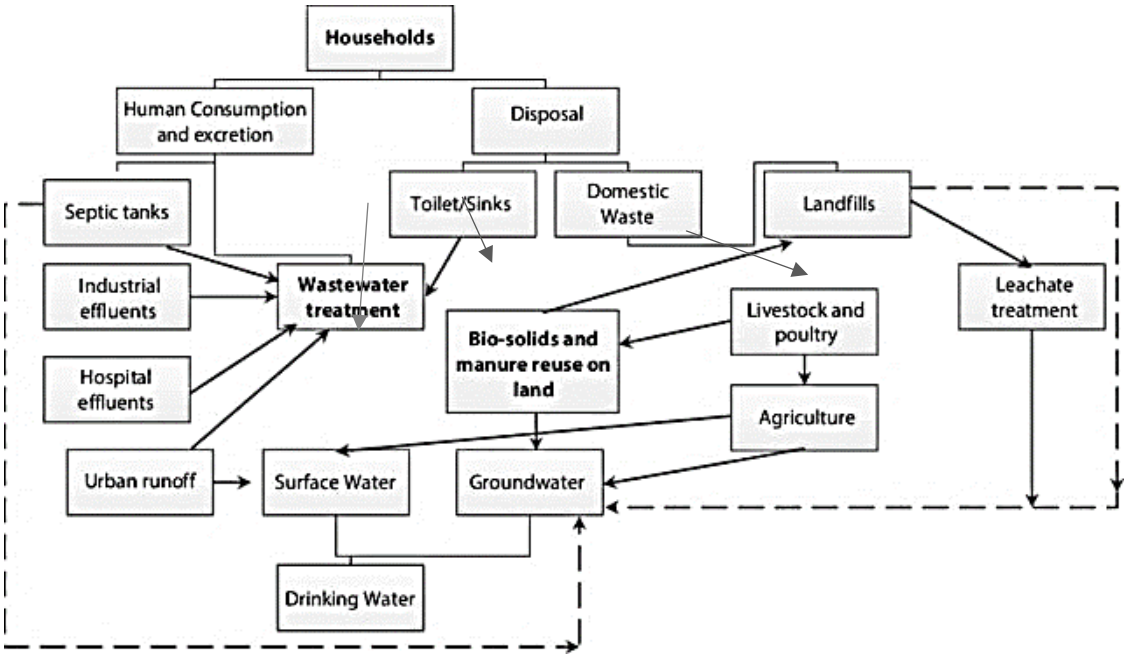


Figure 1. 1: Suspected sources of emerging contaminants in the environment and human health (Stefanakis & Becker, 2016)

Irrigation with treated effluent water

Effluent water is used in agricultural lands to meet crop water needs and supply essential nutrients (Toze, 2006); however, effluent water contains a wide range of ECs, which may accumulate in agricultural lands (Toze, 2006). One of the major concerns of ECs in agricultural lands is their transfer to: (i) the human food chain through crop roots uptake, (ii) groundwater through leaching, and (iii) surface water through runoff (Healy et al., 2017; Lapen et al., 2008; Sabourin et al., 2009). For instance, Lapen et al. (2008) detected ECs, such as triclosan, carbamazepine, atenolol, and cotinine in the tile drainage (0.8 m below surface soil) of plots, exploiting liquid municipal biosolids; this signifies that ECs can be leached from agricultural lands, lower horizons and groundwater.

Commercial inorganic fertiliser

Commercial inorganic fertilisers in agricultural lands are used to improve the soil nutrient status and crop yield (Roba, 2018). These fertilisers contain specific target crop nutrients (s), directly applied to the soil to enhance those nutrients; however, because of their origin (i.e., from the industry), inorganic fertilisers may contain ECs, such as polycyclic aromatic hydrocarbons, phthalic acid esters, and halogenated hydrocarbons (Mo et al., 2008), which may accumulate in agricultural lands and transfer to other environments through various routes, such as surface runoff.

Mulching

Mulching is an agricultural practice where the surface soil is covered with materials to conserve soil moisture, reduce erosion, and minimise weed growth while improving soil properties (Ghouse, 2020). Some of the common mulching materials include plant leaves, straws, cardboard, grass clippings, wood chips, and plastics (Ghouse, 2020). Plastic mulching, however, may lead to agricultural lands and the surrounding environment being contaminated with ECs (Steinmetz et al., 2016). Plastic materials comprise industrial chemicals, such as flame retardants, phthalates, bisphenols, and polyvinyl chlorides, and may, therefore, contaminate the soil when used for mulching (Cooper et al., 2011; Pivnenko et al., 2016; Pivnenko et al., 2017; Turner & Filella, 2021). Plastic mulching may also lead to long-term accumulation of microplastics in the soil as the plastic materials degrade into smaller pieces (Huang et al., 2020).

Pesticides

Pesticides are used to kill pests, control plant diseases, and reduce weed-crop competition; therefore, ensuring healthy plant growth (Arias-Estévez et al., 2008; Cooper & Dobson, 2007); however, when inappropriately used or exploited for a long period, pesticides can pollute the environment, more especially, the agricultural lands (Cooper & Dobson, 2007).

Landfill practices

Landfill refers to the practice of burying solid waste materials in the soil. Landfill practice is one of the commonly known methods of waste management, particularly, solid waste. Landfilled materials include municipal solid, industrial, and hazardous chemical wastes. This practice is one of the most common waste disposal options; however, it is unsustainable, introducing harmful chemical substances, including ECs, into the environment (Eggen et al., 2010; Kotowska et al., 2020). The literature confirms the existence of contaminants in landfill leachates and groundwater underlying landfill sites (Eggen et al., 2010; Sibiya et al., 2017). For instance, Kotowska et al. (2020) observed phthalate contamination in groundwater underlying the municipal solid waste landfill site.

Pit latrines

Pit latrines are also known as pit toilets. According to estimations, 1.8 billion people on Earth use pit latrine systems (Graham & Polizzotto, 2013). In the pit latrine system, human faeces and urine reach the shallow subsurface soil layers. This may lead to groundwater contamination through leaching (Graham & Polizzotto, 2013). The literature confirms a wide range of ECs in pit latrines and their subsequent transfer to groundwater (Lin et al., 2013).

Sewer leakage

A sewer system is observed as a better option than a pit latrine. In the sewer system, the waste materials (faeces and urine) are not released directly into the environment. The waste materials are channelled with pipes from the source (toilet), to be treated before final disposal into the environment; however, owing to improper maintenance, most sewer systems are leaking – more especially in townships, leading to the release of untreated waste materials – containing ECs – into the environment (Held et al., 2006). This is a severe problem in South African

townships. The release of ECs into the subsurface soil layer may lead to the pollution of groundwater through leaching (Dvory et al., 2018; Lee et al., 2015).

Livestock breeding facilities

Livestock breeding facilities use veterinary antibiotics to prevent and treat diseases while enhancing animal growth and reproduction; however, using these chemicals has spread the ECs, especially the veterinary antibiotics, to surrounding environments. Studies confirm the veterinary antibiotics in the soil proximal to livestock breeding facilities (Awad et al., 2014; Ok et al., 2011; Tong et al., 2017); therefore, livestock breeding facilities are sources of ECs in the environment.

Biowaste fertilisers

Biowastes are organic materials comprising biodegradable animal and plant residues (Boelens et al., 1996). These fertilisers are commonly used in agricultural lands as sources of organic matter and plant nutrients (Rigby & Smith, 2014). These materials include composts, animal manure, and biosolids. Despite the benefits of biowaste fertilisers, they may contain ECs, which may accumulate in the soil when used as fertilisers (Bolan et al., 2021; Bourdat-Deschamps et al., 2017). For instance, studies detected a wide range of veterinary antibiotics belonging to tetracyclines, sulphonamides, macrolides, and fluoroquinolones in agricultural lands amended with livestock manure (Gros et al., 2019; Wei et al., 2019).

Discharging effluent water into surface water bodies

The public and scientific communities are concerned with the continuous release of effluent water into surface water bodies. The most concerning issue is the concurrent release of harmful chemical substances, such as ECs, into vulnerable freshwater bodies. Previous studies reported a wide range of ECs in effluent and surface water receiving the effluent water (Ali et al., 2017; Ramirez et al., 2009; Teijon et al., 2010).

1.1.3 Suspected sources of emerging contaminants on human health

Emerging contaminants may enter human health through various routes, but the most common route is through the trophic level transfer and the consumption of contaminated drinking water. Several studies detected ECs in common human food crops, such as carrots, cabbage, spinach,

radish, celery, maize, and soybean (Wu et al., 2014; X. Wu et al., 2012). Previous studies have also detected ECs in drinking water (Carmona et al., 2014; Loraine & Pettigrove, 2006; Pai et al., 2020). The manifestation of ECs in human food crops and drinking water presents a potential entry point into human health.

1.1.4 Effects of emerging contaminants on the environment

Emerging contaminants in the environment can alter environmental processes and cause ecotoxicological risks to organisms. Some influences of ECs on various environmental compartments are briefly discussed below.

Soil

Emerging contaminants in the soil can affect soil processes (Liu, Ying, Tao, et al., 2009; Liu, Ying, Yang, et al., 2009) and alter soil microbial activities (Du & Liu, 2011; Girardi et al., 2011; Liu, Ying, Tao, et al., 2009; Liu, Ying, Yang, et al., 2009; Wei et al., 2009), disturb the structure of the microbial community (Wei et al., 2009), and kill soil biota (McKelvie et al., 2011). For example, soil triclosan concentration levels of up to 10 mg Kg^{-1} inhibited soil respiration (Butler et al., 2011; Waller & Kookana, 2009). In another study, tetracycline concentration levels of up to 100 mg Kg^{-1} inhibited the soil microbial activities and altered the structure of the microbial community (Wei et al., 2009).

This could have serious implications for nutrient recycling in agricultural lands, harming crop production, which leads to food insecurity. Soil organic matter decomposition is an important process attributed to the release of essential plant nutrients; it is mainly facilitated by soil microorganisms (Fleischer et al., 2022). Soil microbial activity inhibition (Wei et al., 2009) could delay the organic matter decomposition process (Svenningsen et al., 2011). This leads to crop nutrient deficiency, making crops vulnerable to diseases (de Bang et al., 2021), and contributing to the decline in crop yield (de Bang et al., 2021).

Plants

Exposure to ECs reduces plant yield by inhibiting germination and growth (Du & Liu, 2011; Eggen et al., 2011; Liu, Ying, Yang, et al., 2009). For instance, Eggen et al. (2011) exposed a carrot (*Dacus carota*) plant to soils with spiked metformin concentration levels of up to 10 mg Kg^{-1}, observing a decline in the plant's growth and development. The sulphadiazine soil levels

between 10 and 200 mg Kg^{-1} (spiked concentrations) caused maize (*Zea mays*) plant death (Michelini et al., 2012). The above studies emphasise that plant exposure to ECs could influence crop production and cause food insecurity challenges. Potential human health risks may emanate from the consumption of contaminated plants (C. Wu et al., 2012).

Water

Emerging contaminants in the aquatic environment can affect aquatic organisms' growth, reproduction, and functioning; for instance, caffeine disrupts the endocrine system of a goldfish (*Carassius auratus*) (Li et al., 2012). Veldhoen et al. (2006) observed a reduction in the body weight and the rate of thyroid hormone production in tadpoles after exposure to triclosan at a concentration of 0.03 $\mu g\ L^{-1}$. These studies emphasise some of the adverse effects of ECs on aquatic organisms. Emerging pollutants might harm food production and food security owing to their effects on aquatic organisms.

1.1.5 Effects of emerging contaminants on human health

Emerging contaminants may threaten human health. Studies reported the influences of various ECs on human health. For example, industrial chemicals, such as bisphenol A, phthalates, and polychlorinated biphenyls, influence the hypothalamic neuroendocrine system in humans (Gore et al., 2019). Children's exposure to phthalates affects their hormonal production (Meeker, 2012). The exact levels of ECs leading to human health problems are unavailable. This is owing to a lack of reliable and sufficient information from previous studies and contradictions in some reported data (Lei et al., 2015).

1.2 Emerging contaminants in biowastes, agricultural lands, water bodies (surface and groundwater) and their dynamics within the soil-plant-water system

This section presents the global and local (South African) EC concentration status in biowastes, agricultural lands, and water bodies (surface and groundwater).

1.2.1 Emerging contaminants concentration of biowastes

Biowastes comprise several sources. Animal manure and treated sludge (biosolids) are the most used biowaste in agricultural lands. This section, therefore, presents the EC concentration status

of animal manure and sewage sludge/biosolids, regarded as potential sources of ECs in agricultural lands.

Sewage sludge

Sewage sludge and biosolids are solid products of wastewater treatment plants. They often contain a wide range of ECs originating from various sources, such as households, hospitals, and industrial sewer systems. These ECs are owing to the failure of wastewater treatment methods to remove them from wastewater. ECs are bound to the sludge, forming part of the biosolids.

Global status of emerging contaminants in sewage sludge/ biosolids

A wide range of ECs is detected in sewage sludge and biosolid samples from wastewater treatment plants around the globe (Chen et al., 2019; Guerra et al., 2014; McClellan & Halden, 2010; Ying & Kookana, 2007) (Table 1.2). This implies that the products of the wastewater treatment plant, in particular sewage sludge, could become potential sources of a wide range of ECs in the environment through disposal in landfills or beneficial agricultural use.

A tremendous variation exists in the concentration levels of ECs detected in sludge and biosolid samples from diverse countries (Table 1.2). For example, nationwide surveys from China and the United States of America report maximum triclosan concentration levels of up to 4870 (Chen et al., 2019) and 133000 ng g^{-1} (dry weight) (USEPA, 2009), respectively in sludge and biosolid samples. This could be due to several factors, as discussed in the next subsections.

A variation exists in the concentration levels of ECs detected in sludge and biosolid samples within each country (Table 1.2). The concentration level of caffeine in 110 biosolid samples collected around the United States of America reached up to 643 ng g^{-1} (dry weight) (McClellan & Halden, 2010); However, Kinney et al. (2008) could not detect caffeine in biosolid samples collected from the same country. This could be owing to several factors discussed in the next subsections.

Among ECs, the concentration of galaxolide (427000 ng g^{-1} dry weight) in biosolids from the United States of America was reported as the highest. The lowest concentration (2290 ng g^{-1} (dry weight)) of galaxolide in sludge was reported in Switzerland (Herren & Berset, 2000).

Table 1. 2: Emerging contaminants in sewage sludge and biosolids globally

Contaminant	Class	Concentrations (ng/g dry wt.)	Country	Reference
Triclosan	Antimicrobial	90 - 16790	Australia	(Ying & Kookana, 2007)
		400 - 8800	Germany	(Bester, 2003)
		530 - 15 600	USA	(Mcavoy et al., 2002)
		420 - 5400	Spain	(Morales et al., 2005)
		≤ 4870	China	(Chen et al., 2019)
		30000[a]	USA	(Heidler & Halden, 2007)
		10500[a]	USA	(Kinney et al., 2008)
		1114 - 1350	USA	(Sherburne et al., 2016)
		1200[a]	India	(Subedi et al., 2015)
		620 - 11550	Canada	(Chu & Metcalfe, 2007)
		90 - 7060	USA	(Cha & Cupples, 2009)
		≤ 11000	Canada	(Guerra et al., 2014)
		≤ 19700	USA	(McClellan & Halden, 2010)
		≤ 4900	Ireland	(Healy et al., 2017)
		190 - 9850	Greece	(Stasinakis et al., 2008)
		330 - 133000	USA	(USEPA, 2009)
Triclocarban	Antimicrobial	≤ 43300	China	(Chen et al., 2019)
		1026 - 1472	USA	(Sherburne et al., 2016)
		≤ 150	Ireland	(Healy et al., 2017)
		≤ 48100	USA	(McClellan & Halden, 2010)
Triclocarban	Antimicrobial	7000[a]	India	(Subedi et al., 2015)
		4300[a]	Canada	(Chu & Metcalfe, 2007)
		≤ 8900	Canada	(Guerra et al., 2014)

Contaminant	Class	Concentrations (ng/g dry wt.)	Country	Reference
		≤ 6900	South Korea	(Subedi et al., 2014)
		51000[a]	USA	(Heidler et al., 2006)
		7500 - 25900	USA	(Sapkota et al., 2007)
		≤ 441000	USA	(USEPA, 2009)
Ciprofloxacin	Antibiotics	≤ 4.0	France	(Thomas et al., 2020)
		≤ 2.0	China	(Jia et al., 2012)
		1780 - 16000	Canada	(Guerra et al., 2014)
		6900[a]	USA	(McClellan & Halden, 2010)
		60 - 2420	Switzerland	(Golet et al., 2002)
		500 - 4800	Sweden	(Lindberg et al., 2005)
		9300 - 11700	Sweden	(Lindberg et al., 2006)
		≤ 10800	USA	(McClellan & Halden, 2010)
		2270 - 2420	Germany	(Golet et al., 2002)
Norfloxacin	Antibiotics	98 - 3300	Canada	(Guerra et al., 2014)
		4700 - 5800	Sweden	(Lindberg et al., 2006)
		≤ 860	China	(Jia et al., 2012)
		≤ 418	USA	(McClellan & Halden, 2010)
Norfloxacin	Antibiotics	2130 - 2370	Germany	(Golet et al., 2002)
		100 - 4200	Sweden	(Lindberg et al., 2005)
Ofloxacin	Antibiotics	5400[a]	USA	(McClellan & Halden, 2010)
		ND - 2000	Sweden	(Lindberg et al., 2005)
		≤ 8140	USA	(McClellan & Halden, 2010)
Diclofenac	NSAIDs	1720 - 11060	China	(Dong et al., 2016)

Contaminant	Class	Concentrations (ng/g dry wt.)	Country	Reference
		≤ 30	Greece	(Samaras et al., 2013)
		≤ 20	Poland	(Kumirska et al., 2015)
Carbamazepine	Anticonvulsant	≤ 0.04	France	(Bourdat-Deschamps et al., 2017)
		44 - 11060	China	(Dong et al., 2016)
		≤ 22	India	(Subedi et al., 2017)
		390a	USA	(Kinney et al., 2008)
		9.0 - 6030	USA	(USEPA, 2009)
Codeine	Analgesic	29.7[a]	USA	(McClellan & Halden, 2010)
Cotinine	Stimulant	38.6[a]	USA	(McClellan & Halden, 2010)
Chlortetracycline	Antibiotics	≤ 43.5	USA	(McClellan & Halden, 2010)
Oxytetracycline	Antibiotics	≤ 114	USA	(McClellan & Halden, 2010)
Azithromycin	Antibiotics	≤ 1220	USA	(McClellan & Halden, 2010)
		8.0 - 5210	USA	(USEPA, 2009)
Tetracycline	Antibiotic	≤ 2790	USA	(McClellan & Halden, 2010)
		38 - 5270	USA	(USEPA, 2009)
Enrofloxacin	Antibiotic	≤ 28.6	USA	(McClellan & Halden, 2010)
Gemfibrozil	Lipid regulator	≤ 159	USA	(McClellan & Halden, 2010)
Metformin	Antidiabetics	≤ 456	USA	(McClellan & Halden, 2010)
Ibuprofen	NSAIDs	18 - 145	India	(Subedi et al., 2015)
		≤ 180	Greece	(Samaras et al., 2013)
		≤ 359	USA	(McClellan & Halden, 2010)
Naproxen	NSAIDs	≤ 273	USA	(McClellan & Halden, 2010)

Contaminant	Class	Concentrations (ng/g dry wt.)	Country	Reference
		23.8 - 72.2	Spain	(Martin et al., 2012)
		11 - 35	China	(Yu & Wu, 2012)
Sulfamethoxazole	Antibiotic	≤ 31	India	(Subedi et al., 2015)
		≤ 3.3	USA	(McClellan & Halden, 2010)
		≤ 68000	Switzerland	(Gobel et al., 2005)
Trimethoprim	Antibiotic	≤ 61	USA	(McClellan & Halden, 2010)
		≤ 103	Japan	(Matsuo et al., 2011)
		ND	USA	(Kinney et al., 2008)
Galaxolide	Synthetic musk	427000[a]	USA	(Kinney et al., 2008)
		3580 - 78600	Hong Kong	(Shek et al., 2008)
		5420 - 21210	China	(Zeng et al., 2005)
		2290 - 12160	Switzerland	(Herren & Berset, 2000)
		7400 - 36000	Switzerland	(Kupper et al., 2004)
		6030 - 11450	Germany	(Heberer, 2002)
Tonalide	Synthetic musk	177000[a]	USA	(Kinney et al., 2008)
		720 - 6200	China	(Zeng et al., 2005)
		120 - 16000	UK	(Stevens et al., 2003)
		475 - 13900	Hong Kong	(Shek et al., 2008)
		2520 - 5070	Germany	(Heberer, 2002)
		740 - 4160	Switzerland	(Herren & Berset, 2000)
Fluoxetine	Antidepressant	≤ 258	USA	(McClellan & Halden, 2010)
		10.0 - 3130	USA	(USEPA, 2009)
Acetophenone	Anaesthetic agent	3450[a]	USA	(Kinney et al., 2008)
Oestrogen (E1)	Hormone	≤ 37	Germany	(Ternes et al., 2002)

Contaminant	Class	Concentrations (ng/g dry wt.)	Country	Reference
		≤ 39	China	(Ben et al., 2018)
		≤ 965	USA	(USEPA, 2009)
17α-Ethinyloestradiol	Hormone	≤ 17	Germany	(Ternes et al., 2002)
		≤ 355	USA	(USEPA, 2009)
		< LOQ	China	(Nie et al., 2009)
Caffeine	Stimulant	≤ 643	USA	(McClellan & Halden, 2010)
		≤ 910	Australia	(Yang et al., 2016)
		ND	USA	(Kinney et al., 2008)
Bisphenol A	Plasticizer	3.0 - 10.0	India	(Karthikraj & Kannan, 2017)
		85.0 - 133	China	(Yu et al., 2011)
		4600[a]	USA	(Kinney et al., 2008)
		100 - 130	China	(Nie et al., 2009)
		4.0 - 1363	Germany	(Fromme et al., 2002)
		≤ 1750	Greece	(Stasinakis et al., 2008)
		4.0 - 158	Australia	(Tan et al., 2007)
		≤ 1860	Greece	(Samaras et al., 2013)

[a] Average concentration; wt. weight; LOQ limit of quantification; ND not detected

wt. weight; NSAIDs nonsteroidal anti-inflammatory drugs

Emerging contaminant content of South African sewage sludge or biosolids

A wide range of ECs in sewage sludge and biosolids from South African wastewater treatment plants have been reported (Ademoyegun et al., 2020b; Bakare & Adeyinka, 2022; Lehutso et al., 2017); however, previous studies focused on sludge and biosolids collected from a few provinces, such as Gauteng, KwaZulu-Natal, Eastern Cape, and Western Cape (Table 1.3).

The concentration levels of some ECs reported in sewage sludge and biosolids from South African wastewater treatment plants are lower compared to those in other countries, such as the USA, Canada, China, South Korea, and Ireland. As an example, triclocarban concentration in South African sewage sludge is reported at 11.8 ng g^{-1} (Lehutso et al., 2017). This contrasts with the reported values from China (43300 (Chen et al., 2019)), the United States of America (441000 (USEPA, 2009)), Canada (8900 (Guerra et al., 2014)), Ireland (150 (Healy et al., 2017)), and South Korea (6900 ng g (dry weight) (Subedi et al., 2014)). This could be attributed to the low consumption pattern of triclocarban-containing products in South Africa relative to the other countries.

A South African study by Lehutso et al. (2017) reports varying effects of wastewater treatment methods on the concentration of triclosan and triclocarban. The study observed that the concentration of triclosan (15 ng g^{-1} (dry weight)) and triclocarban (11.8 ng g^{-1} (dry weight)) was highest for raw sludge and lowest (7.8 ng g^{-1} (dry weight) for triclosan; 8.23 ng g^{-1} (dry weight) triclocarban) for treated (activated) sludge. This study informed on the effect of wastewater treatment on the EC concentration; however, it is impossible to draw any conclusions on the contaminant sources and the effectiveness of wastewater treatment methods in removing them (Table 1.3).

Table 1. 3: Emerging contaminants in local (South African) sewage sludge and biosolids

Contaminant	Class	Concentration (ng/g dry wt.)	Sludge type	Province	Reference
Triclosan	Antimicrobial	3.7 - 15.0	Raw sludge	Gauteng	(Lehutso et al., 2017)
		2.1 - 7.8	Activated sludge	Gauteng	(Lehutso et al., 2017)
		2.16 - 13.5	Biosolids	Gauteng	(Lehutso et al., 2017)
		0.1 - 2.5	Raw sludge	KwaZulu-Natal	(Bakare & Adeyinka, 2022)
		11.0 - 90	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Triclocarban	Antimicrobial	3.7 - 11.8	Raw sludge	Gauteng	(Lehutso et al., 2017)
		1.2 - 9.2	Activated sludge	Gauteng	(Lehutso et al., 2017)
		2.59 - 8.23	Biosolids	Gauteng	(Lehutso et al., 2017)
		0.1 - 8.8	Raw sludge	KwaZulu-Natal	(Bakare & Adeyinka, 2022)
Aspirin	NSAIDs	19 - 60	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Ibuprofen	NSAIDs	11.0 - 97	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
DEET	Pesticide	2.0 - 43	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Caffeine	Stimulant	23 - 85	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Carbamazepine	Anticonvulsant	9.0 - 59	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Trimethoprim	Antibiotic	1.0 - 50	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Diclofenac	NSAIDs	9.0 - 50	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Acetaminophen	NSAIDs	2.0 - 98.9	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Doxycycline	Antibiotic	ND	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Codeine		Analgesic	20 – 43	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020b)
Efavirenz		ARV drug	17000 – 43000	Primary settling tank sludge	Gauteng	(Schoeman et al., 2017)

Contaminant	Class	Concentration (ng/g dry wt.)	Sludge type	Province	Reference
Nevirapine	ARV drug	ND	Primary settling tank sludge	Gauteng	(Schoeman et al., 2017)
Nonylphenol	Phenol	≤ 2079000	Anaerobic digested sludge	Gauteng	(Mamabolo, 2006)
		≤ 821000	Waste activated sludge	Western Cape	(Mamabolo, 2006)
		ND	Anaerobic digested sludge	North West	(Mamabolo, 2006)
		≤ 12200	Waste Activated sludge	KwaZulu-Natal	(Mamabolo, 2006)
p-cresol	Phenol	≤ 57300	Anaerobic digested sludge	Gauteng	(Mamabolo, 2006)
		ND	Anaerobic digested sludge	North West	(Mamabolo, 2006)
		≤ 25700	Waste activated sludge	Western cape	(Mamabolo, 2006)
		≤ 18200	Waste activated sludge	KwaZulu-Natal	(Mamabolo, 2006)
α-Hexachlorocyclohexane (α-BHC)	Pesticide	32 – 160	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
β-Hexachlorocyclohexane (β-BHC)	Pesticide	ND – 32	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
Y-Hexachlorocyclohexane (Y-BHC)	Pesticide	ND – 270	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
δ-Hexachlorocyclohexane (δ-BHC)	Pesticide	ND – 17	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
Heptachlor	Pesticide	ND	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
Aldrin	Pesticide	23 – 121	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
4,4-DEE	Pesticide	12.0 – 45	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
Dieldrin	Pesticide	ND	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
Endrin	Pesticide	ND	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
4, 4, DDD	Pesticide	56 – 145	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
Endosulfan 11	Pesticide	ND	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
4, 4, DDT	Pesticide	57 – 220	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
Endrin Aldehyde	Pesticide	ND	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)

Contaminant	Class	Concentration (ng/g dry wt.)	Sludge type	Province	Reference
Endosulfan sulphate	Pesticide	ND	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
Methoxychlor	Pesticide	ND	Activated sludge	Eastern Cape	(Ademoyegun et al., 2020a)
2,2,4'-tri BDE	Flame retardants	ND - 4.64[a]	Dewatered sludge	Western cape	(Daso et al., 2012)
2,2', 4,4'tetra BDE	Flame retardants	1.03 - 40.5[a]	Dewatered sludge	Western cape	(Daso et al., 2012)
2,2',4,4', 6-penta BDE	Flame retardants	0.68 - 7.98[a]	Dewatered sludge	Western cape	(Daso et al., 2012)
2,2',4,4',5-penta-BDE	Flame retardants	1.44 - 9.24[a]	Dewatered sludge	Western cape	(Daso et al., 2012)
2,2',4,4',5,6'-hexa BDE	Flame retardants	0.33 - 4.24[a]	Dewatered sludge	Western cape	(Daso et al., 2012)
2,2',4,4',5,5'-hexa BDE	Flame retardants	2.25 - 7.88[a]	Dewatered sludge	Western cape	(Daso et al., 2012)
2,2',3,4,4',5',6-hepta BDE	Flame retardants	0.85 - 37.8[a]	Dewatered sludge	Western cape	(Daso et al., 2012)
2,2',3,3',4,4',5,5',6,6'-deca BDE	Flame retardants	ND - 297[a]	Dewatered sludge	Western cape	(Daso et al., 2012)
2,2', 4,4', 5,5' - Hexabromobiphenyl	Flame retardants	ND - 7.32[a]	Dewatered sludge	Western cape	(Daso et al., 2012)

[a] average concentration range; ND not detected; ARV antiretroviral; wt weight; NSAIDs nonsteroidal anti-inflammatory drugs; ND not detected; DEET diethyltoluamide

Factors contributing to emerging contaminant variation among sludges and biosolids

The following factors contribute to the variations in EC concentrations among sludge types and biosolids:

- The variation in the consumption pattern of EC-containing products (Gani et al., 2021)
- The nature and composition of the waste stream reaching the wastewater treatment facility (Bester, 2005)
- The type and the effectiveness of treatment technology to remove ECs (Bester, 2005)
- The competency of individuals operating the wastewater treatment plant (Lehutso et al., 2017)
- The validity of analytical methods to quantify the ECs (Gani et al., 2021)
- Sludge type (Chen et al., 2019)
- Geographic location (Chen et al., 2019)
- Sampling season (Lehutso et al., 2017)
- The size of the wastewater treatment plant from which the sample was taken (Chen et al., 2019)

Chen et al. (2019) observed a significant variation in the contribution of parabens, triclosan, and triclocarban from diverse economic regions of China. The most developed regions contribute significantly to the target ECs in wastewater treatment plants. This indicates that the consumption pattern of products with ECs varies among regions, influencing their occurrence and concentration levels in wastewater treatment plant products. The same study evaluated the influence of wastewater treatment plant size (i.e., small, medium, large, and super large-based on a volume of waste received) and sludge origin (i.e., domestic vs industrial sludge) on the occurrence and concentration levels of parabens, triclosan, and triclocarban in sludge. According to the findings, wastewater treatment plant size and sludge origin influenced the occurrence and concentration levels of target compounds in the sludge (Chen et al., 2019). Higher concentrations of the target compounds were detected in super-large wastewater treatment plants (Chen et al., 2019).

Lehutso et al. (2017) investigated the effect of the season (i.e., summer vs winter) on the occurrence of triclosan and triclocarban in sludge from various wastewater treatment plants in Gauteng (South Africa). Higher concentrations of the target compounds were reported during

winter. This could be attributed to limited dilution from rainfall. When investigating the occurrence and concentration levels of ECs in sludge and biosolids, all the aforementioned factors should be considered.

Livestock manures

Livestock manures used in agricultural lands enhance soil fertility and improves crop yield (Schoenau, 2006); however, animal manures may also contain ECs, such as veterinary antibiotics. Veterinary antibiotics are commonly used in animal breeding facilities to treat and prevent diseases. A high percentage of the administered animal medication is excreted through animal faeces and urine; therefore, it forms part of the animal manure (Kumar et al., 2005).

The global status of emerging contaminants in livestock manures

Several studies detected ECs in livestock manure of various origins (cattle, poultry, pig, and duck) globally (Jacobsen & Halling-Sorensen, 2006; Motoyama et al., 2011; Zhou et al., 2020). Diverse livestock manures may, therefore, constitute potential sources of ECs in the environment through disposal pathways, such as agronomic use of animal manure.

The concentration levels of ECs in animal manure vary between the animal species and the EC type (Table 1.4). These levels are higher in the pig manure than in the poultry, cattle, and duck (Table 1.4). **Error! Reference source not found.**However, this also varies among ECs. For example, Zhou et al. (2020) reported higher concentration levels of tetracycline (up to 187.7 ng g^{-1}); sulphadiazine (up to 136.3 ng g^{-1}); and sulfamethoxazole (up to 157.33 ng g^{-1}) in pig manures than cattle (tetracycline(up to 3.41 ng g^{-1}); sulphadiazine (up to 1.0 ng g^{-1}); and sulfamethoxazole (up to 0.33 ng g^{-1})); poultry (tetracycline(up to 3.61 ng g^{-1}); sulphadiazine (up to 2.16 ng g^{-1}); and sulfamethoxazole (up to 0.53 n g^{-1})); and duck manures (tetracycline(up to 2.80 ng g^{-1}); sulphadiazine (up to 0.80 ng g^{-1}); and sulfamethoxazole (up to 1.94 ng g^{-1})).

The chlortetracycline (125.9 ng g^{-1}) and oxytetracycline (290.5 ng g^{-1}) concentration levels were, however, higher in the poultry manures and relative to cattle (chlortetracycline (up to 0.85 ng g^{-1}) and oxytetracycline (up to 6.20 ng g^{-1})), pig (chlortetracycline (up to 84.60 ng g^{-1}) and oxytetracycline (up to 108.7 ng g^{-1})), and duck (chlortetracycline (up to 35.67 ng g^{-1}) and oxytetracycline (up to 8.40 ng g^{-1})) (Zhou et al., 2020).

Most studies on the occurrence and concentration ranges of ECs in animal manures were conducted in Asia, specifically China (Table 2.3**Error! Reference source not found.**). China is a country with high levels of meat consumption (FAO, 2022); therefore, large quantities of animal manure are produced in animal breeding facilities. China, therefore, prioritises research on the sustainable use of livestock manure to control animal wastes manure.

Veterinary antibiotics are the most studied group of ECs in livestock manures with higher concentration levels than other groups (Table 1.4). It is mainly owing to veterinary antibiotics used in animal breeding facilities to treat the animals and increase their growth (Sarkar et al., 2018).

A wide variation exists in the concentration levels of ECs detected in animal manure globally (Table 1.4**Error! Reference source not found.**). This variation is also vivid within countries, as clearly indicated by Zhou et al. (2020) in China. Oxytetracycline in cattle, poultry, and pig manures varied within a range of 6.20 – 1940 ng g^{-1}, 290.5 – 416750 ng g^{-1}, and 108.7 – 43429 ng g^{-1}, respectively (Zhang et al., 2015). Such variation is attributed to the deviation in the livestock intensity and type of care.

Table 1. 4: Emerging contaminants in global livestock manures

	Concentration (ng/g dry wt.)					
Compound	**Cattle**	**Poultry**	**Pig**	**Duck**	**Country**	**Reference**
Tetracycline	≤ 3.41	≤ 3.61	≤ 187.7	≤ 2.80	China	(Zhou et al., 2020)
	200 - 450				USA	(Wallace et al., 2018)
			≤ 1900		Denmark	(Jacobsen & Halling-Sorensen, 2006)
	17.3 - 2495	21.4 - 8675	15.9 - 30941	132 - 520	China	(Zhang et al., 2015)
	≤ 1.2	< LOD	≤ 15		Japan	(Motoyama et al., 2011)
Caffeine			ND		USA	(Kinney et al., 2008)
Carbamazepine			ND		USA	(Kinney et al., 2008)
	< LOD	≤ 15	< LOD		Japan	(Motoyama et al., 2011)
Chlortetracycline	≤ 0.85	≤ 125.9	≤ 84.60	≤ 35.67	China	(Zhou et al., 2020)
	46 – 340				USA	(Wallace et al., 2018)
			≤ 24400		Denmark	(Jacobsen & Halling-Sorensen, 2006)
	240 - 27590	160 - 17680	160 - 21060		China	(Zhao et al., 2010)
	15.1 - 65.5	13.9 - 129.5	20.6 - 215346	19.1 - 44.3	China	(Zhang et al., 2015)
	≤ 1.3	≤ 1.5	≤ 280		Japan	(Motoyama et al., 2011)
Oxytetracycline	ND – 26				USA	(Wallace et al., 2018)
	≤ 6.20	≤ 290.5	≤ 108.7	≤ 8.40	China	(Zhou et al., 2020)
			≤ 1600		Denmark	(Jacobsen & Halling-Sorensen, 2006)
	320 - 59590	270 - 10560	150 - 59060		China	(Zhao et al., 2010)
	130 - 1940	19.0 - 416750	21.5 - 43429	20.5 - 7150	China	(Zhang et al., 2015)
	≤ 1.0	< LOD	≤ 13		Japan	(Motoyama et al., 2011)
Doxycycline	≤ 1.73	< 43.50	≤ 2.93	≤ 4.47	China	(Zhou et al., 2020)
			≤ 3500		Denmark	(Jacobsen & Halling-Sorensen, 2006)
	440 -10500	920 - 10910	230 - 13500		China	(Zhao et al., 2010)
	15.3 - 2495	19.8 - 8300	15.1 - 30718	122.5 - 505	China	(Zhang et al., 2015)

	Concentration (ng/g dry wt.)					
Compound	**Cattle**	**Poultry**	**Pig**	**Duck**	**Country**	**Reference**
Sulfadiazine	≤ 1.0	≤ 2.16	≤ 136.3	≤ 0.80	China	(Zhou et al., 2020)
			≤ 3200		Denmark	(Jacobsen & Halling-Sorensen, 2006)
	ND	30 - 3120	90 - 800		China	(Zhao et al., 2010)
	5.2 - 65.0	5.5 - 1845	5.1 - 6792	5.3 - 5.5	China	(Zhang et al., 2015)
Galaxolide			ND		USA	(Kinney et al., 2008)
Triclosan			ND		USA	(Kinney et al., 2008)
Acetophenone			1380[a]		USA	(Kinney et al., 2008)
Indone			21500[a]		USA	(Kinney et al., 2008)
Bisphenol A			ND		USA	(Kinney et al., 2008)
Tonalide			ND		USA	(Kinney et al., 2008)
Tylosin A			< LOD		Denmark	(Jacobsen & Halling-Sorensen, 2006)
Trimethoprim			ND		USA	(Kinney et al., 2008)
	< LOD	< LOD	< LOD		Japan	(Motoyama et al., 2011)
Sulfamethazine	≤ 2.43	≤ 5650	≤ 5.07	≤ 67.03	China	(Zhou et al., 2020)
			< LOD		Denmark	(Jacobsen & Halling-Sorensen, 2006)
		5.9 - 22.7	5.7 - 33.7	7.4 - 11.0	China	(Zhang et al., 2015)
	4.7 - 34.0					
Sulfachlorpyridazine	≤ 4.90	≤ 9.63	≤ 4960	≤ 3.40	China	(Zhou et al., 2020)
	≤ 360	200 - 710	90 – 3510		China	(Zhao et al., 2010)
Sulfamethoxazole	≤ 0.33	≤ 0.53	≤ 157.33	≤ 1.94	China	(Zhou et al., 2020)
	≤ 10.0	≤ 37.0	≤ 8.2		Japan	(Motoyama et al., 2011)
	ND	120 - 2800	230 – 840		China	(Zhao et al., 2010)
	4.2 - 7.85	4.1 - 28.8	4.1 - 14.3	4.9 - 8.1	China	(Zhang et al., 2015)
	≤ 10	≤ 61	≤ 35		Japan	(Motoyama et al., 2011)

	Concentration (ng/g dry wt.)					
Compound	**Cattle**	**Poultry**	**Pig**	**Duck**	**Country**	**Reference**
Sulfamethoxypyridazine	≤ 1.96	≤ 2.0	≤ 2.52	≤ 0.61	China	(Zhou et al., 2020)
Sulfamethoxydiazine	ND	≤ 5.95	≤ 7.07	ND	China	(Zhou et al., 2020)
Sulfamonomethoxine	ND	≤ 16.27	≤ 3490	≤ 158.3	China	(Zhou et al., 2020)
	≤ 60	80 - 900	70 – 4080		China	(Zhao et al., 2010)
	2.0 - 2.2	2.1 - 3.9	2.1 - 20.3	ND	China	(Zhang et al., 2015)
	≤ 22	≤ 26	≤ 210		Japan	(Motoyama et al., 2011)
Sulfathiazole	≤ 0.91	ND	ND	ND	China	(Zhou et al., 2020)
Sulfadimethoxine	≤ 3.67	≤ 2.8	≤ 8.97	≤ 6.19	China	(Zhou et al., 2020)
	6.2 - 7.7	6.0 - 8.9	6.1 - 8.6	6.2 - 6.3	China	(Zhang et al., 2015)
	< LOD	≤ 8.0	< LOD		Japan	(Motoyama et al., 2011)
Sulfamethizole	≤ 1.83	≤ 0.69	ND	≤ 1.73	China	(Zhou et al., 2020)
Ciprofloxacin	≤ 39.71	≤ 2860	≤ 63.63	≤ 116	China	(Zhou et al., 2020)
	490 - 29590	680 - 45590	640 – 33980		China	(Zhao et al., 2010)
	28.2 - 331.5	19.1 - 4905	28.4 - 45.0	59.0 - 2475	China	(Zhang et al., 2015)
	≤ 12	≤ 6.3	≤ 6.4		Japan	(Motoyama et al., 2011)
Ofloxacin	≤ 54.57	≤ 5567	≤ 24.62	≤ 154.2	China	(Zhou et al., 2020)
	21.2 - 189.5	17.9 - 4990	12.0 - 124.5	73.5 - 595	China	(Zhang et al., 2015)
Sarafloxacin	≤ 5.47	≤ 7.22	≤ 11.6	≤ 11.5	China	(Zhou et al., 2020)
Norfloxacin	≤ 119.3	≤ 30.23	≤ 27.53	≤ 41.39	China	(Zhou et al., 2020)
	1230 - 2760	850 - 225450	560 – 5500		China	(Zhao et al., 2010)

Compound	Concentration (ng/g dry wt.)				Country	Reference
	Cattle	Poultry	Pig	Duck		
	18.4 - 227	10.2 - 4540	13.8 – 107	16.2 - 384	China	(Zhang et al., 2015)
Fleroxacin	≤ 3.41	≤ 4.63	≤ 2.13	≤ 2.92	China	(Zhou et al., 2020)
	≤ 2220	760 - 99430	1080 – 7460		China	(Zhao et al., 2010)
Roxithromycin	8.3 - 21.8	10.2 - 89	ND	ND	China	(Zhang et al., 2015)
Erythromycin	< LOD	< LOD	< LOD		Japan	(Motoyama et al., 2011)
Danofloxacin	≤ 35.13	≤ 26.82	≤ 5.56	≤ 25.48	China	(Zhou et al., 2020)
	410 - 3060	80 - 2480	80 – 2920		China	(Zhao et al., 2010)
Enrofloxacin	≤ 5.73	≤ 2560	≤ 57.62	≤ 2267	China	(Zhou et al., 2020)
	10.1 - 740	10.6 - 8575	12.5 - 89.0	20.1 - 28.7	China	(Zhang et al., 2015)
	1720 - 46700	330 - 1420760	480 – 33260		China	(Zhao et al., 2010)

LOD limit of detection; ND not detected; LOD limit of detection; wt weight; [a] average concentration

Emerging contaminant status of South African livestock manure

In South Africa, insufficient investigation exists on ECs in livestock manure and their concentration levels. This research presents only one report from South Africa on ECs in animal manures (Ravindran & Mnkeni, 2016). Ravindran and Mnkeni (2016) reported on the occurrence and concentration levels of oxytetracycline (166600 ng g^{-1}), 4-epi-oxytetracycline (22800 ng g^{-1}), α-apo-oxytetracycline (22200) ng g^{-1}, and β-apo-oxytetracycline (19300 ng g^{-1}) in poultry manure. The value of oxytetracycline reported by Ravindran and Mnkeni (2016) in South Africa is relatively higher than those reported for poultry in Japan (< LOD) (Motoyama et al., 2011) but within the ranges reported in China (290.5 ng g^{-1} (Zhou et al., 2020) - 416750 ng g^{-1} (Zhang et al., 2015)).

1.2.2 Emerging contaminants content status of agricultural lands

Significant public and scientific concerns exist over the presence of ECs in agricultural lands. The previous sections discuss potential sources of ECs and their negative influences on the environment, including agricultural lands. This section reports on the global and local (South African) EC concentration levels in agricultural lands.

Global concentration status of emerging contaminants in agricultural lands

Various types of ECs are detected in agricultural lands globally (Hu et al., 2010; Lozano et al., 2010; Malchi et al., 2014; Sanchez-Brunete et al., 2010). The authors include antibiotics, antimicrobials, stimulants, synthetic musks, nonsteroidal anti-inflammatory drugs, and lipid regulators (Table 1.5). Agricultural lands could, therefore, become a potential source of water pollution (surface and groundwater) and food contamination, presenting a serious health threat to humans.

Most studies on the occurrence and concentration levels of ECs in agricultural lands were conducted in Asia and China (Table 1.5). These studies investigated these aspects amended with animal manures (Table 1.5). Most ECs investigated under these agricultural lands were veterinary antibiotics (Table 1.5). It is also apparent that veterinary antibiotics are the most studied EC in livestock manure from China (**Error! Reference source not found.**). China prioritises research on the sustainable use of animal manures in agricultural lands.

Other studies investigated the occurrence and concentration levels of ECs in agricultural lands, amended with biosolids and sewage sludge (Table 1.5). Most studies were conducted in North America (USA) and Europe (i.e., Spain and UK) (Table 1.5). Unlike studies conducted in manure-amended agricultural lands, these studies comprised a wide range of ECs, such as antimicrobials, antibiotics, anticonvulsants, and stimulants (Table 1.5).

Limited studies examined ECs in agricultural lands receiving wastewater irrigation, such as in Israel and China (Table 1.5).

It is unviable to compare the emerging contamination level on agricultural lands amended by various biowastes, such as biosolids, manure, and wastewater irrigation. Most studies focus on compounds suspected of being the source, such as veterinary antibiotics in soils amended with manure, whereas biosolid studies focus on additional compounds, such as antibacterial and anticonvulsants.

The concentration levels of ECs in agricultural lands vary (Table 1.5). The variation is observed not only among countries but also within the same country or region. For example, triclosan concentration levels ranged from 4.1 to 66.6 (Lozano et al., 2010), 2.7 - 4.4 (Sherburne et al., 2016), and 96 - 160 ng g^{-1} (dry weight) (Kinney et al., 2008) in various biosolids and sewage sludge-amended agricultural lands around the United States of America.

Table 1. 5: Emerging contaminants in agricultural lands around the globe

Contaminant	Class	Concentration (ng/g dry wt.)	Country	Fertiliser used	Reference
Triclosan	Antimicrobial	4.1 - 66.6	USA	Biosolids/sludge	(Lozano et al., 2010)
		< LOD - 1.02	USA	Biosolids/sludge	(Cha & Cupples, 2009)
		2.7 - 4.4	USA	Biosolids/sludge	(Sherburne et al., 2016)
		0.8 - 4.7	Spain	Biosolids/sludge	(Sanchez-Brunete et al., 2010)
		96 - 160	USA	Manure/Biosolids/sludge	(Kinney et al., 2008)
		≤ 948.6	UK	Biosolids/sludge	(Butler et al., 2012)
Methyl triclosan	Triclosan metabolite	≤ 2.19	UK	Biosolids/sludge	(Butler et al., 2012)
		0.3 - 3.8	Spain	Biosolids/sludge	(Sanchez-Brunete et al., 2010)
Triclocarban	Antimicrobial	1.20 - 65.10	USA	Biosolids/sludge	(Cha & Cupples, 2009)
		14.8 - 27.3	USA	Biosolids/sludge	(Sherburne et al., 2016)
		131.9[a]	USA	Biosolids/sludge	(Lozano et al., 2018)
Caffeine	Stimulant	ND	USA	Manure/Biosolids/sludge	(Kinney et al., 2008)
		≤ 15	Israel	Wastewater irrigated	(Malchi et al., 2014)
Carbamazepine	Anticonvulsant	ND	USA	Manure/Biosolids/sludge	(Kinney et al., 2008)
		≤ 44.2	USA	Biosolids/sludge	(Wu et al., 2010)
		0.5 - 15	Israel	Wastewater irrigated	(Goldstein et al., 2014)
		≤ 7.0	Israel	Wastewater irrigated	(Malchi et al., 2014)
Trimethoprim	Antibiotics	< LOD	USA	Manure/biosolids/sludge	(Kinney et al., 2008)
		< LOD - 109.6	China	Manure	(Hou et al., 2015)
Galaxolide	Synthetic musk	ND - 2770	USA	Manure/Biosolids/sludge	(Kinney et al., 2008)
Tonalide	Synthetic musk	ND - 773	USA	Manure/Biosolids/sludge	(Kinney et al., 2008)
Tetracycline	Antibiotics	2.5 - 105	China	Manure	(Hu et al., 2010)
		0.9 - 249	China	Manure	(H. Zhang et al., 2016)

Contaminant	Class	Concentration (ng/g dry wt.)	Country	Fertiliser used	Reference
		2.3 - 152. 9	China	Manure	(Hou et al., 2015)
		≤ 10207	China	Manure	(Wei et al., 2016)
		ND - 74	China	Manure	(Li et al., 2011)
		≤ 60.44	China	Manure	(Wei et al., 2019)
		0.16 - 25.66	China	Manure	(Xiang et al., 2016)
		≤ 21.9	China	Wastewater irrigated	(Pan et al., 2014)
Diclofenac	NSAIDs	≤ 0.1	Israel	Wastewater irrigated	(Malchi et al., 2014)
Naproxen	NSAIDs	≤ 5.0	Israel	Wastewater irrigated	(Goldstein et al., 2014)
	NSAIDs	≤ 0.05	Israel	Wastewater irrigated	(Malchi et al., 2014)
Chlortetracycline	Antibiotics	ND - 1079	China	Manure	(Hu et al., 2010)
		1.3 - 101.5	China	Manure	(H. Zhang et al., 2016)
		4.9 - 10967.1	China	Manure	(Hou et al., 2015)
		≤ 86567	China	Manure	(Wei et al., 2016)
		ND - 105	China	Manure	(Li et al., 2011)
		≤ 222	China	Manure	(Wei et al., 2019)
		0.29 - 161.5	China	Manure	(Xiang et al., 2016)
		70 - 100	Turkey	Manure	(Karci & Balcioglu, 2009)
Chlortetracycline	Antibiotics	≤ 1.0	USA	Manure	(Hamscher et al., 2002)
Ibuprofen	NSAIDs	≤ 0.02	Israel	Wastewater irrigated	(Goldstein et al., 2014)
	NSAIDs	≤ 0.2	Israel	Wastewater irrigated	(Malchi et al., 2014)
Oxytetracycline	Antibiotics	< LOD - 2683	China	Manure	(Hu et al., 2010)
		1.0 - 8400	China	Manure	(H. Zhang et al., 2016)
		< LOQ - 571.4	China	Manure	(Hou et al., 2015)

Contaminant	Class	Concentration (ng/g dry wt.)	Country	Fertiliser used	Reference
		≤ 3676	China	Manure	(Wei et al., 2016)
		ND - 80	China	Manure	(Li et al., 2011)
		171[a]	Italy	Manure	(Brambilla et al., 2007)
		≤ 415	China	Manure	(Wei et al., 2019)
		0.04 - 31.85	China	Manure	(Xiang et al., 2016)
		4 - 112	China	Wastewater irrigated	(Chen et al., 2014)
		40 - 500	Turkey	Manure	(Karci & Balcioglu, 2009)
Sulfamethoxazole	Antibiotics	0.03 - 0.9	China	Manure	(Hu et al., 2010)
		ND - 3.1	China	Manure	(H. Zhang et al., 2016)
		< LOD - 58.1	China	Manure	(Hou et al., 2015)
		≤ 1784	China	Manure	(Wei et al., 2016)
		ND - 55	China	Manure	(Li et al., 2011)
		≤ 9.29	China	Manure	(Wei et al., 2019)
		16 - 90	China	Wastewater irrigated	(Chen et al., 2014)
Sulfamethoxazole	Antibiotics	≤ 5	Israel	Wastewater irrigated	(Goldstein et al., 2014)
		≤ 0.25	Israel	Wastewater irrigated	(Malchi et al., 2014)
Sulphadiazine	Antibiotics	ND - 20.1	China	Manure	(H. Zhang et al., 2016)
		< LOD - 3.2	China	Manure	(Hou et al., 2015)
		≤ 682	China	Manure	(Wei et al., 2016)
		ND - 86	China	Manure	(Li et al., 2011)
		≤ 0.67	China	Manure	(Wei et al., 2019)
Sulfathiazole	Antibiotics	50 - 400	Turkey	Manure	(Karci & Balcioglu, 2009)
Sulfadimethoxine	Antibiotics	ND - 40.4	China	Manure	(Li et al., 2011)
Sulfachlorpyridazine	Antibiotics	0.18 - 2.5	China	Manure	(Hu et al., 2010)
		40 - 100	Turkey	Manure	(Karci & Balcioglu, 2009)
Sulfamethazine	Antibiotics	0.3 - 4.3	China	Manure	(H. Zhang et al., 2016)
		≤ 1688	China	Manure	(Wei et al., 2016)

Contaminant	Class	Concentration (ng/g dry wt.)	Country	Fertiliser used	Reference
		ND - 74	China	Manure	(Li et al., 2011)
		≤ 2.48	China	Manure	(Wei et al., 2019)
		≤ 4.4	China	Wastewater irrigated	(Pan et al., 2014)
Ofloxacin	Antibiotics	< LOD -1.6	China	Manure	(Hu et al., 2010)
		1.1 - 66.5	China	Manure	(H. Zhang et al., 2016)
		< LOD - 115.1	China	Manure	(Hou et al., 2015)
Ciprofloxacin	Antibiotics	0.8 - 30.1	China	Manure	(Hu et al., 2010)
		0.3 - 145.5	China	Manure	(H. Zhang et al., 2016)
		< LOD - 83.2	China	Manure	(Hou et al., 2015)
		≤ 7220	China	Manure	(Wei et al., 2016)
		5.3 - 120	China	Manure	(Li et al., 2011)
		≤ 140	China	Manure	(Wei et al., 2019)
Gemfibrozil	Lipid regulator	≤ 0.1	Israel	Wastewater irrigated	(Goldstein et al., 2014)
		≤ 0.1	Israel	Wastewater irrigated	(Malchi et al., 2014)
Clofibric acid	Lipid regulator	≤ 5.0	Israel	Wastewater irrigated	(Goldstein et al., 2014)
		≤ 0.1	Israel	Wastewater irrigated	(Malchi et al., 2014)
Enrofloxacin	Antibiotics	0.2 - 333.5	China	Manure	(H. Zhang et al., 2016)
		< LOD - 96.4	China	Manure	(Hou et al., 2015)
		≤ 3059	China	Manure	(Wei et al., 2016)
		5.1 - 1348	China	Manure	(Li et al., 2011)
Enrofloxacin		≤ 141	China	Manure	(Wei et al., 2019)
		20 - 70	Turkey	Manure	(Karci & Balcioglu, 2009)
Lincomycin	Antibiotics	ND - 11.7	China	Manure	(Hu et al., 2010)

Contaminant	Class	Concentration (ng/g dry wt.)	Country	Fertiliser used	Reference
Bezafibrate	Lipid regulator	≤ 0.25	Israel	Wastewater irrigated	(Malchi et al., 2014)
Norfloxacin	Antibiotics	14.9 - 150.2	China	Manure	(Li et al., 2011)
		≤ 66.7	China	Wastewater irrigated	(Pan et al., 2014)
Erythromycin	Antibiotics	< LOD - 7.2	China	Manure	(Hou et al., 2015)
		≤ 4.4	China	Wastewater irrigated	(Pan et al., 2014)
Perfloxacin	Antibiotics	< LOD	China	Manure	(Hu et al., 2010)
Roxithromycin	Antibiotics	0.1 - 5.0	China	Manure	(H. Zhang et al., 2016)
		< LOD - 96.3	China	Manure	(Hou et al., 2015)

ND not detected; LOD limit of detection; wt weight; [a] average concentration; LOQ limit of quantification; NSAIDs nonsteroidal anti-inflammatory drugs

Emerging contaminants in South African agricultural lands and their prevalence

Limited studies were conducted to determine the status of ECs in South African agricultural lands. This has left several questions, such as: what is the status of ECs in South African agricultural lands? Is the contamination level in South African agricultural lands similar to that reported in other countries? What are the ecotoxicological risks associated with the concentration levels of ECs discovered in South African agricultural lands, if any?

Most studies conducted in South Africa focused on ECs in non-agricultural lands (Chokwe et al., 2019; Chokwe et al., 2017; Chokwe et al., 2016; Gumbi et al., 2022; Matongo et al., 2015a). Table 1.6 presents ECs detected in South African non-agricultural soils. The concentration levels of ECs in non-agricultural soils and sediments were investigated up to 40 cm of the earth's surface. No attempts have been made to examine the correlation between soil samples and groundwater for ECs.

Table 1. 6: Emerging contaminants of South African soil samples collected from golf-course and river sediment

Contaminant	Concentration (ng/g dry wt.)	Matrix and site	Maximum sampling depth (cm)	Province	Reference
Triclosan	≤ 3.0	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
Aspirin	≤ 1.5	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
	≤ 427	River sediment	25	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
Ibuprofen	1.0 - 8.9	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
	≤ 41.41	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	≤ 9.56	River sediment	25	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
Ketoprofen	≤ 57.4	River sediment	25	KwaZulu-Natal	(Ademoyegun et al., 2020b)
DEET	ND	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
Caffeine	≤ 6.0	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
	≤ 224.35	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	≤ 1.32	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015b)
Carbamazepine	1.5 - 3.6	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
	≤ 2.23	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	≤ 3.0	River sediment	30	KwaZulu-Natal	(Rimayi et al., 2018)
	≤ 6.07	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015b)
Trimethoprim	ND	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
	ND	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	≤ 87.55	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015b)
Diclofenac	ND	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
	≤ 309	River sediment	25	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
Acetaminophen	≤ 4.2	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
	≤ 8.92	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	≤ 15.8	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015b)

Contaminant	Concentration (ng/g dry wt.)	Matrix and site	Maximum sampling depth (cm)	Province	Reference
Ampicillin	≤ 369	River sediment	25	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
Chloramphenicol	0.5 - 2.2	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
Diazepam	ND	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
Doxycycline	≤ 2.5	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
Codeine	ND	Soil from golf-course	40	Eastern Cape	(Ademoyegun et al., 2020b)
Sulfamethoxazole	≤ 50.73	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	< LOD	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015b)
Erythromycin	≤ 1.57	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	< LOD	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015b)
Clozapine	≤ 26.65	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	≤ 17.89	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015b)
Sulfamethazine	ND	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
	ND	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015b)
Metronidazole	≤ 61.93	River sediment	10	KwaZulu-Natal	(Matongo et al., 2015a)
Ciprofloxacin	≤ 183	River sediment	25	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
Bezafibrate	≤ 80.3	River sediment	25	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
Nevirapine	ND - 81	River sediment	30	KwaZulu-Natal	(Rimayi et al., 2018)
Efavirenz	ND - 3.0	River sediment	30	KwaZulu-Natal	(Rimayi et al., 2018)
Lamivudine	≤ 0.6	River sediment	30	KwaZulu-Natal	(Rimayi et al., 2018)
Emtricitabine	≤ 1.0	River sediment	30	KwaZulu-Natal	(Rimayi et al., 2018)
Tenofovir disoproxil	≤ 0.3	River sediment	30	KwaZulu-Natal	(Rimayi et al., 2018)
Naphthalene	ND - 652	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
	≤ 500	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Acenaphthylene	ND - 816	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)

Contaminant	Concentration (ng/g dry wt.)	Matrix and site	Maximum sampling depth (cm)	Province	Reference
	≤ 1541	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Acenaphthene	ND - 731	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
	≤ 1135	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Fluorene	ND - 1380	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
	≤ 2160000	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Anthracene	ND - 749	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
Phenanthrene	ND - 476	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
	≤ 778	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Fluoranthene	ND - 456	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
	≤ 15470	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Pyrene	ND - 923	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
	≤ 961	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Benzo(a)anthracene	56.94 - 1490	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
Chrysene	ND - 1015	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
Benzo(b)fluoranthene	33.49 - 1107	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)
	≤ 10740	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Benzo(k)fluoranthene	ND - 772	River sediment		Not specified	Eastern Cape
(Adeniji et al., 2019)	**Benzo(a)pyrene**	ND - 351	River sediment	Not specified	Eastern Cape
(Adeniji et al., 2019)	≤ 3859	River sediment	Not specified	Limpopo	(Edokpayi et al., 2016)
Dibenzo(a,h)anthracene	ND - 2799	River sediment	Not specified	Eastern Cape	(Adeniji et al., 2019)

ND not detected; wt weight; LOD limit of detection

Human and environmental risks from emerging contaminants in agricultural lands

The literature failed to identify the human and environmental risks associated with ECs in South African agricultural lands, owing to a lack of information; however, several studies globally were conducted on this topic (Prosser & Sibley, 2015), as presented in the succeeding subsections.

Human health risks from emerging contaminants in agricultural lands

Human health risks from the presence of ECs in agricultural lands are measured using the maximum EC concentrations in the edible tissues of plants (Prosser & Sibley, 2015). The potential human health hazard of a contaminant is estimated based on the hazard quotient (HQ) ratio—the ratio between the acceptable daily intake (ADI) and the estimated daily intake (EDI) of a contaminant (Prosser & Sibley, 2015). The contaminant concentration level in plant tissue is potentially hazardous to human health when its HQ ratio is ≥ 0.1 (USEPA, 2008).

Studies are contradicting (Aryal & Reinhold, 2011; Holling et al., 2012; Sabourin et al., 2012; Wu et al., 2010). For example, Sabourin et al. (2012) detected atenolol, ciprofloxacin, and naproxen in tomato, carrot, and corn plants grown in biosolids amended agricultural soils at concentration levels of up to 5.57, 2.15, and 0.8 ng g^{-1} dry weight, respectively. Their calculated HQ ratios were 0.01, 0.0001, and 0.0001 in tomato, carrot, and corn, respectively (Prosser & Sibley, 2015), which were far below the HQ limit of 0.1, indicating no/low risk to humans.

Studies, however, are reporting high concentration levels of ECs in edible plant tissues with potential risks to human health (Aryal & Reinhold, 2011; Holling et al., 2012; C. Wu et al., 2012). For example, C. Wu et al. (2012) detected carbamazepine concentration levels of up to 800 ng g^{-1} (dry weight) in collards (*Brassica oleracea*) grown in biosolids amended soils. The calculated HQ ratios were 0.8 and 0.2 for toddlers and adults, respectively (Prosser & Sibley, 2015). The aforementioned studies emphasise that human health risks through trophic level transfer from crops in agricultural lands depend on the concentration levels of the contaminant in the edible tissues and the ADI.

Environmental risks from emerging contaminants in agricultural lands

The literature suggests that ECs in agricultural lands may present a potential risk to the environment, such as interference with the nutrient cycle (Butler et al., 2011; Waller &

Kookana, 2009) and plant toxicity (Michelini et al., 2012). For example, soil triclosan concentration levels of up to 10 mg Kg^{-1} inhibited soil respiration (Butler et al., 2011; Waller & Kookana, 2009). Sulphadiazine soil concentration levels between 10 and 200 mg Kg^{-1} (spiked concentrations) caused maize (*Zea mays*) plant death (Michelini et al., 2012).

1.2.3 Emerging contaminants content status in surface and groundwater

Surface freshwater and groundwater are deteriorating owing to pollution caused by anthropogenic actions. ECs are one of the most concerning pollutants, also deteriorating surface and groundwater resource quality. The global and local (South African) EC concentration status of surface and groundwater is presented below.

The global status of emerging contaminants in surface and groundwater

Several studies investigated the status of ECs in surface and groundwater bodies globally (Barnes et al., 2008; Nannou et al., 2015; Peng et al., 2014). Studies detected a wide range of ECs globally (Table 1.7**Error! Reference source not found.**). This indicates the extent of pollution in the water resources and the threat to aquatic organisms and humans.

The most highly detected compound in groundwater was the insecticide diethyltoluamide (DEET), detected in the USA at a concentration level of 13500 ng L^{-1} (Table 1.7). In surface water, the most highly detected compound is acetaminophen at concentration levels up to 4460 ng L^{-1} (Table 1.7).

It is complex to identify the water environment (surface water or groundwater) with high concentration levels of ECs, owing to their non-uniformity in these environments; however, previous studies reported higher concentration levels in surface water than in groundwater (Lopez-Serna et al., 2013). This is linked to the subsurface flow and transport of ECs within the soil (Barnes et al., 2008).

Table 1. 7: Emerging contaminants in global surface and groundwater

Compound	Concentration (ng/L)	Water Environment (Location)	Country	Reference
Paracetamol	ND - 156	Surface (river and lake)	Greece	(Nannou et al., 2015)
	354 - 4460	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	≤ 380	Groundwater	USA	(Barnes et al., 2008)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
DEET	≤ 13500	Groundwater	USA	(Barnes et al., 2008)
	≤ 13000	Groundwater	USA	(Bernes et al., 2007)
	≤ 1130	surface (river)	USA	(Kolpin et al., 2002)
	≤ 1.8	Groundwater	Zambia	(Sorensen et al., 2015)
Diclofenac	ND - 457	Surface (river and lake)	Greece	(Nannou et al., 2015)
	268 - 1398	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	35 - 477	Groundwater	Spain	(Teijon et al., 2010)
	< LOQ	Groundwater	China	(Peng et al., 2014)
	≤ 3.14	Groundwater	Spain	(Lopez-Serna et al., 2013)
	32.0 - 71	Surface (river)	Denmark	(Matamoros et al., 2012)
Ibuprofen	ND - 1351	Surface (river and lake)	Greece	(Nannou et al., 2015)
	184 - 1106	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	< LOD – 185	Groundwater	Spain	(Teijon et al., 2010)
	≤ 57.9	Groundwater	China	(Peng et al., 2014)

Compound	Concentration (ng/L)	Water Environment (Location)	Country	Reference
	≤ 988	Groundwater	Spain	(Lopez-Serna et al., 2013)
	≤ 3110	Groundwater	USA	(Barnes et al., 2008)
	9.0 – 22	surface (river)	Denmark	(Matamoros et al., 2012)
Naproxen	732 – 4880	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	145 – 263	Groundwater	Spain	(Teijon et al., 2010)
	≤ 86.9	Groundwater	China	(Peng et al., 2014)
	< LOQ	Groundwater	Spain	(Lopez-Serna et al., 2013)
	17 – 36	Surface (river)	Denmark	(Matamoros et al., 2012)
Iopamidol	6 – 396	Groundwater	Spain	(Teijon et al., 2010)
Iopromide	462 – 687	Groundwater	Spain	(Teijon et al., 2010)
Indomethacin	ND	Surface (river and lake)	Greece	(Nannou et al., 2015)
	≤ 362	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	≤ 11.5	Groundwater	China	(Peng et al., 2014)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Ketoprofen	ND – 91	Surface (river and lake)	Greece	(Nannou et al., 2015)
	< LOQ - 215	Groundwater	Spain	(Lopez-Serna et al., 2013)
	≤ 6	Surface (river)	Denmark	(Matamoros et al., 2012)

Compound	Concentration (ng/L)	Water Environment (Location)	Country	Reference
Sulfamethazine	ND	Surface (river and lake)	Greece	(Nannou et al., 2015)
	6 – 446	Groundwater	Spain	(Teijon et al., 2010)
	ND	Groundwater	China	(Peng et al., 2014)
	≤ 360	Groundwater	USA	(Barnes et al., 2008)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Sulfadiazine	ND	Groundwater	China	(Peng et al., 2014)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Cholesterol	≤ 1730	Groundwater	USA	(Barnes et al., 2008)
Naphthalene	≤ 1510	Groundwater	USA	(Barnes et al., 2008)
Sulfamethizole	ND	Groundwater	USA	(Barnes et al., 2008)
Tetracycline	ND	Groundwater	USA	(Barnes et al., 2008)
	< LOQ	Groundwater	Spain	(Lopez-Serna et al., 2013)
Oxytetracycline	ND	Groundwater	USA	(Barnes et al., 2008)
	≤ 12.2	Groundwater	Spain	(Lopez-Serna et al., 2013)
Doxycycline	ND	Groundwater	USA	(Barnes et al., 2008)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Chlortetracycline	ND	Groundwater	USA	(Barnes et al., 2008)
Sulfamethoxazole	ND - 190	Surface (river and lake)	Greece	(Nannou et al., 2015)
	76 - 722	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	2 – 117	Groundwater	Spain	(Teijon et al., 2010)
	≤ 124.5	Groundwater	China	(Peng et al., 2014)
	≤ 1110	Groundwater	USA	(Barnes et al., 2008)
	≤ 65	Groundwater	Spain	(Lopez-Serna et al., 2013)

Compound	Concentration (ng/L)	Water Environment (Location)	Country	Reference
Sulphathiazole	ND	Groundwater	USA	(Barnes et al., 2008)
Trimethoprim	34 - 120	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	≤ 10.5	Groundwater	China	(Peng et al., 2014)
	ND	Groundwater	USA	(Barnes et al., 2008)
	< LOQ	Groundwater	Spain	(Lopez-Serna et al., 2013)
Ciprofloxacin	ND - 115	Surface (river and lake)	Greece	(Nannou et al., 2015)
	ND	Groundwater	China	(Peng et al., 2014)
	ND	Groundwater	USA	(Barnes et al., 2008)
Erythromycin	ND - 137	Surface (river and lake)	Greece	(Nannou et al., 2015)
	≤ 12.4	Groundwater	China	(Peng et al., 2014)
	ND	Groundwater	USA	(Barnes et al., 2008)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Carbamazepine	ND - 406	Surface (river and lake)	Greece	(Nannou et al., 2015)
	8 – 276	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	2 – 118	Groundwater	Spain	(Nannou et al., 2015)
	≤ 38.6	Groundwater	Spain	(Lopez-Serna et al., 2013)
	12.0 - 38	Surface (river)	Denmark	(Matamoros et al., 2012)
Caffeine	124 - 3508	Surface (river and lake)	Greece	(Nannou et al., 2015)
	4 – 505	Groundwater	Spain	(Teijon et al., 2010)
	≤ 130	Groundwater	USA	(Barnes et al., 2008)
	≤ 0.17	Groundwater	Zambia	(Sorensen et al., 2015)
	65 - 382	Surface (river)	Denmark	(Matamoros et al., 2012)
Gemfibrozil	ND - 200	Surface (river and lake)	Greece	(Nannou et al., 2015)
	9 – 368	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	ND	Groundwater	China	(Peng et al., 2014)
	ND	Groundwater	USA	(Barnes et al., 2008)
	12 – 574	Groundwater	Spain	(Teijon et al., 2010)
	≤ 0.82	Groundwater	Spain	(Lopez-Serna et al., 2013)

Compound	Concentration (ng/L)	Water Environment (Location)	Country	Reference
Bezafibrate	< LOQ	Surface (river and lake)	Greece	(Nannou et al., 2015)
	≤ LOQ	Groundwater	Spain	(Lopez-Serna et al., 2013)
	≤ 2100	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	ND	Groundwater	China	(Peng et al., 2014)
Methylparaben	≤ 5000	Groundwater	China	(Peng et al., 2014)
Fenofibrate	ND – 91	Surface (river and lake)	Greece	(Nannou et al., 2015)
	≤ 22.3	Groundwater	Spain	(Lopez-Serna et al., 2013)
Mefenamic acid	< LOQ	Surface (river and lake)	Greece	(Nannou et al., 2015)
	≤ 64.3	Groundwater	Spain	(Lopez-Serna et al., 2013)
Salicylic acid	≤ 3001	Surface (river and lake)	Greece	(Nannou et al., 2015)
	≤ 664	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	≤ 2014.7	Groundwater	China	(Peng et al., 2014)
	≤ 147	Groundwater	China	(Lopez-Serna et al., 2013)
Bisphenol A	≤ 160.3	Groundwater	China	(Peng et al., 2014)
	≤ 2550	Groundwater	USA	(Barnes et al., 2008)
	4.0 – 31	Surface (river)	Denmark	(Matamoros et al., 2012)
Triclocarban	≤ 36.2	Groundwater	China	(Peng et al., 2014)
Triclosan	ND - 150	Surface (river and lake)	Greece	(Nannou et al., 2015)
	≤ 39.9	Groundwater	China	(Peng et al., 2014)
	0.03	Groundwater	Zambia	(Sorensen et al., 2015)
	10.0 - 60	Surface (river)	Denmark	(Matamoros et al., 2012)
Atenolol	< LOQ	Surface (river and lake)	Greece	(Nannou et al., 2015)
	4 – 32	Surface (river)	Mexico	(Rivera-Jaimes et al., 2018)
	18 – 106	Groundwater	Spain	(Teijon et al., 2010)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Codeine	ND	Groundwater	USA	(Barnes et al., 2008)
	106 - 3483	Groundwater	Spain	(Teijon et al., 2010)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)

Compound	Concentration (ng/L)	Water Environment (Location)	Country	Reference
Oestriol	< LOQ	Surface (river and lake)	Greece	(Nannou et al., 2015)
Ofloxacin	4 – 48	Groundwater	Spain	(Teijon et al., 2010)
	≤ 44.2	Groundwater	China	(Peng et al., 2014)
	≤ 43.3	Groundwater	Spain	(Lopez-Serna et al., 2013)
Cotinine	< LOD	Groundwater	USA	(Barnes et al., 2008)
Nicotine	11 – 144	Groundwater	Spain	(Teijon et al., 2010)
Fluoxetine	≤ 56	Groundwater	USA	(Barnes et al., 2008)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Sarafloxacin	ND	Groundwater	USA	(Barnes et al., 2008)
Roxithromycin	ND	Groundwater	USA	(Barnes et al., 2008)
	ND	Groundwater	China	(Peng et al., 2014)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Lincomycin	≤ 320	Groundwater	USA	(Barnes et al., 2008)
Enrofloxacin	ND	Groundwater	USA	(Barnes et al., 2008)
	ND	Groundwater	China	(Peng et al., 2014)
	≤ 65.2	Groundwater	Spain	(Lopez-Serna et al., 2013)
Clofibric acid	≤ 73.9	Groundwater	China	(Peng et al., 2014)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)
Tonalide	8.0 – 10	Surface (river)	Denmark	(Matamoros et al., 2012)
Galaxolide	2 – 359	Groundwater	Spain	(Teijon et al., 2010)
	15 – 28	Surface (river)	Denmark	(Matamoros et al., 2012)

Compound	Concentration (ng/L)	Water Environment (Location)	Country	Reference
Phenazone	ND - 95	Surface (river and lake)	Greece	(Nannou et al., 2015)
Salbutamol	ND	Groundwater	USA	(Barnes et al., 2008)
Tylosin	ND	Groundwater	USA	(Barnes et al., 2008)
	ND	Groundwater	Spain	(Lopez-Serna et al., 2013)

ND not detected; LOD limit of detection; LOQ limit of quantification

The emerging contaminants status of South African surfaces and groundwaters

Several authors reported ECs in the South African surface and groundwater resources (Archer et al., 2017; Omotola & Olatunji, 2020; Rimayi et al., 2018). Various studies reported the occurrence and concentration levels of ECs in surface water bodies (Table 1.8). This could be attributable to easier monitoring of surface water contamination (i.e., sampling, identifying sources, pollution etc.) compared to groundwater. Research on contamination must be prioritised in South Africa considering that half of the population consumes groundwater (WRC, 2017).

A wide range of ECs is detected in South African water environments. These include antiretroviral (ARV) drugs, pesticides, antibiotics, nonsteroidal anti-inflammatory drugs (NSAIDs), and stimulants (Table 1.8). NSAIDs are one of the most studied EC groups in South African water environments. NSAIDs are used as pain killers, prescribed with other medication to most patients; therefore, scientists suspected they might be ubiquitous in the environment. Up to 40% of NSAIDs were prescribed in South Africa between 2009 and 2013 for patients suffering from kidney disease alone (Meuwesen et al., 2016). This signifies the extent of NSAID prescriptions in South Africa; therefore, the motivation for South African studies to suspect their availability in the environment. Another well-studied EC group in South African water environments is ARV drugs. South Africa has a high consumption of ARV drugs, compared globally (WHO, 2022).

A profoundly detected group of ECs in South African water environments are NSAIDs with ibuprofen as prominent with reported concentration levels of 85000 ng L^{-1} in surface water (Matongo et al., 2015b).

Table 1. 8: Emerging contaminants of local (South African) surface and groundwater

Compound	Class	Concentration (ng/L)	Water environment (location)	Province	Reference
Nevirapine	ARV	8.0 - 13	Groundwater	Gauteng	(Rimayi et al., 2018)
		25 - 40	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 68	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
Efavirenz	ARV	2.0 - 5	Groundwater	Gauteng	(Rimayi et al., 2018)
		10 - 62	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 138	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
Lamivudine	ARV	ND	Groundwater	Gauteng	(Rimayi et al., 2018)
		ND	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 0.15	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
Emtricitabine	ARV	ND	Groundwater	Gauteng	(Rimayi et al., 2018)
		ND	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 8	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
Tenofovir disoproxil	ARV	ND	Groundwater	Gauteng	(Rimayi et al., 2018)
		ND	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		ND	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
Carbamazepine	Anticonvulsant	6.0 - 13	Groundwater	Gauteng	(Rimayi et al., 2018)
		19 - 39	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 94	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
		(279.5)[a], (157.1)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Methocarbamol	Muscle relaxant	≤ 0.15	Groundwater	Gauteng	(Rimayi et al., 2018)
		6.0 - 33	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 3	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)

Compound	Class	Concentration (ng/L)	Water environment (location)	Province	Reference
Etilefrine HCL	Stimulant	ND	Groundwater	Gauteng	(Rimayi et al., 2018)
		ND	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		ND	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
Venlafaxine HCL	Stimulant	ND	Groundwater	Gauteng	(Rimayi et al., 2018)
		ND - 2	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 1	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
Bromacil	Pesticide	ND	Groundwater	Gauteng	(Rimayi et al., 2018)
		4.0 - 7	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 10	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
p-Chloroaniline	Pesticide	ND	Groundwater	Gauteng	(Rimayi et al., 2018)
		ND	Surface (Dam)	Gauteng	(Rimayi et al., 2018)
		≤ 0.76	Surface (River)	KwaZulu-Natal	(Rimayi et al., 2018)
Methylparaben	Paraben	(146.1)[a], (58.7)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Bisphenol A	Plasticizer	(396.4)[a], (239.0)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Sulfamethoxazole	Antibiotic	(1013.2)[a], (757.4)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Trimethoprim	Antibiotics	(898.7)[a], (383.0)b	Surface (River)	Gauteng	(Archer et al., 2017)
Acetaminophen	NSAIDs	(63.7)[a], (20.8)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Diclofenac	NSAIDs	(1461.5)[a], (467.4)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
		≤ 82	Surface (River)	Gauteng	(Mhuka et al., 2020)
		≤ 51940	Surface (River)	KwaZulu-Natal	(Omotola & Olatunji, 2020)
		≤ 3670	Surface (Not specified)	Western Cape	(Fatoki et al., 2018)
		≤ 2580	Surface (River)	KwaZulu-Natal	(Madikizela et al., 2017)

Compound	Class	Concentration (ng/L)	Water environment (location)	Province	Reference
		≤ 1010	Surface (River)	KwaZulu-Natal	(Gumbi et al., 2017)
		≤ 1200	Surface (River)	KwaZulu-Natal	(Sibeko et al., 2019)
		≤ 5300	Surface (River)	KwaZulu-Natal	(Madikizela & Chimuka, 2017)
		< LOQ	Surface (River)	KwaZulu-Natal	(Madikizela & Chimuka, 2016)
		≤ 10000	Surface (River)	KwaZulu-Natal	(Hlengwa & Mahlambi, 2020)
		≤ 8170	Surface (River)	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
Ibuprofen	NSAIDs	(312.1)[a], (153.3)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
		≤ 12800	Surface (River)	Gauteng	(Mhuka et al., 2020)
		≤ 278	Surface (River)	KwaZulu-Natal	(Ngubane et al., 2019)
		≤ 2570	Surface (River)	KwaZulu-Natal	(Gumbi et al., 2017)
Ibuprofen	NSAIDs	≤ 6720	Surface (River)	KwaZulu-Natal	(Madikizela et al., 2017)
		ND	Surface (River)	Eastern Cape	(Vumazonke et al., 2020)
		≤ 1400	Surface (River)	KwaZulu-Natal	(Sibeko et al., 2019)
		445 - 689	Surface (River)	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
		≤ 11000	Surface (River)	KwaZulu-Natal	(Madikizela & Chimuka, 2017)
		≤ 85000	Surface (River)	KwaZulu-Natal	(Matongo et al., 2015b)
		≤ 28900	Surface (River)	KwaZulu-Natal	(Hlengwa & Mahlambi, 2020)

Compound	Class	Concentration (ng/L)	Water environment (location)	Province	Reference
		≤ 11400	Surface (River)	KwaZulu-Natal	(Madikizela & Chimuka, 2016)
Ketoprofen	NSAIDs	(330.3)[a], (642.2)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
		≤ 39	Surface (River)	Gauteng	(Mhuka et al., 2020)
		≤ 437	Surface (River)	KwaZulu-Natal	(Agunbiade & Moodley, 2016)
		≤ 9220	Surface (River)	KwaZulu-Natal	(Gumbi et al., 2017)
Naproxen	NSAIDs	(1112.8)[a], (224.3)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
		≤ 355	Surface (River)	KwaZulu-Natal	(Ngubane et al., 2019)
		≤ 9710	Surface (River)	KwaZulu-Natal	(Hlengwa & Mahlambi, 2020)
Naproxen	NSAIDs	≤ 680	Surface (River)	KwaZulu-Natal	(Madikizela & Chimuka, 2016)
		≤ 2770	Surface (River)	KwaZulu-Natal	(Madikizela et al., 2017)
		≤ 3800	Surface (River)	KwaZulu-Natal	(Madikizela & Chimuka, 2017)
		< LOQ	Surface (River)	KwaZulu-Natal	(Gumbi et al., 2017)
		≤ 487	Surface (River)	Gauteng	(Mhuka et al., 2020)
Fenoprofen	NSAIDs	≤ 10500	Surface (River)	KwaZulu-Natal	(Hlengwa & Mahlambi, 2020)
		≤ 418	Surface (River)	Gauteng	(Mhuka et al., 2020)
Iopromide	X-ray contrast	(598.3)[a], (265.8)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Atenolol	Beta-blocker	(272.0)[a], (156.2)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Metformin	Diabetes	(174.6)[a], (73.3)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Fluoxetine	Antidepressant	(109.2)[a], (34.4)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Codeine	Analgesic	(128.9)[a], (11.3)[b]	Surface (River)	Gauteng	(Archer et al., 2017)

Compound	Class	Concentration (ng/L)	Water environment (location)	Province	Reference
Nicotine	Stimulant	(245.5)[a], (154.3)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Cotinine	Nicotine metabolite	(31.7)[a], (25.5)[b]	Surface (River)	Gauteng	(Archer et al., 2017)
Caffeine	Stimulant	(2077.5)[a], (812.2)[b]	Surface (River)	Gauteng	(Archer et al., 2017)

[a] downstream mean; [b] upstream mean; NSAIDs nonsteroidal anti-inflammatory drugs; LOQ limit of quantification; ARV antiretroviral drugs; ND not detected

Human and environmental risks from emerging contaminants in South African water environments

Limited studies determined the environmental risks associated with the concentration levels of ECs in South African surface water environments (Gani et al., 2021; Madikizela & Ncube, 2021). Environmental risk is determined using the risk quotient (RQ) ratio derived from the maximum reported concentration levels of ECs (such as from South African surface water) and the predicted no-effect concentration levels of the most sensitive test organisms discovered in aquatic environments (Gani et al., 2021). RQ values of less than 0.1, between 0.1 and 1, and above 1 were less risk, medium risk, and high risk, respectively (Gani et al., 2021; Madikizela & Ncube, 2021).

Several aquatic organisms, including fish, crustaceans, and algae, were selected as test organisms (Gani et al., 2021; Madikizela & Ncube, 2021). Test organisms from South African water bodies exhibited varying RQ values and risk levels from ECs. A concentration of ibuprofen up to 689 ng L^{-1} in river water was associated with medium risks to algae (RQ = 0.12) (Madikizela & Ncube, 2021); however, the same concentration had a lower risk to fish (RQ = 0.004). In South Africa, NSAIDs were identified as one group of compounds with high concentration levels in water environments (Table 1.7), with the highest risk to aquatic organisms; of these, ibuprofen (Madikizela & Ncube, 2021) and diclofenac (Gani et al., 2021) were identified as the compounds with the highest risk.

1.3 Dynamics and transfer of emerging contaminants within the soil-plant-water continuum

Once ECs are present in the environment, they can undergo various pathways among the soil-plant-water systems. The subsequent subsections briefly discuss the dynamics of ECs in the soil-plant-water.

1.3.1 Dynamics of emerging contaminants in the soil

Emerging contaminants in the soil may undergo several transformations and transport processes and destinies. Some of these processes are discussed below.

Degradation and transformation

Degradation of ECs in soils has been reported under laboratory and field conditions (Lozano et al., 2010; Thelusmond et al., 2019; Ying et al., 2007). Several conduits were reported for ECs degradation from the soil. Microbial degradation is one of the possible degradation pathways (Thelusmond et al., 2019). An example is an investigation by Zhang et al. (2013), comparing caffeine degradation and metronidazole, tinidazole, and chloramphenicol degradation in sterilised and non-sterilised agricultural soils. The authors established that degradation was significantly reduced in sterilised soil.

Pan and Chu (2016) also established that chloramphenicol, erythromycin, norfloxacin, sulfamethazine, and tetracycline degrade faster under aerobic than anaerobic soil conditions. According to these studies, soil microorganisms contribute significantly to the degradation of ECs. Photodegradation is also a potential EC degradation pathway from the soil (Vulava et al., 2016).

During the microbial degradation of ECs in the soil, ECs may form metabolites or transformation products (Butler et al., 2012). For example, Butler et al. (2012) observed a concurrent increase in the methyl triclosan (triclosan metabolite) concentration in the soil as the triclosan (parent compound) concentration decreased, indicating that methyl triclosan is formed from triclosan in the soil. One concern with the formation of emerging contaminant metabolites in the environment is that some metabolites are more persistent than their parent compounds. For example, Lozano et al. (2012) reported a half-life of up to 104 days and 443 days for triclosan and methyl triclosan, respectively, indicating methyl triclosan (triclosan metabolite) is more persistent than triclosan in the soil.

Microbial distribution in the soil

Soil faunas move within the soil from one part to another to find shelter and food. Evidence demonstrates that soil fauna can ingest ECs present in the soil into their body (Carter et al., 2016; Kinney et al., 2008). Kinney et al. (2008) detected a wide range of pharmaceuticals and other compounds in earthworms collected from agricultural lands, amended with biosolids and swine manure. The concentrations in earthworm tissues were as high as over 1000 $\mu g\ Kg^{-1}$ (Kinney et al., 2008), indicating significant bioaccumulation of ECs from the soil by earthworms. Soil faunas can translocate ECs to parts other than where they were placed or

applied. Transportation (i.e., ingestion and movement) of ECs in the soil-by-soil faunas may vary between soil organisms and their type (Carter et al., 2016). Carter et al. (2016) compared the uptake of pharmaceuticals in two earthworm species (*E. fetida and L. terrestris*), observing a higher accumulation of fluoxetine in *E. fetida* earthworms than in the *L. terrestris* earthworms.

Leaching from the soil

Contaminated soil can leach ECs to groundwater by infiltrating water (Gottschall et al., 2013; Gottschall et al., 2012; Lapen et al., 2008). Studies reported the leaching potential of various ECs from soil to groundwater (Gottschall et al., 2013; Gottschall et al., 2012; Lapen et al., 2008). Lapen et al. (2008) established that applying 93,500 L ha^{-1} of a liquid municipal biosolid to agricultural lands could rapidly contaminate subsurface drainage water and shallow groundwater (0.6, 1.2, and 2 m below soil surface) with pharmaceuticals and personal care product compounds.

Edwards et al. (2009) assessed the concentrations and mass loads of selected pharmaceuticals and personal care products in subsurface drainage water, following dewatered municipal biosolids application to agricultural land at 8 Mg ha^{-1} (dry weight). They detected both products in subsurface drainage. Gottschall et al. (2012) monitored pharmaceuticals and personal care product compounds in subsurface drainage and groundwater (2, 4 and 6 m below soil surface) following a single high 22 Mg ha^{-1} (dry weight) of dewatered municipal biosolids application to agricultural land. They detected both products in subsurface drainage and groundwater at concentrations ranging between five and 74 ng L^{-1} and 10 and 19 ng L^{-1}, respectively (Gottschall et al., 2012). Gottschall et al. (2013) monitored hormone and sterol concentrations in groundwater (2, 4 and 6 m below soil surface) and subsurface drainage water, following dewatered municipal biosolids application to agricultural land at a single high 22 Mg ha^{-1} (dry weight). They detected hormones and sterols in subsurface drainage water but not in groundwater (Gottschall et al., 2013).

Leaching behaviour of emerging is, however, controlled by several factors, including soil organic matter, soil moisture, soil pH, soil texture, contaminant attention coefficient, and climate. These factors are discussed in the succeeding Subsections.

Soil organic matter

Soil organic matter can influence the leaching behaviour of ECs in the soil (Joshi et al., 2019; Qin et al., 2017). An increase in soil organic matter decreases the leaching of ECs by enhancing their sorption (Qin et al., 2017). Joshi et al. (2019) examined the efficacy of two amendments, cereal straw and fresh cow dung slurry, in preventing the leaching of sulfosulfuron to groundwater and reported that both cereal straw and fresh cow dung slurry reduced the leaching of sulfosulfuron into groundwater. They concluded that adding organic matter from the two amendments to the soil enhanced the sorption of sulfosulfuron (Joshi et al., 2019).

Soil moisture

Soil moisture can influence the leaching of ECs by increasing their solubility and facilitating their movement in the soil (Blackwell et al., 2009). Blackwell et al. (2009) evaluated the leaching behaviour of veterinary antibiotics (i.e., sulfachloropyridazine) under various soil moisture treatment conditions. They observed sporadic sulfachloropyridazine in leachates under typical irrigation conditions and more frequent detection under extreme irrigation conditions (Blackwell et al., 2009), indicating that the availability and the level of moisture in the soil can affect the extent of EC leaching to the groundwater.

Soil pH

According to Kahle and Stamm (2007), negatively charged compounds are repelled by the soil colloidal surfaces and could easily be leached from the soil compared with positively charged compounds. This is because negative charges mostly dominate soil colloidal surfaces at pH levels suitable for most crops (Kahle & Stamm, 2007), attracting positively charged compounds. This could lead to more presence of positively charged compounds in the soil because of their retention by sorption; however, studies revealed that the fluctuation in soil pH can alter the contaminant charge forms, influencing their sorption on soil colloidal surfaces (Biel-Maeso et al., 2019). Biel-Maeso et al. (2019) reported the transformation of three sulphonamides compounds (i.e., sulfamethoxypyridazine, sulphathiazole, sulfamethoxazole) into anionic or negatively charged forms at pH levels above 7.2 (i.e., pH value above their acid-dissociation constant). This could lead to low sorption in the soil (Kahle and Stamm (2007) exposing its leaching.

Soil texture

Another factor affecting leaching is soil texture, which influences the sorption of ECs in the soil (Biel-Maeso et al., 2019). According to Biel-Maeso et al. (2019), high clay content encourages strong sorption and greater retention of ECs in the soil. Al-Khazrajy and Abdallh (2020) investigated the sorption, degradation, and mobility of antihistamine ranitidine to groundwater under two textured soils. They observed that the sand percentage has a negative influence on the absorption of ranitidine in soil. Xu et al. (2009) assessed the leaching potential of triclosan, 4-n-nonylphenol, estrone, bisphenol A, ibuprofen, diclofenac, clofibric acid, 4-tert-octylphenol, and naproxen in irrigated turf grass fields; coarser-textured soil enhanced the downward movement of the target compounds in the soils. The above studies indicate that soil texture plays a significant role in the level of EC leaching from the soil to the groundwater.

Contaminant sorption

According to Gottschall et al. (2012), the attention coefficient of a contaminant (Kd) has a notable function in influencing the EC level, leaching from the soil. ECs with higher Log K_{ow} (≥ 4) have strong sorption and are not easily leached from the soil compared with contaminants with low Log K_{ow} (< 4). Triclosan and triclocarban, for example, have Log K_{ow} values above four (i.e. triclosan = 4.8 and triclocarban = 4.9), reported low leaching potentials (Cha & Cupples, 2010). Because ECs differ in their Log K_{ow}, their sorption and leaching potentials are influenced by these parameters, as explained by Gottschall et al. (2012).

Climatic factors

Climatic factors, such as rainfall, can influence the leaching potential of ECs in the soil (Gottschall et al., 2012). Gottschall et al. (2012) monitored pharmaceutical and personal care product compounds in subsurface drainage and groundwater (2, 4 and 6 m below soil surface) following a single high 22 Mg ha^{-1} (dry weight) of dewatered municipal biosolids application to agricultural land. None of the studied pharmaceuticals and personal care product compounds were present in the groundwater post-application of biosolids (Gottschall et al., 2012); however, the target compounds were detected in groundwater two days following the first rainfall event (Gottschall et al., 2012), indicating that rainfall influenced the leaching potentials of ECs in the soil.

Plant uptake

Plants can remove ECs from the soil (Beltran et al., 2020; Fu et al., 2016; Mendez et al., 2016; Nie et al., 2022; Sanchez-Brunete et al., 2010). Previous studies indicate ECs enter the plant through the root epidermis and cross to the cortex and endodermis (Christou et al., 2019). Figure 1.2 presents the potential of crops to accept ECs. In contrast to cereals and fruits, leafy, root, and tuber vegetables are much more inclined to absorb ECs.

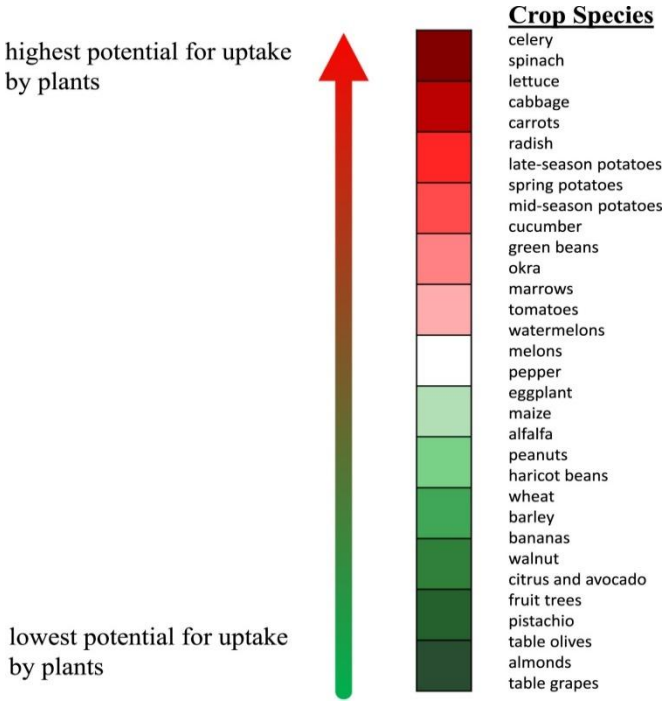


Figure 1.2: The potential of crops to absorb emerging contaminants (Christou et al., 2019)

Several factors influence plant realisation of ECs from the soil. Such aspects include the soil properties (e.g. Soil organic matter, pH, texture, aeration) (Karnjanapiboonwong et al., 2011; Malchi et al., 2014; Y. Zhang et al., 2016), environmental factors (e.g. air humidity, wind speed, ambient temperature, transpiration rate) (Dodgen et al., 2015; Y. Zhang et al., 2016), plant species, genotype, and physiology (e.g. lipid content of the roots, root system) (Eggen et al., 2011; Goldstein et al., 2014; Hepworth et al., 2015), and the contaminant properties (e.g. Water solubility, sorption to the soil, molecular size, and ionic charge form) (Christou et al., 2019).

For example, Karnjanapiboonwong et al. (2011) conducted a laboratory study to determine the uptake of triclosan in pinto bean (*Phaseolus vulgaris*) plant grown in two soils, sand (OC: 0%)

and loamy sand (OC: 1.3%). The authors detected triclosan root concentrations levels (mean ± standard deviation) of 2940 ± 329 μg g^{-1} and 6.4 ± 1.6 μg g^{-1}, respectively, indicating that soil properties, in particular organic matter, had an influence on the uptake of triclosan by the bean plant. Soil organic matter enhances triclosan sorption in the soil and therefore reduces its bioavailability for plant uptake (Fu et al., 2016).

1.3.2 Dynamics of emerging contaminants in the plants

Emerging contaminants may undergo these pathways in the plants following plant uptake.

Translocation within the plant

Once ECs are present in the plant roots, they are transported through the phloem by mass water flow driven by transpiration to aerial plant organs (Christou et al., 2019). The transport of ECs from the plant roots to aerial plant parts (i.e., shoots, leaves, and fruits) is estimated using the translocation factor (TF)—the ratio between the root and aerial parts concentrations. The EC's TF varies considerably between contaminants and plants. For example, Mathews et al. (2014) reported root to shoot TFs of up to 3.7% and 1.9% for triclosan and triclocarban, respectively, in a wide range of vegetable crops including asparagus, celery, tomato, cabbage, cucumber, potato, onion, pepper, beet and okra grown under the hydroponic system, indicating that contaminant properties influence the TFs.

Metabolism and transformations in plants

Emerging contaminants can experience metabolism in the plant to form metabolites (Huynh et al., 2018; Wu et al., 2016). The metabolism of ECs in plant tissues occurs in three phases. In Phase I—metabolism, the reactivity and polarity of a contaminant are enhanced by oxidation, hydrolysis, or hydroxylation processes. In Phase II—metabolism, the solubility of the contaminant is enhanced by conjugating it with polar biomolecules (e.g., carbohydrates, glutathione, or amino acids). Last, in Phase III—metabolism, the contaminant is trapped in the vacuole or cell wall of the roots as a bound residue or a non-extractable residue. Studies reported evidence of ECs' metabolism in plants and the formation of metabolites. For example, Huynh et al. (2018) reported that triclocarban experiences Phase I and Phase II metabolism in plants to form hydroxyl triclocarban metabolites, 2′ hydroxyl triclocarban and 6′ hydroxyl triclocarban (Huynh et al., 2018).

Back-conversions in plants

Several studies reported back-conversion from metabolites/ transformation products to parent compounds (Fu et al., 2018). For example, Fu et al. (2018) exposed lettuce and carrot seedlings to methyl triclosan in a nutrient solution, observing that lettuce and carrot seedlings can convert methyl triclosan to triclosan (parent compound) in less than five days of exposure.

1.3.3 Dynamics of emerging contaminants in aquatic environments

Emerging contaminants may undergo the following conduits in aquatic environments.

Sorption of suspended solids and sediments

Emerging contaminants may experience sorption on the suspended solids and sediments in water (Wilkinson et al., 2017). According to Chen et al. (2016), compounds with higher hydrophobicity have stronger sorption on solid material than those with lower hydrophobicity. da Silva et al. (2011) investigated the occurrence and distribution of over 40 pharmaceutical compounds in river water, sediments, and suspended solids, reporting higher concentration levels of some pharmaceuticals (i.e., mostly the hydrophobic compounds with acid-dissociation constant (pKa) values above seven) in suspended solids than in river water.

Emerging contaminants, especially those with hydrophobic nature, can, therefore, be adsorbed on suspended solids in water. Luo et al. (2011) studied the occurrence and transport of antibiotics in river water, reporting that sediments' cation exchange capacity and organic matter affected the transport of antibiotics in river water. The authors also observed that a high flow rate of the river water reduced the sorption of antibiotics owing to limited contact time between sediments and antibiotics (Luo et al., 2011).

Sorption on microplastics

Microplastics refers to all plastic materials with a diameter size less than 5 mm (Barnes et al., 2009). Several studies detected microplastics in an aquatic environment (Elizalde-Velazquez & Gomez-Olivan, 2021; Vivekanand et al., 2021; Xu et al., 2020). Studies reported that microplastics can adsorb ECs in aquatic environments (Hirai et al., 2011; Mato et al., 2001). For example, Mato et al. (2001) detected nonylphenols (0.1 – 16 ng g^{-1}), DEE (0.2 – 3.0 ng g^{-1}), and polychlorinated biphenyls (4.0 – 117 ng g^{-1}) on microplastics collected from the marine

environment. Adsorption of ECs could present microplastics as a transport medium in aquatic environments (Mato et al., 2001).

Bioaccumulation

Emerging contaminants may be transferred to aquatic organisms including plants through uptake, following their presence in the aquatic environment (Kurade et al., 2019; Ravichandran & Philip, 2021; Wang et al., 2019) and to animals through ingestion (Alvarez-Ruiz et al., 2021; Maulvault et al., 2018; Previsic et al., 2020). For example, Ravichandran and Philip (2021) investigated the uptake of carbamazepine, diclofenac, and atenolol in two aquatic plant species, *Chrysopogon zizanioides* and *Canna indica*, grown under hydroponic conditions and detected all target compounds in both plants, indicating that aquatic plants can absorb ECs. Rose et al. (2012) assessed the levels of naphthalene in crayfish and crab collected from local markets in Nigeria, reporting naphthalene concentration levels up to 24.9 ng g^{-1}.

Volatilisation

According to Wilkinson et al. (2017), ECs could volatilise from the water to the atmosphere. Several relevant studies (Salgueiro-Gonzalez et al., 2013) confirmed that ECs can move to the atmosphere through volatilisation. Rudel et al. (2003) investigated polybrominated diphenyl ethers, pesticides, alkylphenols, and phthalates in the atmosphere, detecting them at concentration levels between 50 and 150 ng m^{-3}.

Degradation and transformation

Emerging contaminants may experience a photodegradation process by solar radiation (Wilkinson et al., 2017) and microbial degradation by microorganisms (Ferrando-Climent et al., 2012) in the aquatic environment forming transformation products. During the photodegradation process, solar radiation energy disintegrates the covalent bond from ECs, forming metabolites (Richard & Canonica, 2005). During the microbial degradation process, microorganisms decompose ECs through various pathways (i.e., mineralisation, hydrolysis, and oxidation-reduction processes) to form metabolites (Tran et al., 2013).

CHAPTER 2: CONCENTRATION OF SELECTED EMERGING CONTAMINANTS OF CONCERN IN AGRICULTURAL SOILS AND THEIR UNDERLYING GROUNDWATER IN TSHWANE, WEST RAND, AND EKURHULENI DISTRICTS OF GAUTENG PROVINCE, SOUTH AFRICA

2.1. Materials and Methods

2.1.1 Study area

The research was carried out on agricultural lands situated in three metropolitan municipalities of Gauteng province, South Africa. Gauteng province falls under the sub-humid agroecological zone of South Africa and receives summer rains between October and March. The dominant soil types in Gauteng include Vertisols, Acrisols, Leptosols, Lixisols, and Luvisols (Figure 2.1).

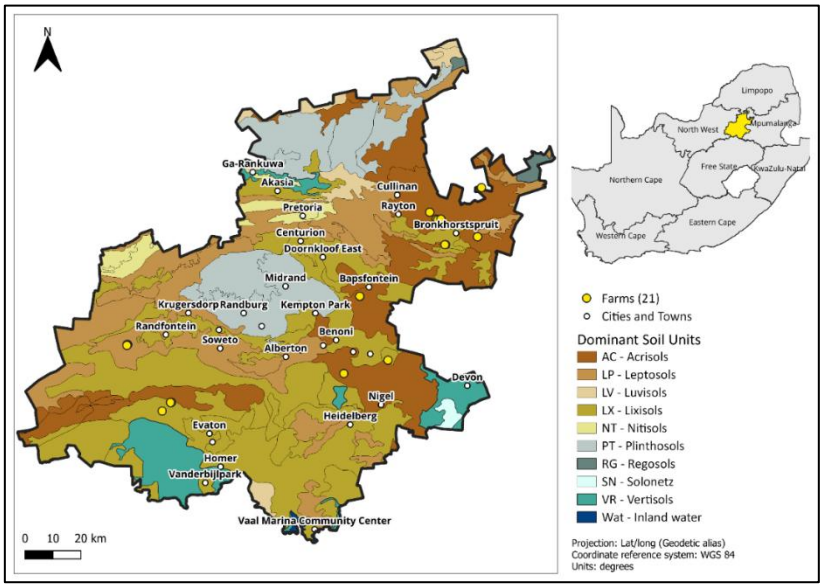


Figure 2.1: Map showing dominant soil forms in Gauteng province, South Africa (Source: International Soil Reference and Information Centre)

Being an industrialized province and the economic hub of South Africa, Gauteng has a denser population compared to other provinces (StatsSA, 2022). With a population of approximately 61 million, 27 percent of them reside in Gauteng (StatsSA, 2022). Due to the higher population size, greater number of medical research institutes, and a higher number of pharmaceutical industries, it is expected that the consumption pattern of pharmaceuticals, lifestyle chemicals,

and industrial chemicals in Gauteng would be comparatively higher. Hence, carrying out studies in Gauteng province could provide a worst-case scenario for examining the occurrence and concentration of the target compounds being investigated.

2.1.2 Site selection

Soil and water samples were collected from 21 representative agricultural lands from the Tshwane, Ekurhuleni, and West Rand district municipalities in Gauteng, South Africa. The sampling sites consisted of i) two farming systems (rainfed and irrigated), ii) three fertilizer types (commercial inorganic fertilizer, animal manure, and municipal sludge), and iii) three cropping systems (cereal, legume, and vegetables). Details of the farms are presented under the Supplementary Table 1. Figure 2.2 below shows the map of South Africa (top right) and Gauteng (left) and the location of the sampling sites under the study.

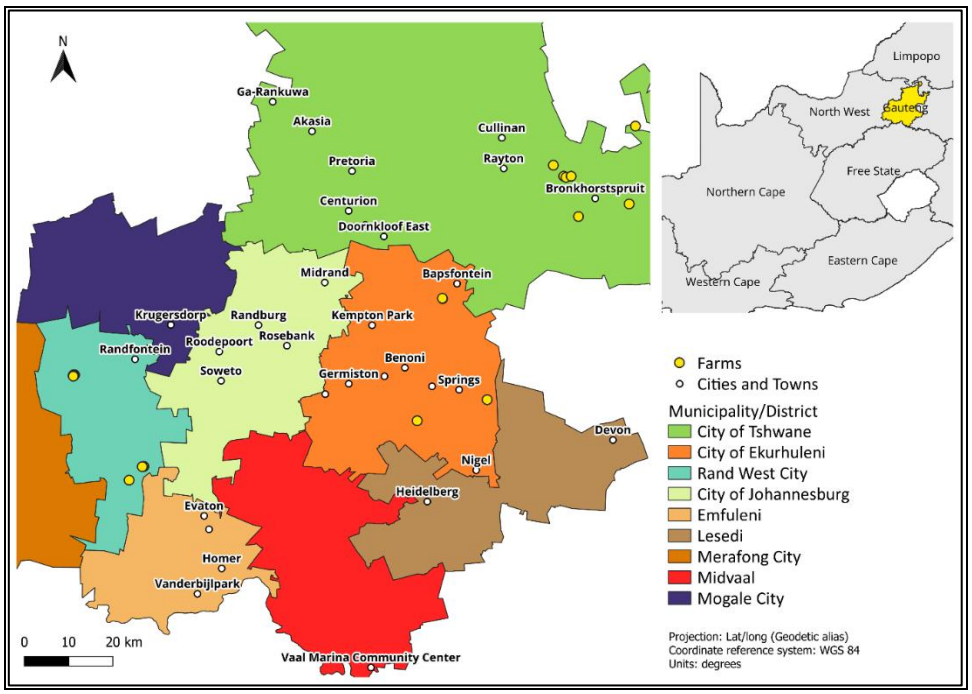


Figure 2.2: Shows the map of South Africa (top right) and Gauteng (left) and the location of the sampling sites under the study

The Tshwane district's agricultural lands were predominantly comprised of Haplic Lixisols (LXh) and Haplic Acrisols (ACh) soils (refer to Figure 2.3: Top). Acrisols and Lixisols are both highly weathered soils that are commonly found in humid regions (International Soil Reference and Information Centre). They are characterized by the presence of the Bt horizon

and low-activity clays in the Bt horizon (International Soil Reference and Information Centre). The key difference between the Acrisols and Lixisols is that the former has low base saturation, whereas the latter has moderate to high base saturation (International Soil Reference and Information Centre). The soils in the Tshwane district's representative agricultural lands were formed from parent materials of dolerite and Sandstone (Greywacke, Arkose) (refer to Figure 2.3: Bottom).

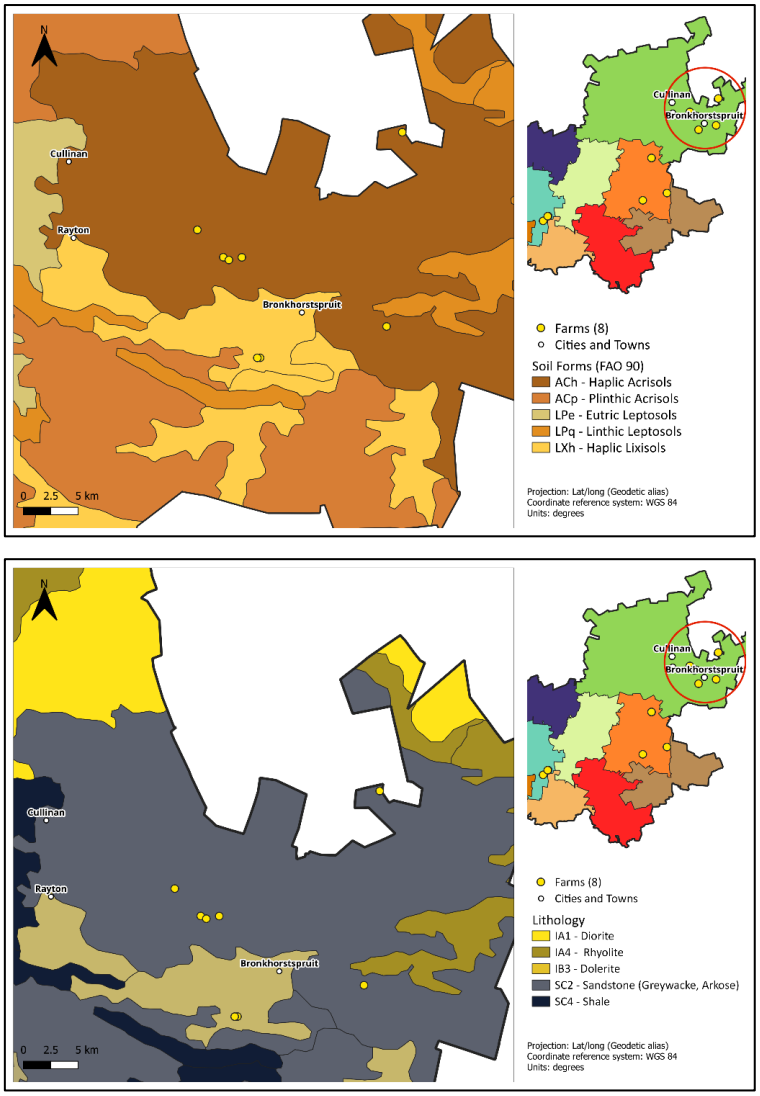


Figure 2.3: Map showing different soil forms (top) and geology (bottom) at the sampling sites from the Tshwane district municipality (Source: International Soil Reference and Information Centre)

The predominant soil type found in agricultural lands of the Ekurhuleni district is Plinthic Acrisols (ACp) soils, as depicted in Figure 2.4 (Top). The parent material for these soils is Sandstone (Greywacke, Arkose), as shown in Figure 2.4 (Bottom).

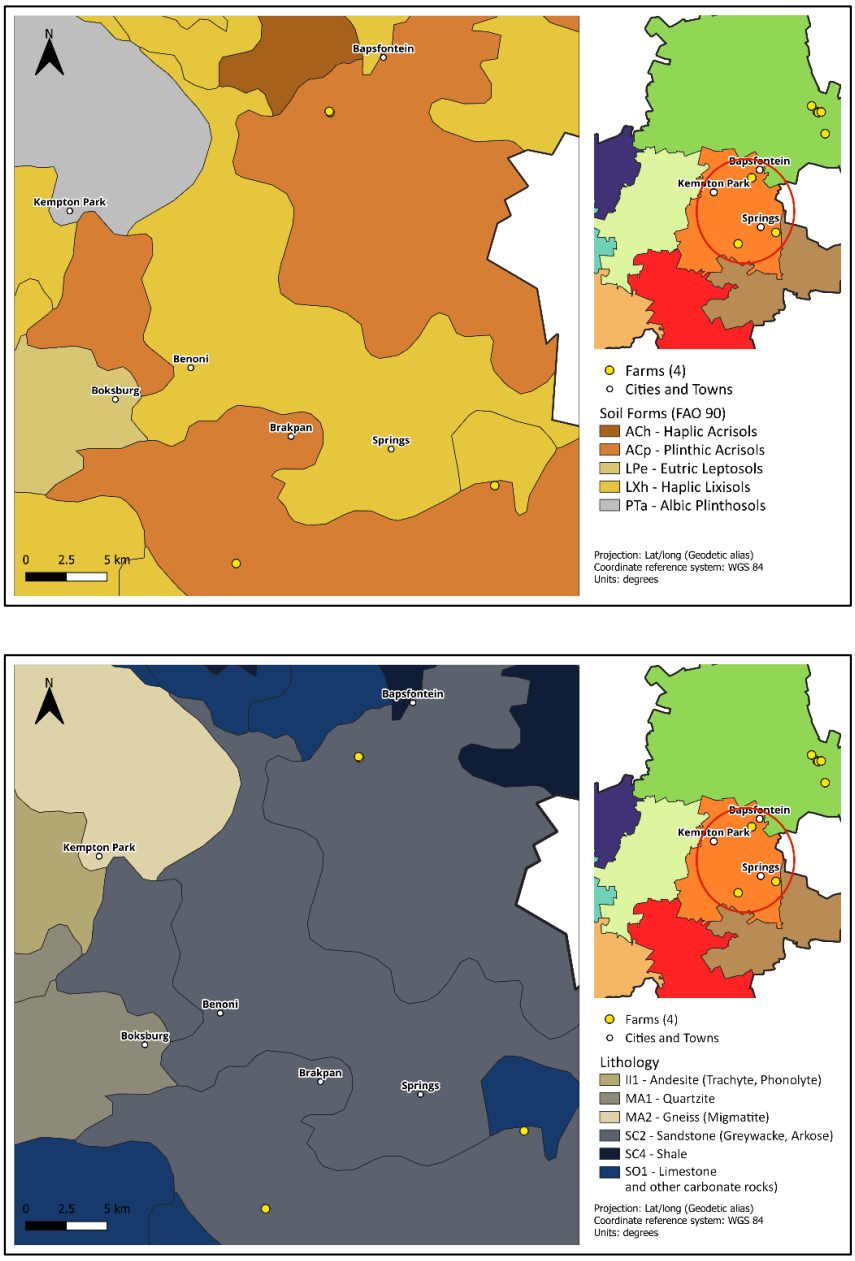


Figure 2.4: Map showing different soil forms (top) and geology (bottom) at the sampling sites from the Ekurhuleni district municipality (Source: International Soil Reference and Information Centre)

The dominant soils in farms located in the West Rand district are Haplic Lixisols (LXh) and Eutric Leptosols (LPe), as shown in Figure 2.5 (Top). Leptosols are commonly found in mountainous regions and are characterized by their shallow depth or deeper depth with an extremely high gravel content, according to the International Soil Reference and Information Centre. The Leptosols in representative agricultural lands under the current study were formed from Andesite (Trachyte, Phonolite) and Quartzite parent materials (Figure 2.5: Bottom).

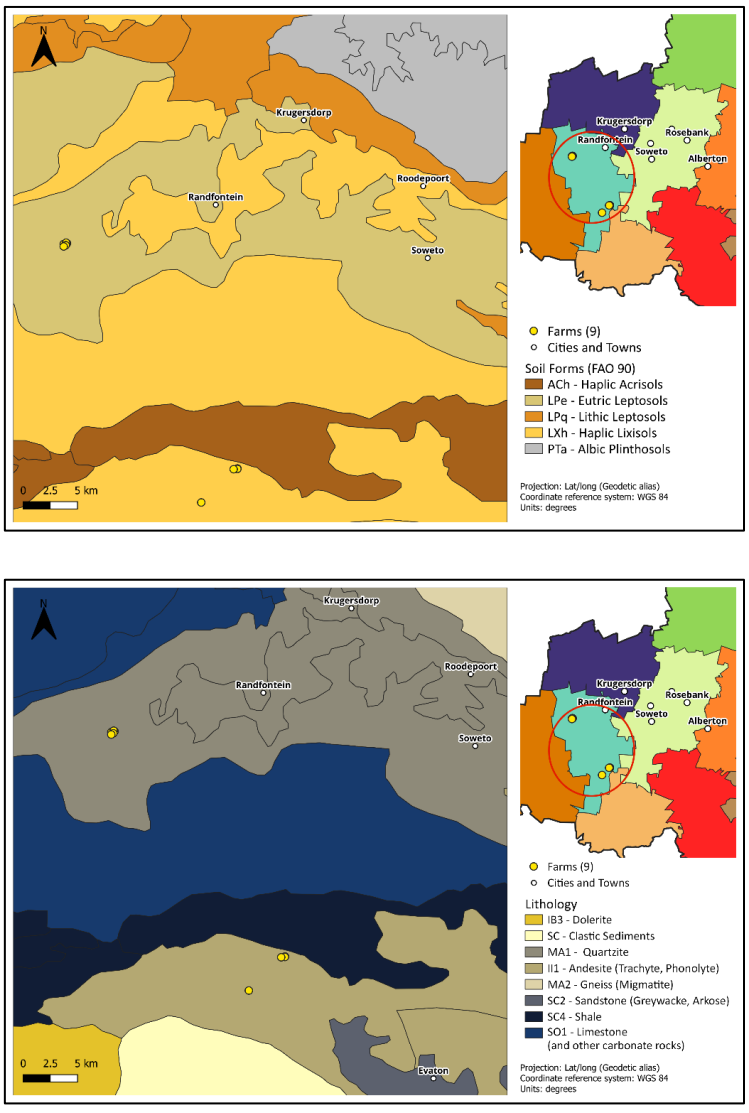


Figure 2.5: Map showing different soil forms (top) and geology (bottom) at the sampling sites from the West Rand district municipality (Source: International Soil Reference and Information Centre)

2.1.3 Selection of pharmaceutical and personal care product compounds and their metabolites

This study focused on the analysis of certain pharmaceutical and personal care product compounds, including carbamazepine (CBZ), caffeine (CAFF), bisphenol A (BPA), diclofenac (DCF), and sulfamethoxazole (SMX). Additionally, the two main metabolites of sulfamethoxazole (N4-acetyl-sulfamethoxzole (N4-Acetyl-SMX) and Sulfamethoxazole-N1-beta-D-Glucoside (SMX-N_1-Glu)), and carbamazepine (carbamazepine-10,11-epoxide (CBZ-10,11-epox) and cis-10,11-Dihydroxy-10,11-carbamazepine (CBZ-DiOH)) were also examined. The selection of these contaminants was based on their inclusion in the priority list of contaminants of emerging concern for evaluating water quality for direct potable reuse in South Africa (Swartz et al., 2018), as well as their recognition as contaminants of concern in drinking water by the European Union (Commission implementing Decision 2015/495), and the United States Environmental Protection Agency (U.S. EPA, 2022). The physico-chemical parameters of these compounds and their metabolites are presented in Table 2.1.

Table 2.1: Physico-chemical parameters of the target compounds and their metabolites

Contaminant	Molecular formula	Molecular weight (g mol^{-1})	Water solubility (mg L^{-1})	Log K_{ow}	pK_a
BPA	$C_{15}H_{16}O$	228.29	120	3.32	9.6
CAF	$C_8H_{10}N_4O_2$	194.19	2.16 X 10 4	-0.07	14
CBZ	$C_{15}H_{12}N_2O$	236.27	18	2.45	13.9
CBZ-10,11-epox	$C_{15}H_{12}N_2O_2$	252.27	NA	NA	NA
CBZ-DiOH	$C_{15}H_{14}N_2O_3$	270.28	NA	NA	NA
DCF	$C_{14}H_{11}C_{12}NO_2$	296.1	2.37	4.51	4.15
SMX	$C_{10}H_{11}N_3O_3S$	253.28	610	0.89	1.6; 5.7
N4-Acetyl-SMX	$C_{12}H_{13}N_3O_4S$	295.32	NA	NA	NA
SMX-N1-Glu	$C_{16}H_{21}N_3O_8S$	415.4	NA	NA	NA

NA is not available.

2.1.4 Sampling and sample preparation

2.1.4.1 Soil

Prior to planting in September 2022, soil samples were taken from representative sampling points, as well as reference sites adjacent to the sampling points with no history of farming. The samples were collected at random intervals of 20 cm to a depth of 100 cm using a galvanised metal auger. To avoid cross contamination, the auger was washed with water, rinsed with deionised water and methanol after every layer of sampling. At least 10 subsamples were collected from each sampling point and mixed according to their respective layers to prepare composite representative samples per layer. The composite samples were divided into two parts: one for analysing physico-chemical parameters, and the other for analysing emerging contaminants. The second set of samples were transferred to aluminium foils and kept in a CAMP MASTER electric cooler box (Model CB46) for transportation to the laboratory. The soil samples for physico-chemical parameter analysis were transferred inside zip-lock plastic bags and transported to the laboratory. Soil samples for emerging contaminants analysis were freeze-dried, sieved with a 2 mm diameter sieve, and stored at - 20 ^{O}C for analyses. Soil samples for physico-chemical parameter analysis were air-dried to a constant weight and sieved with a 2 mm diameter sieve.

2.1.4.2 Fertilizers and water

The fertilizers utilized by the farmers were gathered from each individual farm. Approximately 100 grams of fertilizer were then placed in an aluminium foil which was subsequently stored in a CAMP MASTER electric cooler box (Model CB46) for transportation to the laboratory. Following similar procedures to those used for the analysis of soil samples for emerging contaminants, the samples were prepared and then stored at a temperature of -20 ^{O}C until analysis.

Water samples were collected using SinkFastTM polyethylene bailers with a capacity of 1 liter. In instances where borehole water was unavailable, supplementary water samples were obtained from nearby rivers or dams. The guidelines published by the Water Research Commission (WRC, 2007) were followed to ensure that the water samples were properly collected. Each sample was immediately transferred into a clean amber bottle with a capacity

of 2.5 liters and transported to the laboratory for analysis. The samples were stored in a -20 ^{O}C freezer and were analysed within a month of collection.

2.1.5 Analytical procedures

2.1.5.1 Chemicals, reagents, and storage conditions

The following chemicals and standard materials were purchased from Merck, South Africa: bisphenol A (BPA), N4-acetyl-sulfamethoxzole (N4-Actyl-SMX), sulfamethoxazole (SMX), sodium hydroxide, ethylenediaminetetraacetic acid disodium salt dehydrate (Na2EDTA.2H2O), hydrochloric acid (HCl), and phosphate buffer. The following standards were purchased from Redchem, South Africa: Caffeine (CAF), caffeine 13C3 (CAF 13C3), carbamazepine (CBZ), carbamazepine 13C6 (CBZ 13C6), carbamazepine-10,11-epoxide (CBZ-10,11-epox), and cis-10,11-Dihydroxyl-10,11-dihydrocarbamazepine (CBZ-DiOH). Sulfamethoxazole-N1-beta-D-Glucoside (SMX-N1-Glu), diclofenac acid (DCF), diclofenac D4 (DCF D4), and sulfamethoxazole 13C6 (SMX 13C6) were purchased from Industrial Analytical (South Africa). HiPerSolv Chromanorm-grade methanol, acetonitrile, and acetone were purchased from Moncon (South Africa). Ultrapure water was collected using a water purifier (PURELAB® Chorus 1, Labotec). All stock solutions were prepared in ultra LC methanol and stored in glass amber vials at -20 °C.

2.1.5.2 Physico-chemical analysis

Core samplers were used to collect soil samples from the top 20 cm for bulk density determination. The wet-sieving technique was employed to determine the soil aggregate stability. A Decagon Mini-Disc infiltrometer was used to determine the unsaturated hydraulic conductivity. Total soil C and N were analyzed using a Carlo Erba NA1500 C/N analyzer (Carlo Erba Strumentazione, Milan, Italy). Total P was determined by wet acid digestion and analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES) (SpectroFlame Modula; Spectro, Kleve, Germany). Soil electrical conductivity and pH levels were assessed using Consort EC (C861 model) and pH (C830 model) meters, respectively, on a 1:2 soil: water ratio extract.

Water samples from boreholes on the farms were analyzed for pH, EC, dissolved oxygen, and total dissolved solids using a Lovibond multiparameter water sensor (SensoDirect 150).

2.1.5.3 Pharmaceutical and personal care products and their metabolites analysis

Extraction and clean-up

The EPA method 1694, with certain modifications, was utilized to extract pharmaceutical and personal care products from water samples.(USEPA, 2007). Water samples were subjected to filtration through a 0.7 µm glass fibre filter to remove solid residues. Subsequently, a 500 mL sample was extracted through the solid phase extraction (SPE) approach, utilizing Oasis HLB cartridges. Initially, the sample was acidified by adding HCl to obtain pH 2 and then spiked with 100 µL of 1000 ng mL^{-1} isotope-labelled internal standards. The sample was loaded into the Oasis cartridges, which were conditioned sequentially with 6 ml methanol, 6 ml ultrapure water, and 6 ml acidified ultrapure water (pH = 2). After loading the spiked sample, interfering materials were washed with 20 mL ultrapure water. The cartridges were then dried under vacuum (at 5 bar pressure) for 5 min. Target analytes were eluted using 3 x 4 mL aliquots of methanol, which was then evaporated using GeneVac (EZ-2 Plus series) at a heating temperature of 45 ^{O}C and a pressure of ≤ 200 mbar. Finally, analytes were recovered by a 1 mL methanol: water solvent (50:50, v/v). The solution was vortexed for 1 min, transferred to the injection amber glass vial, and analytes were immediately quantified by the LC MS/MS method.

Samples of soil, sludge, and manure were extracted using the EPA method 1694, with modifications based on the approach developed by de Santiago-Martin et al. (2020). A pre-prepared sample weighing 1g was subjected to spiking with 100 µL of a 1000 ng/mL isotope-labelled internal standard mixture. Methanol was allowed to evaporate under a fume hood after the spiking process. The process involved three sequential extractions. The first extraction involved adding 20 mL of acetonitrile to the spiked sample and sonicated for 30 minutes. The second extraction involved adding 15 mL of phosphate buffer solution (pH 2) to the previously extracted sample and vortexed to suspend solids. The final extraction involved adding 15 mL of acetonitrile to the previously extracted sample and sonicated for 30 minutes. After each extraction, the mixture was centrifuged at a speed of 3000 rpm for 5 minutes and the aqueous were removed into a clean test tube. The extracts from the three sequential extractions were combined inside a Bunchi flask and the solvents were evaporated using a rotary evaporator to a volume of about 20 mL. The extracts were then transferred to a 100 mL volumetric flask and

a 250 mg $Na_2EDTA.2H_2O$ was added to the extracts. Following the addition of Na2EDTA.2H2O, the volume was filled to a 100 mL mark with ultrapure water. The same SPE procedure used during the extraction of liquid samples was performed using the pre-conditioned Oasis HLB cartridge. Elution and reconstitution were also performed the same way as was in the case of the liquid samples.

Quantification using LC MS/MS and method performance

Target pharmaceutical and personal care products and their metabolites were quantified using the Waters ® Synapt G2 high-definition mass spectrometry (HDMS) system (Waters Inc., Milford, Massachusetts, USA). The system was equipped with a Waters Acquity Ultra Performance Liquid Chromatography (UPLC) system hyphenated to a quadrupole time-of-flight (QTOF) instrument. The instrument was equipped with A Kinetex® 1.7 µm EVO C18 100 Å (2.1 mm ID × 100 mm length) column for chromatographic separation of the target compounds. The column temperature was kept constant at 50 °C, and the flow rate was set at 0.3 mL/min for the entire run, giving a total run time of 20 min. Separation was performed using a reverse-phase gradient elution scheme from 97% H2O (with 0.1% formic acid) to 100% methanol (with 0.1% formic acid). The injection volume was 5 µl. After testing the samples, the data were processed using the MassLynx™ (version 4.1) software (Waters Inc., Milford, Massachusetts, USA). Additional instrument parameters and chromatographic separation details are summarized in Supplementary Table 2.

2.2 Results and discussion

2.2.1 Occurrence and concentration levels of selected pharmaceuticals and personal care products in different fertilizer samples

The following subsections present results and discussion on the occurrence and concentration levels of selected pharmaceuticals and personal care products in commercial inorganic fertilizers, sewage sludge, compost, and manure.

Commercial inorganic fertilizers

None of the nine target compounds were found in three selected commercial inorganic fertilizers, except for carbamazepine 10,11 epoxide, which was detected in all three (Figure 2.6). The concentration of carbamazepine 10,11 epoxide in superphosphate fertilizer (39.9 ng/g dry weight) was higher than in potassium chloride (13.9 ng/g dry weight) and lime ammonium nitrate (13.3 ng/g dry weight) fertilizers (Figure 2.6). There is currently no literature on the occurrence and concentration levels of pharmaceuticals and personal care products, including carbamazepine 10,11 epoxide, in commercial inorganic fertilizers. This study is the first to report such information, and further research is needed to validate these findings and identify sources of carbamazepine 10,11 epoxide in these commercial inorganic fertilizers.

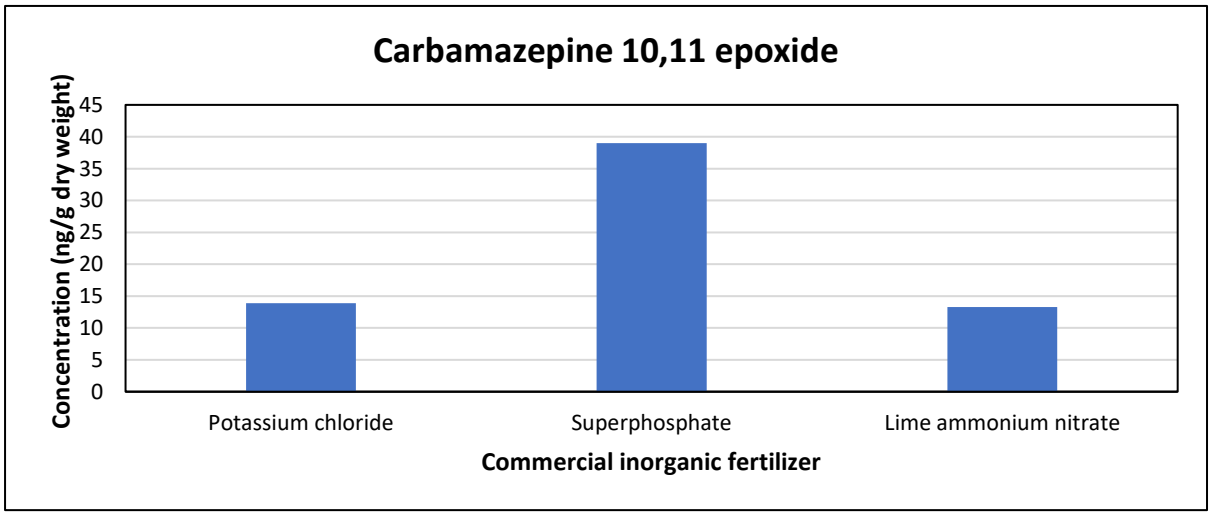


Figure 2.6: Occurrence and concentration levels of carbamazepine 10,11 epoxide in three popular types of commercial inorganic fertilizers

Sludge

Four out of nine target compounds, including caffeine, carbamazepine, and two metabolites of carbamazepine (carbamazepine 10,11 epoxide and cis-10,11-dihydroxy-10,11-dihydrocarbamazepine), were found in sludge samples collected from four wastewater treatment plants across the Gauteng province, South Africa (see Figure 2.7). It is worth noting that cis-10,11-dihydroxy-10,11-dihydrocarbamazepine was only detected in sludge samples from wastewater treatment plants B and C (Figure 2.7). The concentration levels of caffeine, carbamazepine, carbamazepine 10,11 epoxide, and cis-10,11-dihydroxy-10,11-dihydrocarbamazepine were reported to be as high as 27, 151, 602, and 89 ng/g dry weight, respectively (Figure 2.7).

The concentration level of caffeine, as reported in this study, is lower than that found in sludge samples collected from Canada (≤ 166 ng/g dry weight) (Miao et al., 2005 However, the concentration levels of carbamazepine reported in this study are considerably higher than those reported in sludge samples from France (≤ 0.04 ng/g dry weight) (Bourdat-Deschamps et al., 2017) and the USA (≤ 60.30 ng/g dry weight) (USEPA, 2009). Similarly, the concentration levels of carbamazepine 10,11 epoxide in this study are higher than those reported in sludge samples from Canada (not detected) (Miao et al., 2005), as are the levels of cis-10,11-dihydroxy-10,11-dihydrocarbamazepine, which are also higher than those reported in sludge samples from Canada (≤ 15.4 ng/g dry weight) (Miao et al., 2005).

Furthermore, diclofenac, sulfamethoxazole, sulfamethoxazole N1 glucuronide, and N4 acetyl sulfamethoxazole were not detected in any of the sludge samples.

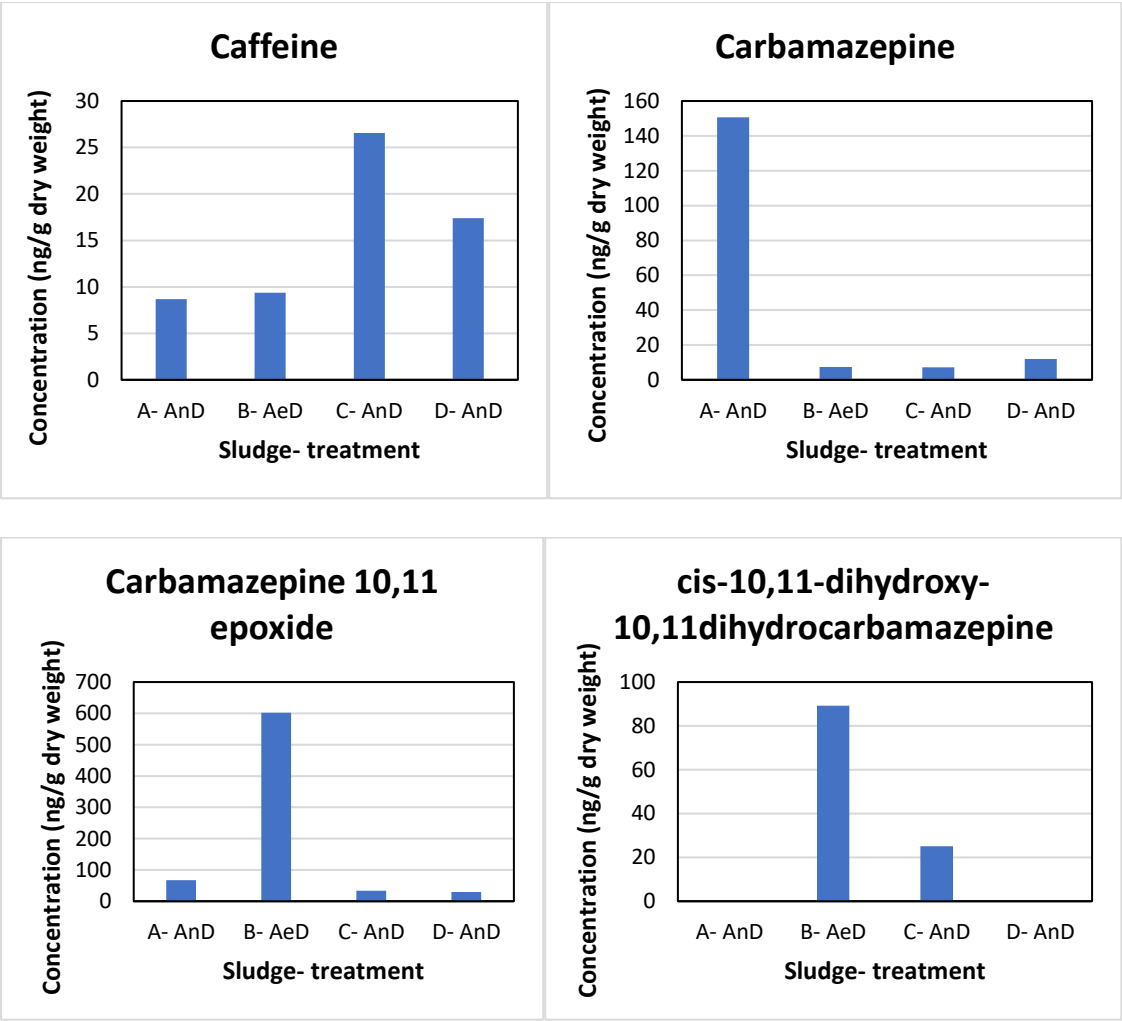


Figure 2.7: Occurrence and concentration levels of selected pharmaceuticals and personal care products in four varying sludge samples collected around Gauteng province, South Africa. Alphabetical letters represent the four wastewater treatment plants. AnD means anaerobic digested and AeD means aerobic digested.

Compost and manure

Caffeine and carbamazepine 10,11 epoxide were identified in compost and cattle manure samples. Additionally, cis-10,11-dihydroxy-10,11-dihydrocarbamazepine was found in cattle manure. The results indicate that the concentration levels of these compounds were higher in cattle manure compared to plant-based compost. Specifically, the concentration levels of caffeine, carbamazepine 10,11 epoxide, and cis-10,11-dihydroxy-10,11-

dihydrocarbamazepine in compost were found to be up to 17, 24.2, and 0 ng/g dry weight, respectively (Figure 2.8). In cattle manure, the concentration levels of caffeine, carbamazepine 10,11 epoxide, and cis-10,11-dihydroxy-10,11-dihydrocarbamazepine were measured to be up to 27, 56, and 31 ng/g dry weight, respectively (Figure 2.8). Additionally, the levels of caffeine detected in this study were higher than those reported in cattle manure from the USA (not detected) (Kinney et al., 2008). Currently, there is no available information regarding the occurrence and concentration levels of the two carbamazepine metabolites in compost and cattle manure.

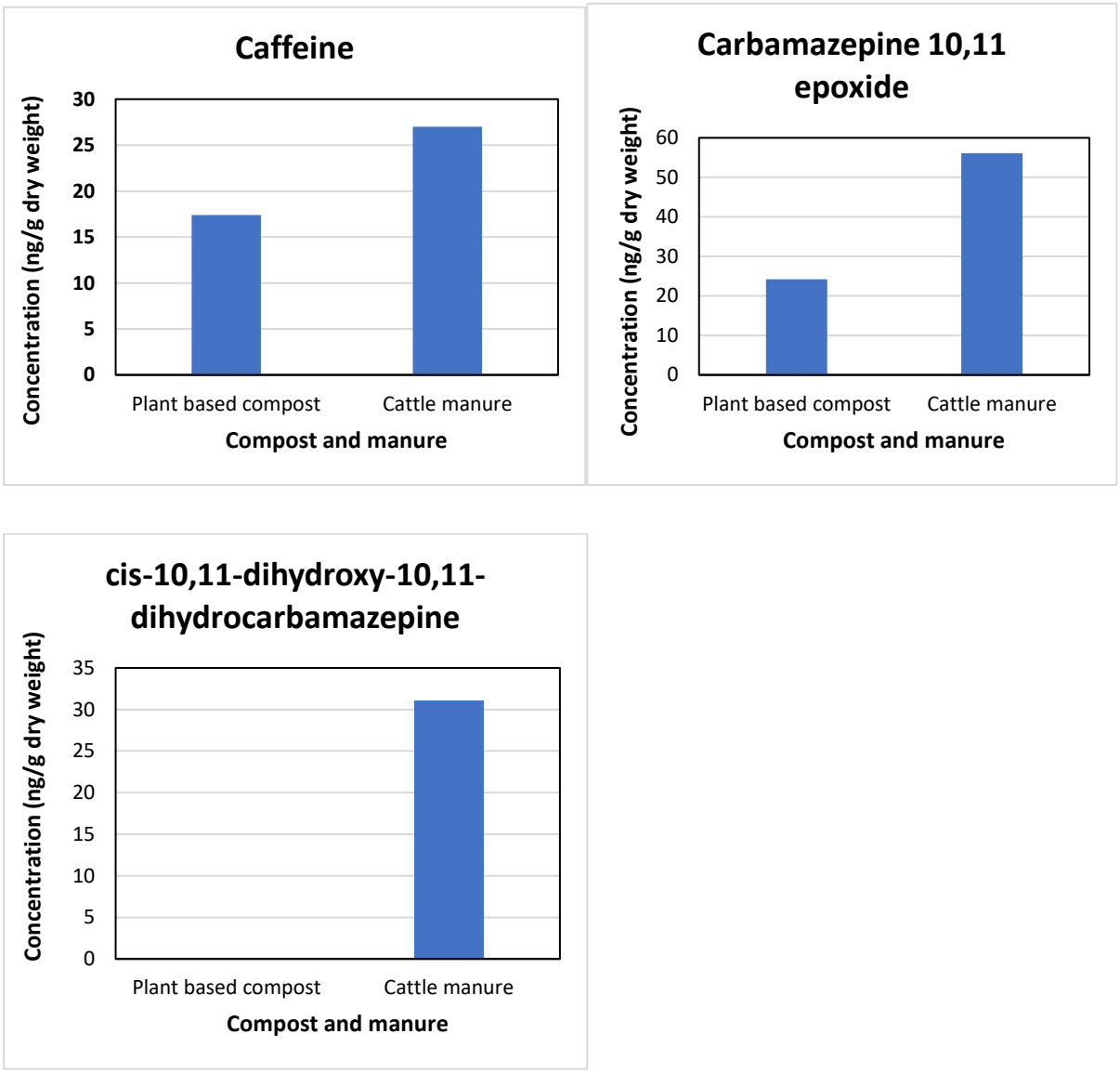


Figure 2.8: Occurrence and concentration of sleeted pharmaceuticals and personal care products in plant-based compost and cattle manure

2.2.2 Occurrence and concentration level of pharmaceutical and personal care product compounds and their metabolites in agricultural lands in Gauteng

Agricultural soils are one of the major sinks for pharmaceutical and personal care products (PPCPs) in the terrestrial environment (Biel-Maeso et al., 2018, Qin et al., 2024, Saha et al., 2022). This is because agricultural soils are treated with various organic amendments such as sewage sludge, animal manure, and wastewater, which are known potential sources of PPCPs in the terrestrial environment. Several studies have reported the presence of PPCPs in soils that received sewage sludge (Kinney and Heuvel, 2020, Prosser and Sibley, 2015), animal manure (Prosser and Sibley, 2015), and wastewater (Liu et al., 2020, Prosser and Sibley, 2015).

The research findings revealed that three out of ten target compounds (carbamazepine-10,11 epoxide, 10,11-dihydroxy carbamazepine, and N4-acetyl sulfamethoxazole) were detected in the agricultural soils of Gauteng (refer to Figure 2.9). This suggests a low level of PPCPs pollution in the region's agricultural soils, possibly due to their low consumption and rapid degradation after accumulating in the soil. Specifically, the detection rates for carbamazepine-10,11 epoxide, 10,11-dihydroxy carbamazepine, and N4-acetyl sulfamethoxazole were 33.3%, 33.3%, and 28.6% respectively (see Figure 2.9). Additionally, caffeine, carbamazepine, ibuprofen, bisphenol A, diclofenac, sulfamethoxazole, and sulfamethoxazole-N1-glucuronide were included in the analysis but were not found in any of the samples (refer to Figure 2.9).

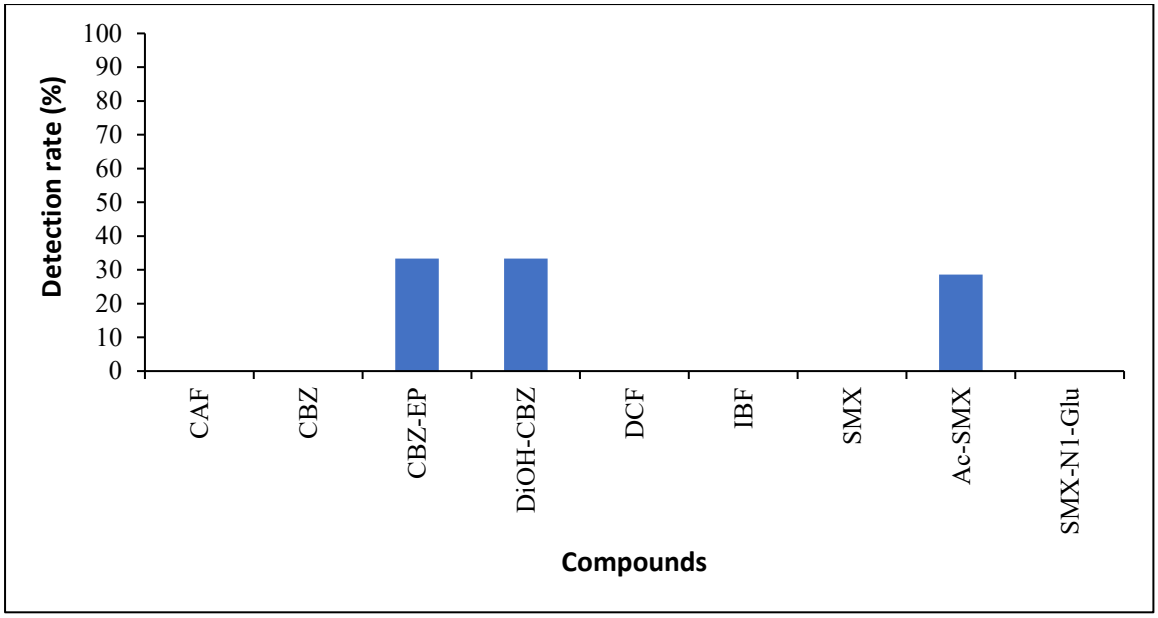


Figure 2.9: Detection rates of targeted PPCPs in cultivated agricultural soils: CBZ = Carbamazepine, CAF = Caffeine, BPA = Bisphenol A, DFC = Diclofenac, IBF = Ibuprofen, SMX = Sulfamethoxazole, Ac-SMX = N4 acetyl sulfamethoxazole, SMX-N1-Glu = Sulfamethoxazole-N1-beta-D-Glucuronide, CBZ-EP = Carbamazepine-10,11-epoxide and DiOH-CBZ = 10,11-dihydro-10,11-dihydroxy-10,11-carbamazepine

The levels and prevalence of certain target compounds align with findings from various studies conducted worldwide. For instance, a study in the USA by Karnjanapiboonwong et al. (2011) found no caffeine in soil samples collected from agricultural lands irrigated with treated wastewater. Similarly, Aznar et al. (2014) found no diclofenac in soil samples from agricultural areas in three Spanish cities (Segovia, Murcia, and Valencia). In Saudi Arabia, Picó et al. (2019) did not detect carbamazepine-10,11 epoxide in soil samples from agricultural areas irrigated with treated wastewater. However, some target compounds were less prevalent in our study compared to findings in other countries. For example, Liu et al. (2020) reported a 100% detection rate of N4-acetyl sulfamethoxazole in soil samples from Chinese agricultural lands irrigated with reclaimed wastewater. In Spain, Biel-Maeso et al. (2018) recorded detection rates of 100% for IBF and CBZ, and 75% for SMX in agricultural soils irrigated with wastewater. These higher occurrence rates in their studies may be attributed to the use of treated wastewater for irrigation, which was not the case in our study.

Table 2.2 provides a summary of the range and average concentrations of the target compounds found in the soils. The concentration levels of carbamazepine-10,11 epoxide, 10,11-dihydro-10,11-dihydroxy carbamazepine, and N4-acetyl sulfamethoxazole reached up to 10.0, 353.5, and 59.1 ng/g dry weight, respectively. In a comparative context, Liu et al. (2020) reported slightly higher to significantly higher N4-acetyl sulfamethoxazole concentration levels (Mean ± SD) of 10.9 ± 2.4, 22.1 ± 2.6, and 23.2 ± 3.1 ng/g dry weight in the top 30 cm soil layer of the three cultivated agricultural fields subjected to reclaimed wastewater irrigation for 20, 30, and 40 years, respectively. However, Paz et al. (2016) reported lower concentration levels of both carbamazepine-10,11 epoxide and 10,11-dihydro-10,11-dihydroxy carbamazepine (0.1 - 0.8 ng/g dry weight) in soils irrigated with reclaimed wastewater. Additionally, Picó et al. (2019) did not detect carbamazepine-10,11 epoxide in three cultivated Saudi Arabian agricultural field soils that were irrigated with wastewater. The authors also noted the absence of carbamazepine-10,11 epoxide in the reclaimed wastewater used (Picó et al. 2019).

Table 2.2: Concentration (n = 21) of studied compounds and their metabolites in agricultural soils in Gauteng, South Africa.

Compound	Range (ng/g dry weight)	Mean ± SD (ng/g dry weight)
CAF	n.d	n.d
CBZ	n.d	n.d
CBZ-EP	n.d - 10.0	2.51 ± 3.8
DiOH-CBZ	n.d - 353.5	52.42 ± 108.2
DCF	n.d	n.d
IBF	n.d	n.d
SMX	n.d	n.d
Ac-SMX	n.d - 59.1	9.23 ± 19.6
SMX-N1 Glu	n.d	n.d

n.d means not detected; SD means standard deviation. CBZ = Carbamazepine, CAF = Caffeine, BPA = Bisphenol A, DFC = Diclofenac, IBF = Ibuprofen, SMX = Sulfamethoxazole, Ac-SMX = N4 acetyl sulfamethoxazole, SMX-N1-Glu = Sulfamethoxazole-N1-beta-D-Glucuronide, CBZ-EP = Carbamazepine-10,11-epoxide and DiOH-CBZ = 10,11-dihydro-10,11-dihydroxy-10,11-carbamazepine

The Kruskal-Wallis procedure was used to conduct a nonparametric test in order to analyze the significant differences between the mean concentrations observed in the three district municipalities (Tshwane, Ekurhuleni, and West Rand). Based on the results presented in Table 2.3, the nonparametric test indicated that there was no statistically significant difference ($p \leq 0.05$) between the mean concentrations of N4-acetyl sulfamethoxazole and 10,11-dihydro-10,11-dihydroxy carbamazepine across the three district municipalities. However, a statistically significant difference ($p \leq 0.05$) was observed in the mean concentrations of carbamazepine-10,11 epoxide among the three districts (Table 2.3).

Table 2.3: Nonparametric test ANOVA for the studied compounds and metabolites

Compounds	Observed value	Critical value	DF	p-value*
CBZ-EP	8.13	5.99	2	0.02
DiOH-CBZ	1.15	5.99	2	0.56
Ac-SMX	1.77	5.99	2	0.41

* One tailed; DF means degree of freedom. Ac-SMX = N4 acetyl sulfamethoxazole, CBZ-EP = Carbamazepine-10,11-epoxide and DiOH-CBZ = 10,11-dihydro-10,11-dihydroxy-10,11-carbamazepine

The results of the multi-pairwise comparison indicated a statistically significant ($p \leq 0.05$) difference in the mean concentration of carbamazepine-10,11 epoxide between the Tshwane and West Rand districts (Figure 2.10). However, there were no statistically significant ($p \leq 0.05$) differences in the mean concentration of carbamazepine-10,11 epoxide between the Ekurhuleni and West Rand districts, as well as between the Ekurhuleni and Tshwane districts (Figure 2.10).

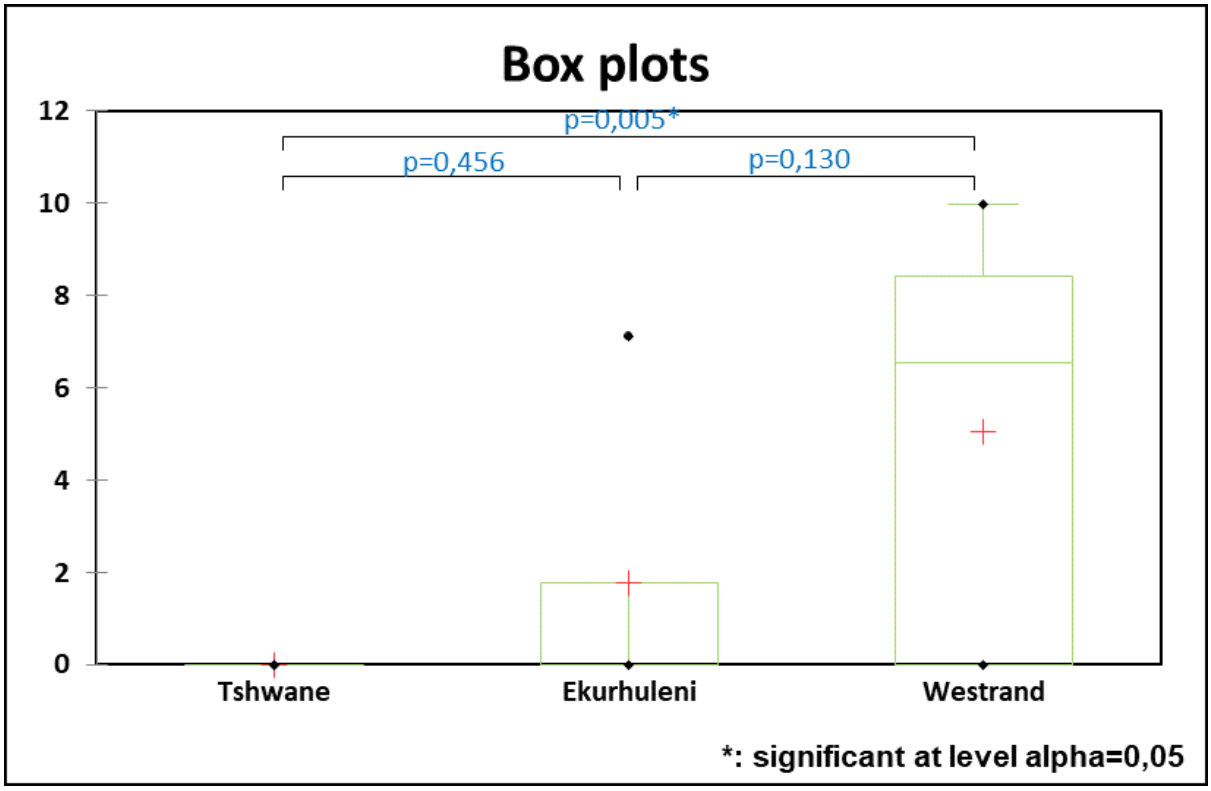


Figure 2.10: Multi-pairwise comparison of carbamazepine-10,11 epoxide means between the three districts

2.2.1.1. Relationship between farming practices and concentration levels of studied compounds and their metabolites

In order to identify potential relationships of targeted pharmaceuticals and personal care products (PPCPs) in cultivated agricultural soils, the data was subjected to principal component analysis (PCA) for further analysis. The first three principal components (PCs) collectively explained 79% of the total observed variation (PC 1 = 39.9%, PC 2 = 22.1%, and PC 3 = 17%). As depicted in Figure 2.11, the concentration levels of N4-acetyl sulfamethoxazole and 10,11-dihydro-10,11-dihydroxy-carbamazepine are positively correlated with both the crop type and cropping system. Additionally, these two compounds exhibit a strong association with farms C, D, E, J, and L, all of which utilize irrigation systems (Figure 2.11). Conversely, the concentration levels of carbamazepine-10,11 epoxide are negatively associated with both the cropping system and crop type, but positively correlated with the fertilization system (Figure 2.11). Farms S, U, Q, O, K, R, and N, all of which rely on rainfed systems, are strongly linked

with carbamazepine-10,11 epoxide. The presence of carbamazepine in these farms can be attributed to the fertilization system rather than the water management and cropping system.

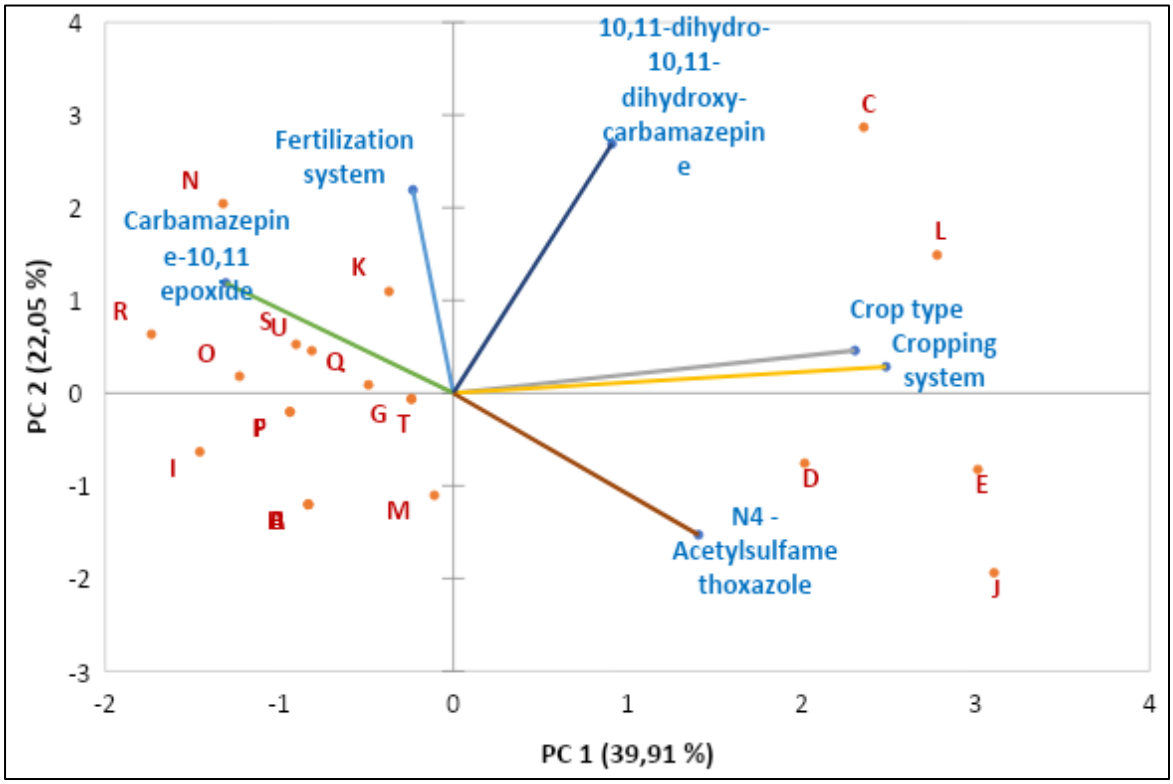


Figure 2.11: Relationship between farming practices and the studied compounds and metabolites

2.2.1.2. Relationship between soil parameters and concentration levels of studied compounds and their metabolites

In order to examine the correlation between soil parameters and PPCP (Pharmaceuticals and Personal Care Products) concentration levels in the soil, the data underwent principal component analysis (PCA). The first three principal components (PCs) collectively explained 76.49% of the total observed variation (PC 1 = 36.82%, PC 2 = 23.25%, and PC 3 = 16.43%). As illustrated in Figure 2.12, the concentration levels of N4-acetyl sulfamethoxazole and 10,11-dihydro-10,11-dihydroxy-carbamazepine are negatively influenced by the sand fraction of the soil. Conversely, the concentrations of these two compounds appear to be positively associated with the clay and organic matter content of the soil (Figure 2.12). This can be attributed to their

limited adsorption in the presence of increased sand fraction, and heightened adsorption in soils with higher organic matter and clay content. Another noteworthy insight from the biplot is the positive correlation between soil pH and the concentration levels of N4-acetyl sulfamethoxazole in the soil, particularly associated with farm E, which is an irrigated farm (Figure 2.12).

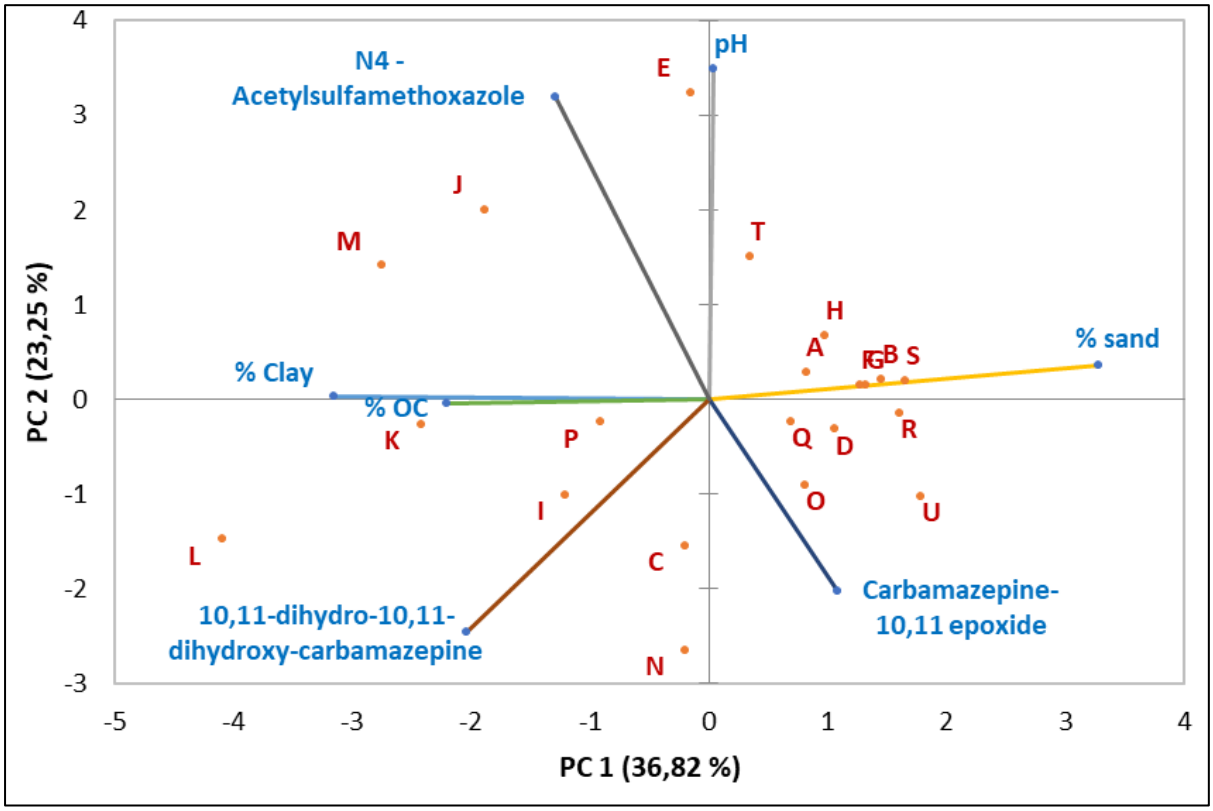


Figure 2.12: Relationship between farming practices and the studied compounds and metabolites

2.2.3 Occurrence and concentration level of pharmaceutical and personal care product compounds and their metabolites in groundwater underlying representative agricultural lands in Gauteng

A widespread occurrence of pharmaceutical and personal care products (PPCPs) in the environment has resulted in their frequent detection in groundwater over the past few years (Abdallat et al. 2022; Khan et al. 2022; Lee et al. 2019; Ebele et al. 2020; Ma et al. 2022). Agronomic practices such as the application of biowaste (i.e, animal manure, municipal sludge,

and treated wastewater) in agricultural soils are some of the major suspected entry points of PPCPs in the environment. Consequently, the PPCPs are transported from the contaminated soils into groundwater via leaching (Khan et al. 2022) and other water bodies (i.e, rivers, dams, lakes, estuaries, and oceans) through runoff. The current study investigated the occurrence and concentration levels of ten PPCPs in groundwater sources adjacent to cultivated agricultural lands around Gauteng under varying cropping systems and fertilisation practices. Overall, four out of the ten targeted PPCPs were detected in groundwaters (Figure 2.13). Of the four detected PPCPs, N4-acetyl sulfamethoxazole and carbamazepine-10,11 epoxide had the highest detection rates of 77.8% and 72.2%, respectively (Figure 2.13). Caffeine had the lowest detection rate of up to 33.3% (Figure 2.13). All detected compounds, except caffeine, were also found in the top 20 cm soil layers of farms under investigation, which suggests there is a relationship between farming practices and PPCP content in underlying groundwater. In contrast, carbamazepine, ibuprofen, bisphenol A, diclofenac, sulfamethoxazole, and sulfamethoxazole-N1-glucuronide were measured but not detected in any of the eighteen groundwater samples (Figure 2.13)

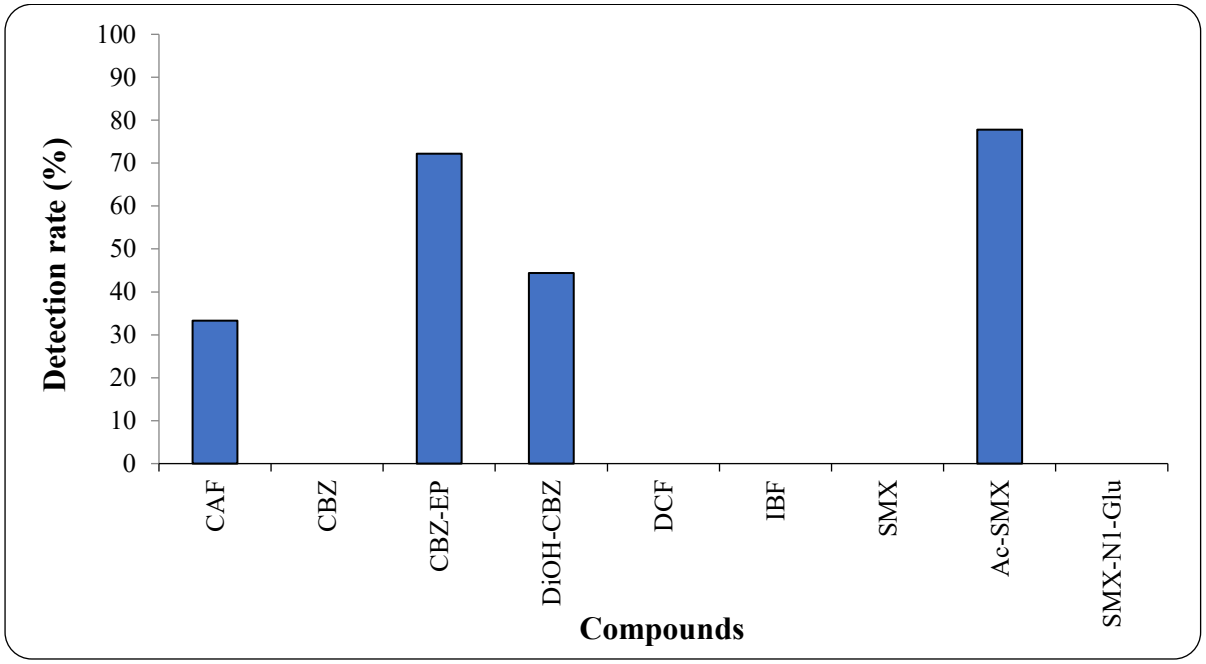


Figure 2.13: Detection rates of targeted PPCPs in groundwater sources adjacent to cultivated soils. CBZ = Carbamazepine, CAF = Caffeine, BPA = Bisphenol A, DFC = Diclofenac, IBF = Ibuprofen, SMX = Sulfamethoxazole, Ac-SMX = N4 acetyl sulfamethoxazole, SMX-N1-Glue = Sulfamethoxazole-N1-beta-D-Glucuronide, CBZ-EP = Carbamazepine-10,11-epoxide and DiOH-CBZ = 10,11-dihydro-10,11-dihydroxy-10,11-carbamazepine

Globally, there have been relatively few extensive studies on the presence of PPCPs in groundwater beneath agricultural areas (Abdallat et al. 2022; Khan et al. 2022). In our study, the frequency of detecting caffeine is comparable to findings in Nigerian groundwaters (33%) (Ebele et al. 2020), but lower than those in Korea (88%) (Lee et al. 2019) and China (90%) (Ma et al. 2022). According to Table 2.4, we have summarized the range and average concentration levels of the ten PPCPs investigated in groundwater. The carbamazepine metabolite, 10,11-dihydro-10,11-dihydroxy carbamazepine, exhibited the highest concentration level of up to 506.7 ng/L, followed by the N4-acetyl sulfamethoxazole and carbamazepine-10,11 epoxide at concentration levels up to 113.8 ng L-1 and 106.7 ng L-1, respectively. It is evident that 10,11-dihydro-10,11-dihydroxy carbamazepine showed the highest concentration level in the soils, implying a potential link between PPCPs content in the soil and groundwater. Caffeine registered the lowest concentration level of up to 67.1 ng L-1 (Table 2.4), which was higher than reported in Korea (15 ng L-1) (Lee et al. 2019) and China (11 ng L-1) (Ma et al. 2022), but lower than in Nigeria (166 ng L-1) (Ebele et al. 2020).

Table 2.4: Concentration (n = 18) of targeted PPCPs in groundwater samples in Gauteng, South Africa.

Compound	Range (ng/L)	Mean ± SD (ng/L)
CAF	n.d – 67.1	8.95 ± 3.2
CBZ	n.d	n.d
CBZ-EP	n.d – 106.7	16.05 ± 13.2
DiOH-CBZ	n.d – 506.7	94.8 ± 29.5
DCF	n.d	n.d
IBF	n.d	n.d
SMX	n.d	n.d
Ac-SMX	n.d – 113.8	43.3 ± 65.3
SMX-N1 Glu	n.d	n.d

n.d means not detected; SD means standard deviation. CBZ = Carbamazepine, CAF = Caffeine, BPA = Bisphenol A, DFC = Diclofenac, IBF = Ibuprofen, SMX = Sulfamethoxazole, Ac-SMX = N4 acetyl sulfamethoxazole, SMX-N1-Glue = Sulfamethoxazole-N1-beta-D-Glucuronide, CBZ-EP = Carbamazepine-10,11-epoxide and DiOH-CBZ = 10,11-dihydro-10,11-dihydroxy-10,11-carbamazepine

2.2.2.1. Relationship between farming practices and concentration levels of studied compounds and their metabolites in groundwater

The relationship between farming practices and PPCPs content in groundwater was investigated by conducting a principal component analysis (PCA) on the data. The first three principal components (PCs) explained 81.9% (PC 1 = 39.6%, PC 1 = 27.1%, and PC 3 = 15.2%) of the total observed variation. Figure 2.14 illustrates that the concentration levels of caffeine and 10,11-dihydro-10,11-dihydroxy-carbamazepine were positively correlated with the type of cropping system. Soil findings also suggested a positive relationship between 10,11-dihydro-10,11-dihydroxy-carbamazepine and the cropping system employed, particularly with farms using irrigation water. However, caffeine showed a negative association with the fertilisation system (Figure 2.14). In conclusion, the PCA results indicate that the presence of caffeine and 10,11-dihydro-10,11-dihydroxy-carbamazepine in groundwater is likely due to the application of contaminated irrigation water rather than the specific fertilisers used.

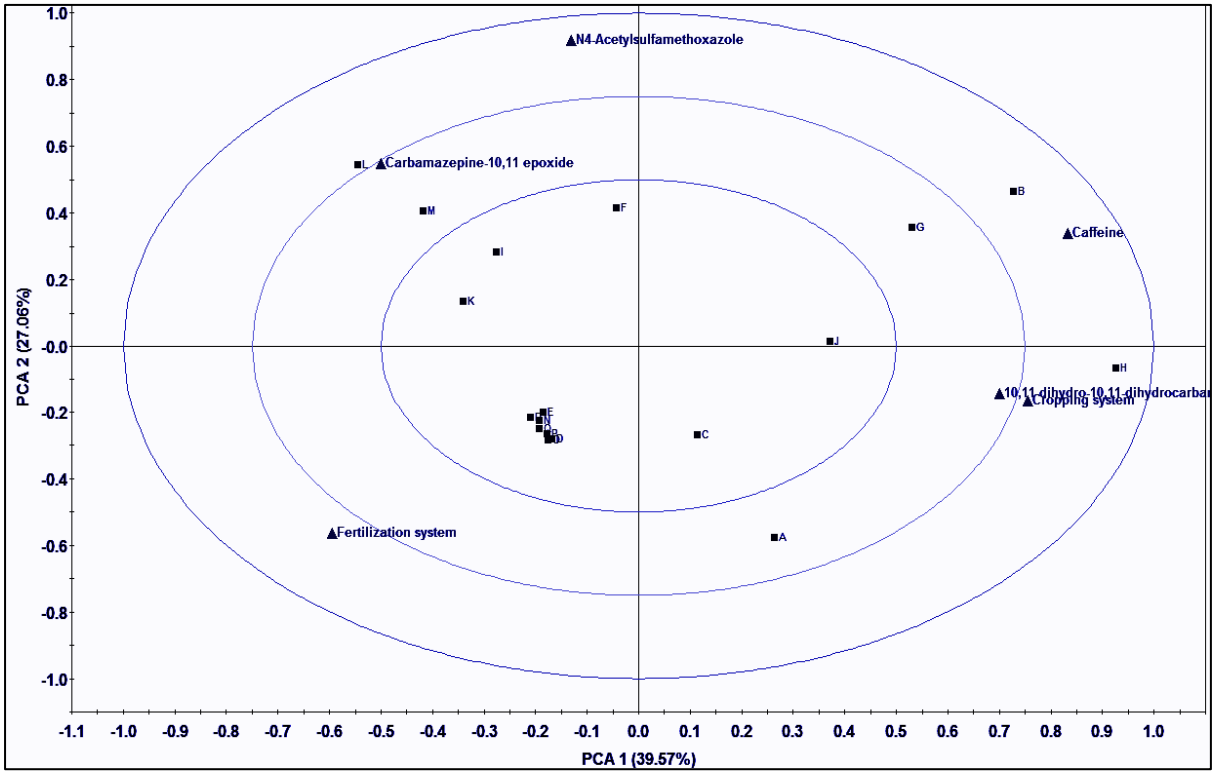


Figure 2.14: Relationship between farming practices and the studied compounds and metabolites

2.2.2.2. Relationship between water parameters and concentration levels of studied compounds and their metabolites in groundwater.

In order to examine the correlation between water parameters and PPCPs content in the soils, the data underwent principal component analysis (PCA). The first three principal components (PCs) represented 76.6% of the total variance (PC 1 = 33.5%, PC 1 = 28.3%, and PC 3 = 14.8%) as illustrated in Figure 2.15. As depicted in the figure, N4-acetyl sulfamethoxazole and carbamazepine-10,11 epoxide exhibited a positive correlation with electrical conductivity. Moreover, 10,11-dihydro-10,11-dihydroxy-carbamazepine and caffeine showed a positive relationship with pH (Figure 2.15).

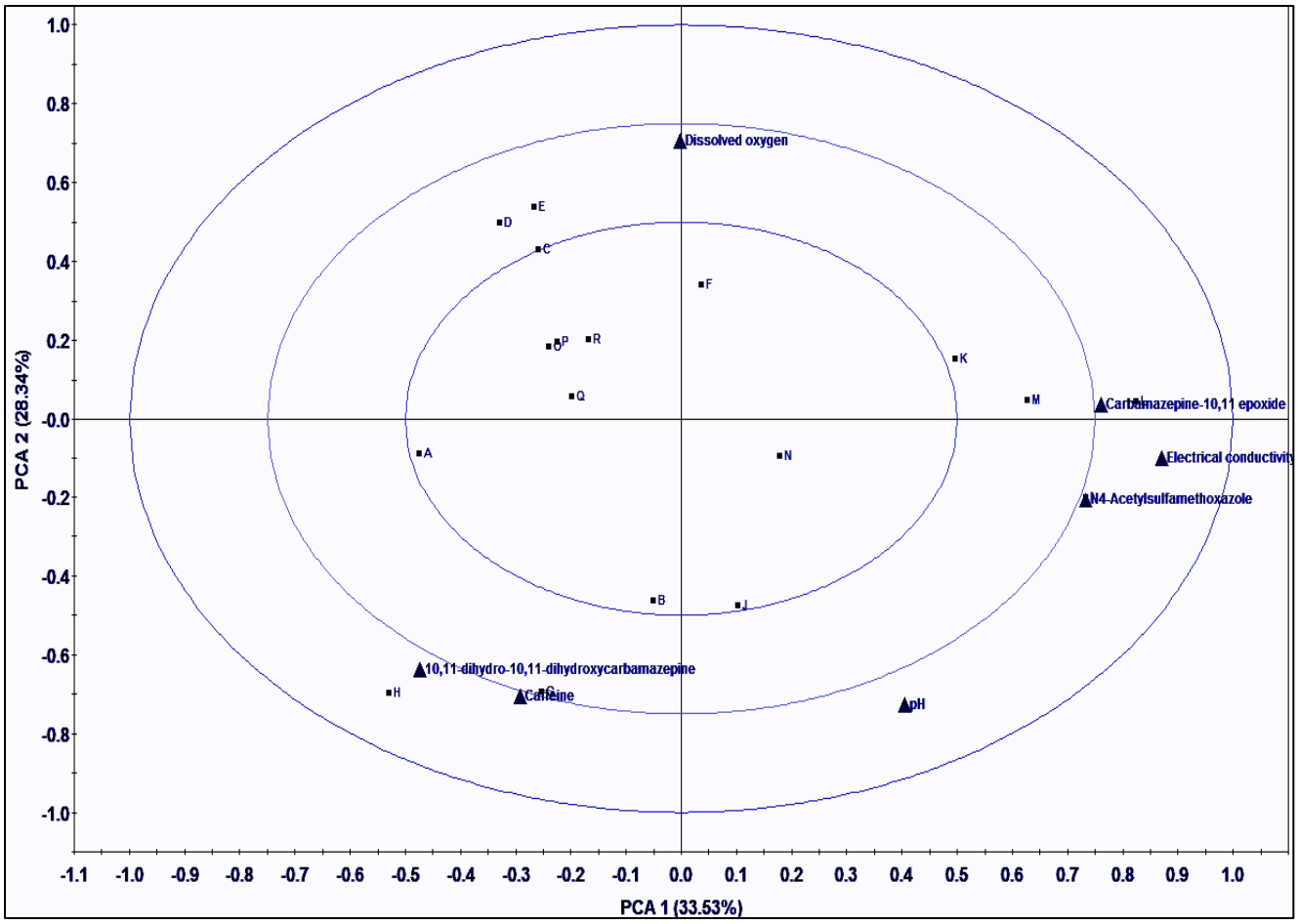


Figure 2.15: Relationship between water and the studied compounds and metabolites.

2.3 Conclusion

The study's findings indicate that three of the nine compounds analyzed, namely caffeine, carbamazepine 10,11 epoxide, and 10,11-dihydro-10,11-dihydroxy-carbamazepine, were detected in various types of fertilizers such as commercial inorganic fertilizer, sludge, compost, and animal manure. Carbamazepine 10,11 epoxide was the most frequently detected compound among these fertilizers. In agricultural soils from Tshwane, Ekurhuleni, and West Rand in the Gauteng province of South Africa, three of the nine compounds were found. The results revealed that the presence of N4-acetyl sulfamethoxazole and 10,11-dihydro-10,11-dihydroxy-carbamazepine in the soil was impacted negatively by the sand fraction but positively by the clay and organic matter content, indicating a higher retention of these compounds with greater clay and organic matter content. The concentration levels of carbamazepine-10,11 epoxide, 10,11-dihydro-10,11-dihydroxy carbamazepine, and N4-acetyl sulfamethoxazole were 10.0, 353.5, and 59.1 ng L-1 dry weight for carbamazepine-10,11 epoxide, respectively. The study also suggested that farming practices, including water management, cropping systems, and fertilization practices, had an impact on the concentration levels of the target compounds in the soil. Principal component analysis (PCA) indicated that the concentration levels of N4-acetyl sulfamethoxazole and 10,11-dihydro-10,11-dihydroxy-carbamazepine in the soil were positively influenced by water management and cropping systems, possibly due to direct accumulation during irrigation. Conversely, the concentration levels of carbamazepine-10,11 epoxide in the soil were positively affected by the type of fertilization practice, suggesting that its presence in the soil mainly originates from fertilizers. Similarly, the findings of the current study reveal the presence of certain targeted pharmaceuticals and personal care products (PPCPs) such as caffeine, carbamazepine-10,11 epoxide, 10,11-dihydro-10,11-dihydroxy-carbamazepine, and N4-acetyl sulfamethoxazole in groundwater sources near agricultural soils in the Gauteng province of South Africa. N4-acetyl sulfamethoxazole and carbamazepine-10,11 epoxide were the most frequently detected PPCPs in groundwater, with detection rates as high as 77.8% and 72.2%, respectively. Although 10,11-dihydro-10,11-dihydroxy-carbamazepine had lower detection rates, it exhibited the highest concentration level (506.7 ng L-1), suggesting that detection rates do not necessarily correlate with PPCPs concentration in the study sites' groundwater. Principal component analysis (PCA) results suggest that the presence of caffeine and 10,11-dihydro-10,11-dihydroxy-carbamazepine in groundwater is

likely due to irrigation water rather than fertilizers used in the soil, or that irrigation water facilitates the compounds' mobility into the groundwater.

CHAPTER 3: THE DYNAMICS OF EMERGING CONTAMINANTS OF CONCERN IN SLUDGE-AMENDED SOILS PLANTED TO CROPS: A CONTROLLED LYSIMETER STUDY

3.1. Materials and Methods

3.1.1 Experimental site

Two parallel lysimeter studies were conducted at the Hillcrest University of Pretoria experimental farm, South Africa (GPS coordinates: 25º45′S; 28º16′E). The experimental farm is situated at an altitude of 1370 m above sea level and receives an average annual summer rainfall ranging between 600 and 700 mm, distributed mainly from October to March.

The research study was conducted using two different sets of lysimeters, namely macro and micro lysimeters, that varied in size. The setup details of both lysimeter sets are provided below for reference.

3.1.2 Experiment 1: Micro-lysimeter

In this experiment, we employed 12 micro-lysimeters made of concrete with a rectangular shape. Each lysimeter measured 0.9 meters in length, 0.50 meters in width, and 1.2 meters in height (as shown in Figure 3.1).

Figure 3.1: Field experimental layout and structure of the micro-lysimeters

To ensure proper drainage, the lysimeters were outfitted with holes in the centre of their bottoms (as shown in Figure 3.2a). Additionally, to minimize soil temperature fluctuations on the edges caused by solar radiation, the lysimeters were externally covered with a fibre glass wool insulator (as depicted in Figure 3.2b). The drained solution was collected in the collection cans placed at the bottom of the lysimeters (as seen in Figure 3.2c).

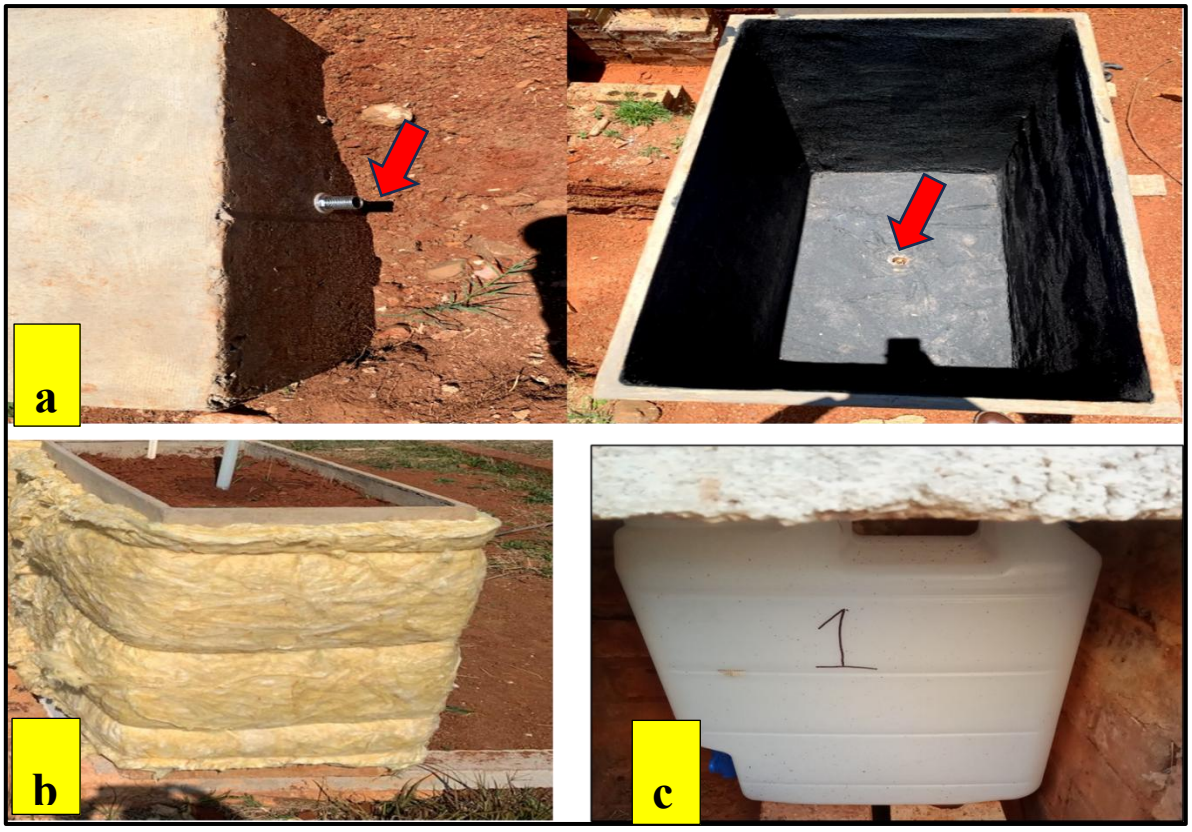


Figure 3.2: Detailed structural features of each micro-lysimeter, (a) drainage hole at the centre of the lysimeter, (b) fibre glass wool covering the outside of the lysimeter, and (c) collection cans placed at the bottom of each lysimeter

Out of the twelve lysimeters, half were filled with sandy clay loam soils and the remaining half with clay. Before the soil was packed, drainage materials were laid out in layers starting with gravel at the bottom (as shown in Figure 3.3a), followed by coarse sand (as shown in Figure 3.3b), and medium-fine sand (as shown in Figure 3.3c). These materials were arranged based on the standard guidelines for constructing drainage lysimeters.

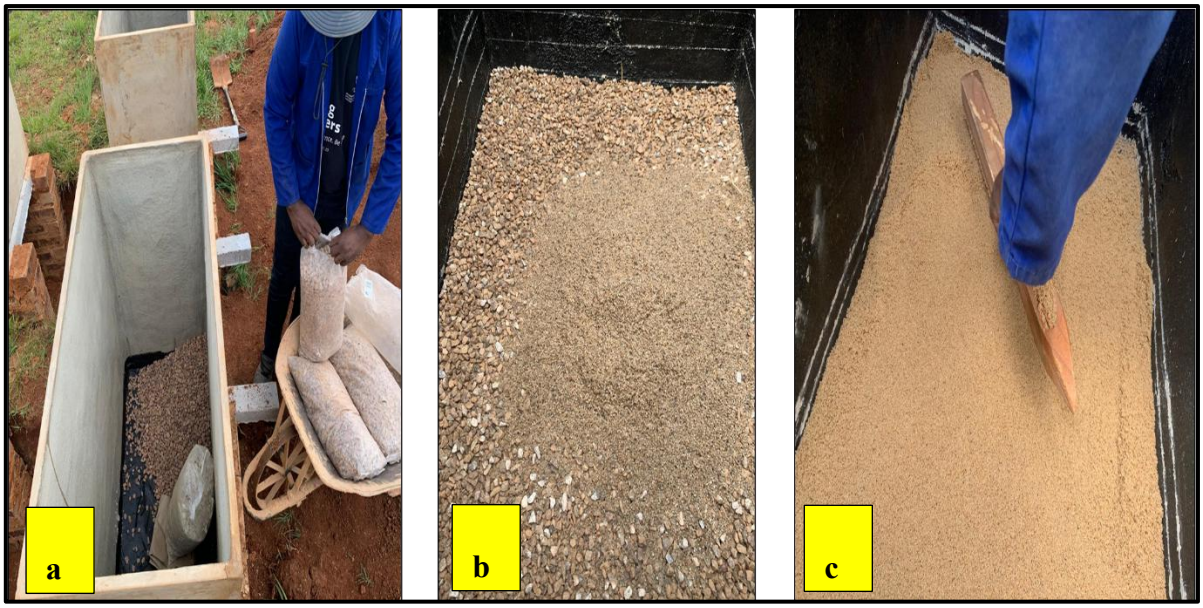


Figure 3. 3: Drainage material placed at the bottom of each lysimeter. (a) gravel at the bottom of the lysimeter, (b) coarse sand above the gravel, (c) medium-fine sand above the coarse sand

The lysimeters were filled with two distinct soil types that were carefully collected to maintain their natural stratification. The topsoil was placed on the surface, followed by the subsoil layers, in order to replicate their natural arrangement (Figure 3.4).

Figure 3.4: Soil packing inside the micro-lysimeters. (a) 60 - 70 cm layer placed above the medium-fine sand, (b) 40 - 60 cm layer placed above the 60 - 70 cm layer, (c) 20 - 40 cm layer placed above the 40 - 60 cm layer, and (d) 0 - 20 cm layer place above the 20 – 40 cm layer

The lysimeters were then allowed to settle for a year, receiving regular watering and growing canola without any additional fertilization (Figure 3.5).

Figure 3.5: Canola plant inside the micro-lysimeter during the soil settling period

3.1.3 Experiment 2: Macro-lysimeter

For this experiment, we utilized 12 circular macro-lysimeters with an inner diameter of 2.4 m, a depth of 1.3 m, and a volume of 6.1 m^3 each (as shown in Figure 3.6). These macro-lysimeters are made of metal and contain a uniform soil type (sandy clay loam) that has undergone natural processes of plant growth and death for over four to five decades, resulting in a well-established profile that is almost in its natural state.

Figure 3.6: Field experimental layout and the structure of the macro-lysimeters

The lysimeters are equipped with drainage collection tanks housed underground, as well as established lighting and an excess water discharge pumping system (as depicted in Figure 3.7).

Figure 3. 7: Drainage collection tanks for macro-lysimeter housed underground

3.1.4 Experimental treatments and design

3.1.4.1 Micro-lysimeter treatments and experimental design

There were four treatments in total, with each soil type receiving two: sludge treated according to the SARA model recommendation and a zero-sludge control. The four treatments included sludge-treated sandy clay loam, sludge-treated clay, zero-sludge sandy clay loam, and zero-sludge clay. The treatments were arranged in a completely randomized design, with each treatment replicated three times on the field. The sludge applied to the sludge treatments was manually incorporated into the top 20 cm after being applied on the surface, as shown in Figure 3.8.

Figure 3.8: Sludge application and incorporation inside micro-lysimeters

Maize (PAN6479) was planted at a density of 133,000 plants per hectare in the micro-lysimeters as a test crop. Weeds were removed manually as needed by hand.

3.1.4.2 Macro-lysimeters treatments and experimental design

The macro-lysimeter experiment consisted of four treatments: sludge-treated irrigated, sludge-treated rainfed, inorganic-fertilizer-treated irrigated, and inorganic-fertilizer-treated rainfed. Each treatment was replicated three times and arranged in a completely randomized design. The treatments were established in November 2018 (Tesfamariam et al., 2022) and have been running since then, with maize (IMP 52-11R) planted inside each lysimeter as a test crop. The planting density for maize was 40,000 and 80,000 seeds under rainfed and irrigation systems, respectively. Before planting, sludge and commercial inorganic fertilizers were applied and incorporated into the top 20 cm soil layer. Sludge was applied according to the recommendations generated by the SARA model, while commercial inorganic fertilizers were

applied according to the recommendations of the South African Fertilizer Handbook. Unlike sludge, commercial inorganic fertilizers were split-applied at various maize-growing stages. Moisture content under irrigated systems was monitored using a neutron probe and were irrigated to field capacity every three days.

3.1.5 Sampling and sample preparation

3.1.5.1 Water

Following each rainfall event that triggered drainage, samples of drainage water were collected. The volume of drainage water from each lysimeter was recorded prior to collecting samples in clean 2.5 L amber glass bottles for analysis (Figure 3.9). These samples were extracted within 24 hours of collection using the solid phase extraction method (Figure 3.9). Along with drainage water samples, samples of irrigation and rainwater were also collected in 2.5 L amber glass bottles.

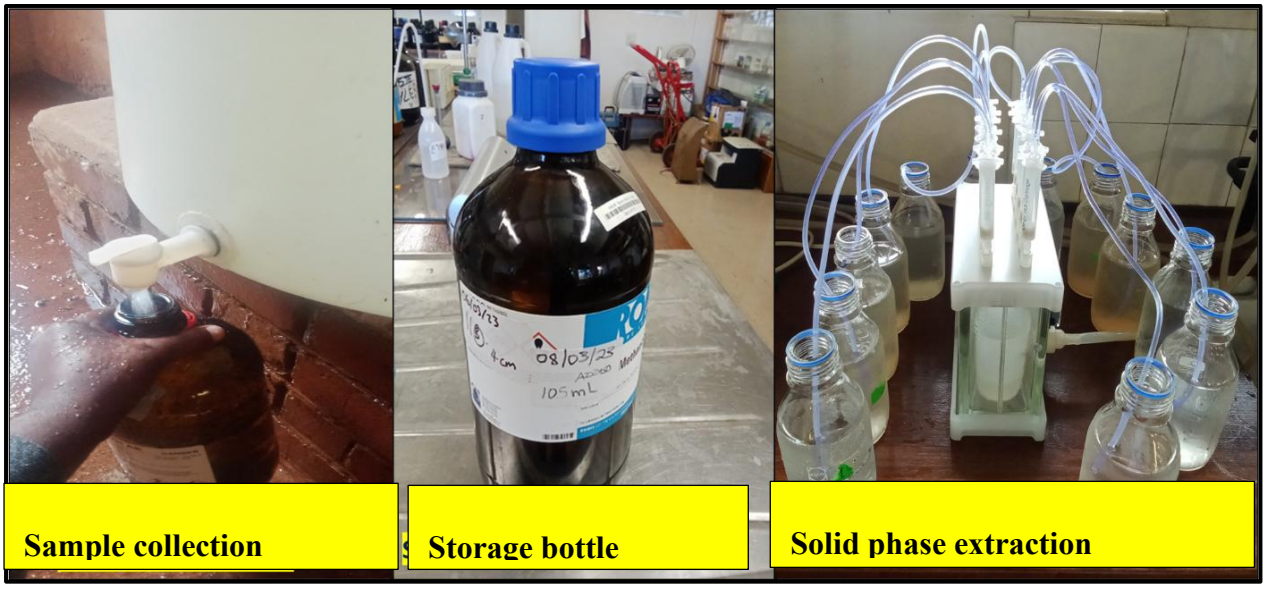


Figure 3.9: Drainage sample collection inside an amber glass bottle

3.1.5.2 Plant

Samples of maize plants were collected when they reached physiological maturity from the lysimeters. To minimize the border effect, the plant samples were collected from the inner rows and were all taken 5 cm above the soil surface. The samples were then washed with deionised water and separated into stems, leaves, and grains. After collection, the plant samples were freeze-dried, ground into a fine powder, homogenized, and stored at -20 ^{O}C until extraction.

3.1.5.3 Soil

Soil samples were collected using a galvanized metal auger immediately after plant sampling. To avoid cross-contamination, the auger was washed with deionized water and rinsed with methanol after every sampling. In Experiment 1 (micro-lysimeter), soil samples were collected randomly from 0-20 cm, 20-40 cm, and 40-70 cm layers. In Experiment 2 (macro-lysimeter), soil samples were collected randomly at 0-30 cm, 30-60 cm, and 60-100 cm layers. The soil samples were then dried at room temperature, sieved with a 2 mm diameter sieve, and stored at -20 ^{O}C before extraction.

3.1.6 Analytical procedures

3.1.6.1 Water

Water samples were extracted using the EPA method 1694, with modifications based on the approach developed by de Santiago-Martin et al. (2020). Briefly, a 500 mL sample was extracted through the solid phase extraction (SPE) approach, utilizing Oasis HLB cartridges. The sample was loaded into the Oasis cartridges, which were conditioned sequentially with 6 mL methanol, 6 mL ultrapure water, and 6 mL acidified ultrapure water (pH = 2). After loading the sample, interfering materials were washed with 20 mL ultrapure water. The cartridges were then dried under vacuum (at 5 bar pressure) for 5 min. Target analytes were eluted using 3 x 4 mL aliquots of methanol, which was then evaporated using a nitrogen gas. Finally, analytes were recovered by a 1 mL methanol. The solution was vortexed for 1 min, transferred to the injection amber glass vial, and analytes were immediately quantified by the UHPLC-QTOFMS method.

3.1.6.2 Soil

Soil and sludge samples were extracted using the EPA method 1694, with modifications based on the approach developed by de Santiago-Martin et al. (2020). A pre-prepared sample weighing 1g was subjected to three sequential extractions using acetonitrile. The first extraction involved adding 20 mL of acetonitrile to the sample and sonicated for 30 minutes. Prior to the second extraction, 15 mL of phosphate buffer solution (pH 2) was added to the sample to suspend solids. The suspended solids were then extracted for the second time with 20 mL of acetonitrile in an ultrasonic water bath for 30 minutes. The final extraction involved adding 15 mL of acetonitrile to the previously extracted sample and sonicated for 30 minutes. After each extraction, the mixture was centrifuged at a speed of 3000 rpm for 5 minutes and the aqueous were removed into a clean test tube. The extracts from the three sequential extractions were combined inside a Bunchi flask and the solvents were evaporated using a rotary evaporator to a volume of about 20 mL. The extracts were then transferred to a 100 mL volumetric flask and 250 mg $Na_2EDTA.2H_2O$ was added to the extracts. Following the addition of $Na_2EDTA.2H2O$, the volume was filled to a 100 mL mark with ultrapure water. The same SPE procedure used during the extraction of liquid samples was performed for both sludge and soil samples using the pre-conditioned Oasis HLB cartridge. Elution and reconstitution were also performed in the same way as was the case with the liquid samples.

3.1.6.3 Plant

The stems, leaves, and grains of maize were extracted using the method developed by de Santiago-Martin et al. (2020). To summarize, a mixture of salts, consisting of 4g magnesium sulphate, 1g sodium chloride, 1g sodium citrate tribasic dihydrate, and 0.5g sodium hydrogen citrate sesquihydrate, was added to 1g of the sample, which was then extracted with 30 mL of methanol using an ultrasonic water bath for 15 minutes. After centrifugation at 4000 rpm for 15 minutes, the aqueous was transferred to a clean test tube. This process was repeated twice using the same conditions. The extracts from the three sequential extractions were combined in a Bunchi flask, and the methanol was evaporated using a rotary evaporator. The extracts were recovered with 25 mL ultrapure water and 25 mg EDTA was added. The solution underwent the previously explained SPE procedure.

3.1.7 Quantification and method validation

3.1.7.1 UHPLC-QTOFMS instrument

3.1.7.1.1 Instrument description

Target analytes were quantified using the Waters ® Synapt G2 high-definition mass spectrometry (HDMS) system (Waters Inc., Milford, Massachusetts, USA). The system was equipped with a Waters Acquity Ultra Performance Liquid Chromatography (UPLC) system hyphenated to a quadrupole time-of-flight (QTOF) instrument. The instrument was equipped with A Kinetex® 1.7 µm EVO C18 100 Å (2.1 mm ID × 100 mm length) column for chromatographic separation of the target compounds. The column temperature was kept constant at 50 °C, and the flow rate was set at 0.3 mL/min for the entire run, giving a total run time of 20 min.

3.1.7.1.2 Operating conditions

Separation was performed using a reverse-phase gradient elution scheme from 97% H_2O (with 0.1% formic acid) to 100% methanol (with 0.1% formic acid). The injection volume was 5 µl. After testing the samples, the data were processed using the MassLynx™ (version 4.1) software (Waters Inc., Milford, Massachusetts, USA).

3.1.7.2 Method validation

3.1.7.2.1 Quality assurance and control measures

More than 5 levels of standard solutions in a range of 1 ng/mL to 500 ng/mL were used to obtain calibration curves for targeted PPCPs (see Supplementary Table 3). The correlation coefficients (r^2) of calibration curves were greater than 0.99 (see Supplementary Table 3). At least one method blank was analysed with every batch of samples to determine the availability of the target compounds in the blanks. None of the target compounds were detected in the method blanks. In addition, LC MS grade methanol which was used as a mobile phase was injected after every 10 samples to check cross contamination.

3.1.7.2.2 Limit of detection and limit of quantification

Limits of detection (LODs) and limits of quantification (LOQ) were calculated from the calibration curves as concentrations that give a signal to noise (S/N) ratio of 3 and 10, respectively. Detailed information is given in the supplementary information Table 3 and 4.

$$\text{LOD} = \frac{Lowest\ concentration\ of\ the\ standard\ in\ the\ calibration\ curve}{Instrumental\ S/N\ \ for\ the\ lowest\ concentration\ of\ the\ standard\ in\ the\ calibration\ curve}\ X\ 3$$

$$\text{LOQ} = \frac{Lowest\ concentration\ of\ the\ standard\ in\ the\ calibration\ curve}{Instrumental\ S/N\ \ for\ the\ lowest\ concentration\ of\ the\ standard\ in\ the\ calibration\ curve}\ X\ 10$$

3.2 Results and discussions

3.2.1 Experiment 1: Micro-lysimeter

The subsequent sections outline the results regarding the presence of specific pharmaceuticals and personal care products (PPCPs) in municipal sludge, their buildup in the soil profile and maize plants after application, and the movement of these substances below the plant root zone.

3.2.1.1 Occurrence of targeted PPCPs in municipal sludge

It is a widespread occurrence to find PPCPs in treated municipal sludges worldwide (Chen et al., 2019; McClellan and Halden, 2010). This is largely due to the influx of waste containing animal and human excretions, as well as household and hospital chemicals (McClellan and Halden, 2010). Some of the PPCPs do not break down, but instead become adsorbed by the solid organic fraction of the sludge (McClellan and Halden, 2010).

In the present study, seven out of the eight candidate PPCPs, such as antibiotics, anticonvulsants, stimulants, non-steroidal anti-inflammatory drugs, and their primary metabolites, were identified in the sludge utilized for the macro and micro lysimeter studies

(see Table 3.1). The compound that was not detected in the sludge used in the micro lysimeter study was sulfamethoxazole (SMX), and in the macro lysimeter study, it was Caffeine (CAF). The concentrations of the PPCPs in the current study ranged from non-detection for SMX and CAF (lower than reported levels in other countries) to less than 152 ng/g dry wt. for Caffeine (CAF) (which falls within the range reported in Canada).

The levels of the metabolite N_4-Acetylsulfamethoxazole (AcSMX) in sludge for the current study are relatively higher (≤ 19.21 ng g^{-1}) compared to those reported in Turkey (< LOQ) (Dolu and Nas, 2023) and Spain (≤ 9.81 ng g^{-1}) (García-Galán et al., 2013). Similarly, the concentrations of the metabolite Sulfamethoxazole-N1 glucuronide (SMX-N1-glu) (≤ 17.77 ng g^{-1}) and the metabolite Carbamazepine-10,11-epoxide (CBZ-E) (≤ 21.73 ng g^{-1}) for sludge from our study were higher than those reported in Turkey (<LOQ) and Canada (N.D), respectively. On the other hand, diclofenac (DCF) (≤ LOD), carbamazepine (CBZ) (≤ 16.94 ng g^{-1}), CAF (N.D - ≤ 152.15 ng g^{-1}), and the metabolite Cis-10,11-Dihydro-10,11-dihydrocarbamazepine (cis-iOH-CBZ) (≤ 12.09 – 17.11 ng g^{-1}) fell within the ranges reported in Canada, Turkey, USA, France, and China, respectively (Table 3.1). In the following sections the dynamics of the targeted compounds within the soil-plant-water system are presented.

Table 3. 1: Concentration levels of targeted PPCPs in municipal sludges around the globe vs the current study

Contaminant	Concentrations (ng/g dry wt.)	Country	Reference
Diclofenac (DCF)	17.20 – 110.60	China	(Dong et al., 2016)
	1.03 – 6.16	Turkey	(Dolu & Nas 2023)
	≤ LOD	South Africa	Sludge used in micro lysimeter
	< LOQ	South Africa	Sludge used in macro lysimeter
Carbamazepine (CBZ)	≤ 0.04	France	(Bourdat-Deschamps et al., 2017)
	9.0 – 60.30	USA	(USEPA, 2009)
	≤ 10.77	South Africa	Sludge used in micro lysimeter
	≤ 16.94	South Africa	Sludge used in macro lysimeter
Sulfamethoxazole (SMX)	≤ 31	India	(Subedi et al., 2015)

Contaminant	Concentrations (ng/g dry wt.)	Country	Reference
	≤ 3.3	USA	(McClellan & Halden, 2010)
	N.D	South Africa	Sludge used in micro lysimeter
	≤ 8.83	South Africa	Sludge used in macro lysimeter
Caffeine (CAF)	165.8	Canada	(Miao et al., 2005)
	≤ 152.15	South Africa	Sludge used in micro lysimeter
	N.D	South Africa	Sludge used in macro lysimeter
N_4-Acetylsulfamethoxazole (AcSMX)	< LOQ	Turkey	(Dolu & Nas 2023)
	≤ 9.81	Spain	(García-Galán et al., 2013)
	≤ 17.62	South Africa	Sludge used in micro lysimeter
	≤ 19.21	South Africa	Sludge used in macro lysimeter
Sulfamethoxazole-N1 glucuronide (SMX-N_1-glu)	< LOQ	Turkey	(Dolu & Nas 2023)
	≤ 12.09	South Africa	Sludge used in micro lysimeter
	≤ 17.77	South Africa	Sludge used in macro lysimeter
Carbamazepine-10,11-epoxide (CBZ-E)	N.D	Canada	(Miao et al., 2005)
	≤ 21.73	South Africa	Sludge used in micro lysimeter
	≤ 16.52	South Africa	Sludge used in macro lysimeter
Cis-10,11-Dihydro-10,11-dihydrocarbamazepine (cis-DiOH-CBZ)	≤ 15.4	Canada	(Miao et al., 2005)
	≤ 12.09	South Africa	Sludge used in micro lysimeter
	≤ 17.11	South Africa	Sludge used in macro lysimeter

N.D means not detected, LOQ means limit of quantification, LOD means limit of detection.

3.2.1.2 Dynamics of targeted PPCPs in Municipal sludge amended soils

The movement of the eight targeted compounds in the plant-soil-water system of sludge-amended clay and sandy clay loam soils planted with maize is outlined below. Prior to the

application of sludge, none of the eight target PPCPs were found in either the clay or clay loam soils. Likewise, none of these eight PPCPs were detected in the plants or leachate from the untreated soils throughout the growing season. As a result, the results presented are solely from the sludge-treated soils. Additionally, sulfamethoxazole (SMX) was not detected in the sludge, and therefore was also not found in the soil, plants, or leachate. Consequently, it will not be included in the subsequent sections of the discussion.

3.2.1.2.1 Diclofenac (DCF)

Diclofenac is a negatively charged compound characterized by a poor sorption (Log K_{ow} = 0.96) (Goldstein et al. 2014) and low water solubility (2.37 mg/L at 25^{O}C) (Goldstein et al. 2014). These features of DCF makes it 1) less persistent in the soil (Grossberger et al., 2014) and 2) not easily taken up by the plant roots (Trapp 2004). According to Trapp (2004) negatively charged compounds cross the cell membranes (i.e., tonoplast and plasma membrane) at a slower rate than the neutral compounds (i.e., compounds with both positive and negative sites). This is due to the repulsions between the negatively charged cell membranes (i.e., tonoplast and plasma membrane) and the negatively charged compound (Trapp, 2000). Following the harvesting of the maize crop, DCF was not detected throughout the soil profile (0 - 70 cm depth) of both clay and sandy clay loam soils. It was also not detected in the maize stems, leaves, grains and drainage water below the root zone during the entire growing season. There is limited information available on the fate of DCF in the soil-plant-water system after municipal sludge application. Previous studies have primarily focused on DCF's behaviour in the soil-plant-water system following wastewater irrigation (Malchin et al. 2012; Paz et al. 2016; Fenet et al. 2012). However, the findings of our study align with those of Malchin et al. (2014) in Israel, where DCF was not detected in the soil and plants (i.e., sweet potato and carrot) after irrigation with treated wastewater. The absence of DCF in the soil, plants, and water in our study can be attributed to the rapid degradation in the soil following municipal sludge application (Grossberger et al., 2014).

3.2.1.2.2 Caffeine (CAF)

Caffeine is a polar neutral compound with low sorption (Log Kow = -0.07) (Paz et al. 2016) and very high water solubility (2.16 x 10^4 mg/L at 25°C) (The National Library of Medicine's Toxnet system, 2009). These characteristics make caffeine 1) easily absorbed by plants from the soil solution (Dettenmaier et al. 2009), 2) readily transported from roots to aboveground plant parts through mass water flow (Dettenmaier et al. 2009), and 3) highly prone to leaching into deeper soil layers (Trapp 2000). After the maize crop was harvested, no CAF was found in the soil profile (0 - 70 cm depth) of both clay and sandy clay loam soils. Additionally, no CAF was detected on the maize stem and leaves (Figure 3.1). However, CAF was detected in the maize grain at levels ranging from 15.87 ng/g d.w (clay) to 19.23 ng/g d.w (sandy clay loam) (Figure 3.10). The results of this study align with those reported elsewhere. In the United States, Kinney et al. (2008) conducted a study on the presence of CAF in agricultural soils amended with municipal sludge and found no detectable CAF in the soils. The absence of CAF in the soil from our study can be attributed to 1) rapid uptake by the maize plant (Figure 3.8) and 2) leaching below the root zone (Figure 3.9). In maize stems and leaves, the lack of CAF can be explained by its translocation to the grains (Figure 3.8).

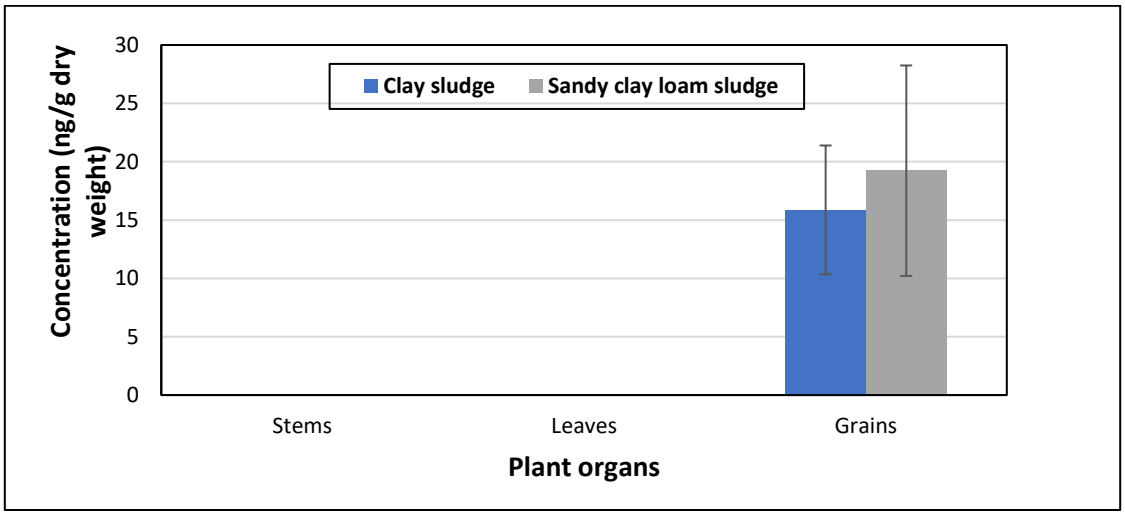


Figure 3.10: Concentration of caffeine in stems, leaves, and grains of maize planted to clay and sandy clay loam soils amended with municipal sludge

Furthermore, CAF was found in the drainage water from both clay soils and sandy clay loam soils (Figure 3.11a). The concentration of CAF in drainage collected from clay soils ranged from 4.58 ng/L to 12.82 ng/L, while in the clay loam soils, it ranged from 1.83 ng/L to 7.10 ng/L (Figure 3.11a). These leaching events took place during the early growing season following high and intensive rainfall events (Figure 3.11b). The early-season presence of CAF in drainage water can be attributed to the high solubility of CAF in the soil, which is a result of elevated soil moisture levels. This leads to the migration of CAF to deeper soil layers below the root zone, as explained by Trapp (2000).

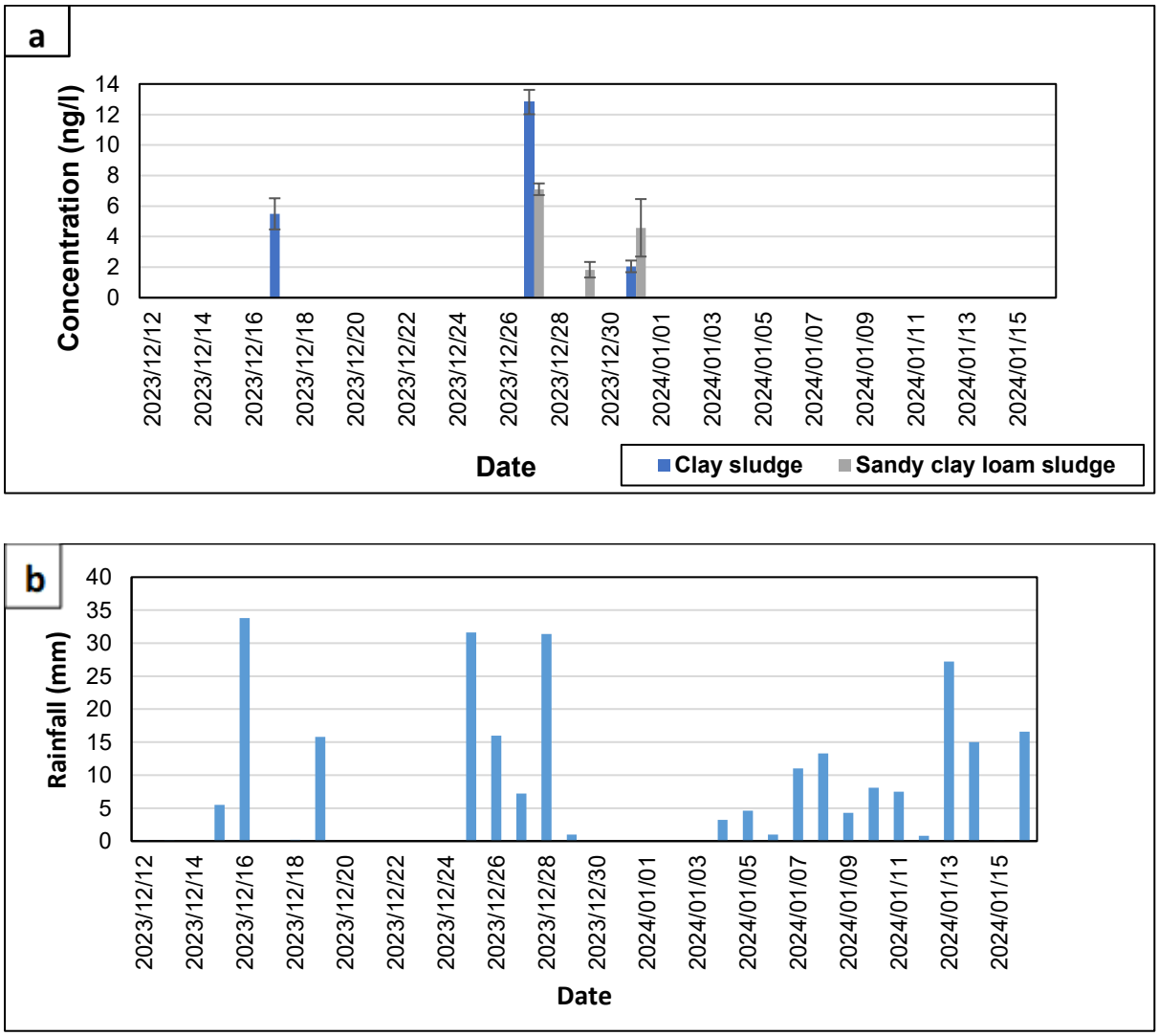


Figure 3.11: Concentration of caffeine in drainage water collected below the 70 cm maize root zone from clay and sandy clay loam soils amended with municipal sludge (a) and the amount of rainfall received throughout the planting season (b)

3.2.1.2.3 Carbamazepine (CBZ)

Carbamazepine is a polar, neutral compound with a strong sorption characteristic (Log Kow = 2.77) (Paz et al. 2016) and a moderate to high water solubility (125 mg/L at 25°C) (Paz et al. 2016). Due to these properties, CBZ has the tendency to 1) persist in the soil (Fenet et al. 2012), 2) be absorbed by plant roots (Malchin et al. 2014), and 3), to a lesser extent, be leached out to deeper soil layers due to strong sorption (Gottschall et al. 2012). Carbamazepine was found in the soil (0 - 20 cm and 20 - 40 cm layers) immediately after the crop harvest and on the maize crop under both the clay and sandy clay loam soils that were fertilized with municipal sludge. Regardless of soil type, the concentration of CBZ in the soil was, however, below the method limit of quantification (2.077 ng/g dry weight, see Supplementary Table 3) for both the 0 - 20 cm and 20 - 40 cm layers and not detected for the 40 - 70 cm layer. Similarly, CBZ was detected below the method of quantification (2.077 ng/g dry weight, see Supplementary Table 3) in maize stems and grains and not detected in maize leaves under both soils. The results of this study are consistent with those reported in Canada by Gottschall et al. (2012). In their research, Gottschall et al. (2012) investigated the presence of CBZ in agricultural soils and wheat grains after the application of municipal sludge. They found no detectable levels of CBZ in the wheat grains, but observed the presence of carbamazepine in the soil at a concentration of 30 ng/g dry weight, one year after the sludge application (Gottschall et al. 2012). The high concentration of CBZ in the soil observed by Gottschall et al. (2012) can be attributed to the elevated levels of CBZ in the applied sludge (183 ng/g dry weight).

Furthermore, CBZ was detected below the limit of quantification (4.154 ng/L, see Supplementary Table 4) in drainage collected from both clay and sandy clay loam soils. The findings from this study indicate that, regardless of soil type, CBZ exhibit limited mobility and uptake in the soils following municipal sludge application. In a study by Gottschall et al. (2012), it was found that carbamazepine (CBZ) was below the limit of quantification in tile drainage at a depth of 1.2 meters after the application of municipal sludge, except for one instance during the season following the first rain event, where a concentration of 13 ng/L was recorded. We can conclude that there are minimal potential CBZ food and groundwater contamination risks from sludge-amended soils provided that similar quality of municipal sludge, in terms of their CBZ content, is applied based on the crop nutrient demand.

3.2.1.2.4 Sulfamethoxazole N_1 glucuronide (SMX-N_1-glu)

Following the time of maize harvest, SMX-N_1-glu was found in the 0 - 20 cm and 40 - 70 cm layers of both clay and sandy clay loam soils but was not found in the 20 - 40 cm layer of the two soils. The concentration of SMX-N_1-glu was, however, below the method limit of quantification under both 0 - 20 cm and 40 - 70 cm layers (6.65 ng/g dry weight, see Supplementary Table 3).

In plant samples, SMX-N_1-glu was found only in stems of maize planted to clay soils (Figure 3.3). SMX-N_1-glu was below the limit of quantification (6.65 ng/g dry weight, see Supplementary Table 3) in stems and leaves of maize planted to sandy clay loam soils and not detected in leaves of maize planted to clay soils. Furthermore, SMX-N_1-glu was not detected in grains of maize planted in both soils (Figure 3.12).

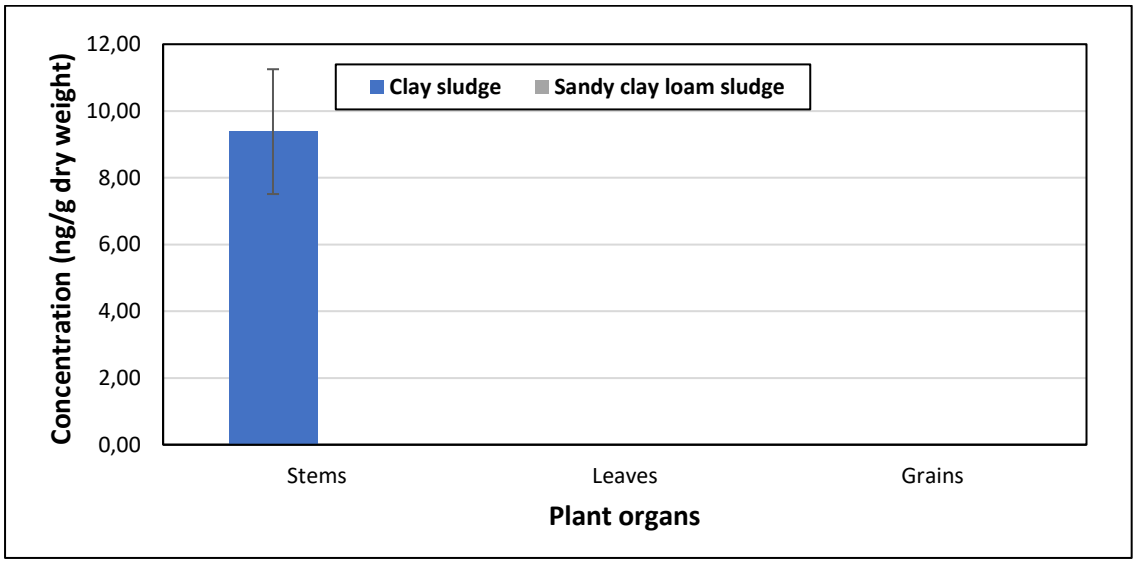


Figure 3.12: Concentration of sulfamethoxazole N_1 glucuronide in stems, leaves, and grains of maize planted to clay and sandy clay loam soils amended with municipal sludge

Sulfamethoxazole N_1 glucuronide found below the limit of quantification (13.30 ng/L, see Supplementary Table 4) in drainage water collected from both clay and sandy clay loam soils amended with municipal sludge.

3.2.1.2.5 N_4 Acetyl sulfamethoxazole (AcSMX)

N_4 Acetyl sulfamethoxazole was not detected in the stems, leaves, and grains of maize planted in both clay and sandy clay loam soil that had been amended with municipal sludge. The study also found that AcSMX was not present in the 20 - 40 cm layer of clay soils, as shown in Figure 3.4, and was below the method limit of quantification (3.41 ng/g dry weight, see supplementary data) in the 40 - 70 cm layer of both clay and sandy clay loam soils. However, AcSMX was detected in the 0 - 20 cm and 20 - 40 cm layers of sandy clay loam soils, as depicted in Figure 3.13. Additionally, AcSMX was found in the 0 - 20 cm layer of clay soil, as illustrated in Figure 3.13. The concentration of AcSMX was observed to decrease with soil depth, under the sandy clay loam soil, as indicated in Figure 3.13.

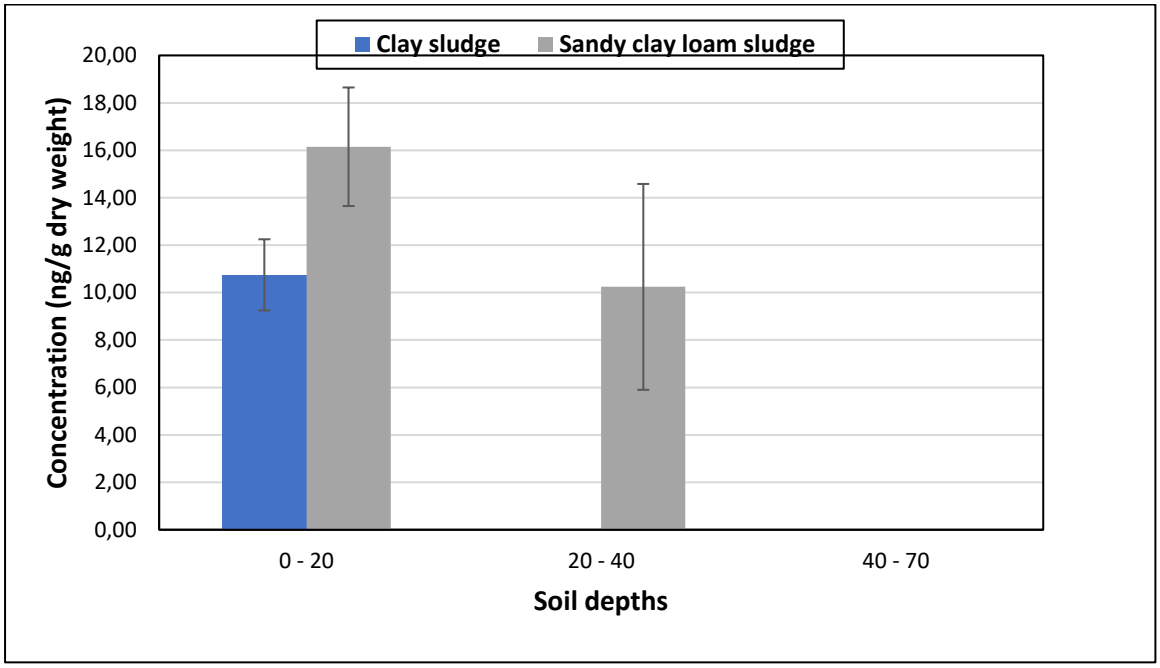


Figure 3.13: Concentration of N_4 acetylsulfamethoxazole in clay and sandy clay loam soils amended with municipal sludge

N4 acetylsulfamethoxazole was detected in drainage water samples collected from both clay and sandy clay loam soil that had been treated with municipal sludge (Figure 3.14a) following heavy rainfall events (Figure 3.14b). The presence of N4 acetylsulfamethoxazole in the drainage water was only observed a few days after the sludge application and planting. Subsequent occurrences of AcSMX were not observed after this initial period (Figure 3.14a).

This timeframe coincided with the early stage of maize crop growth, when the roots were not fully established.

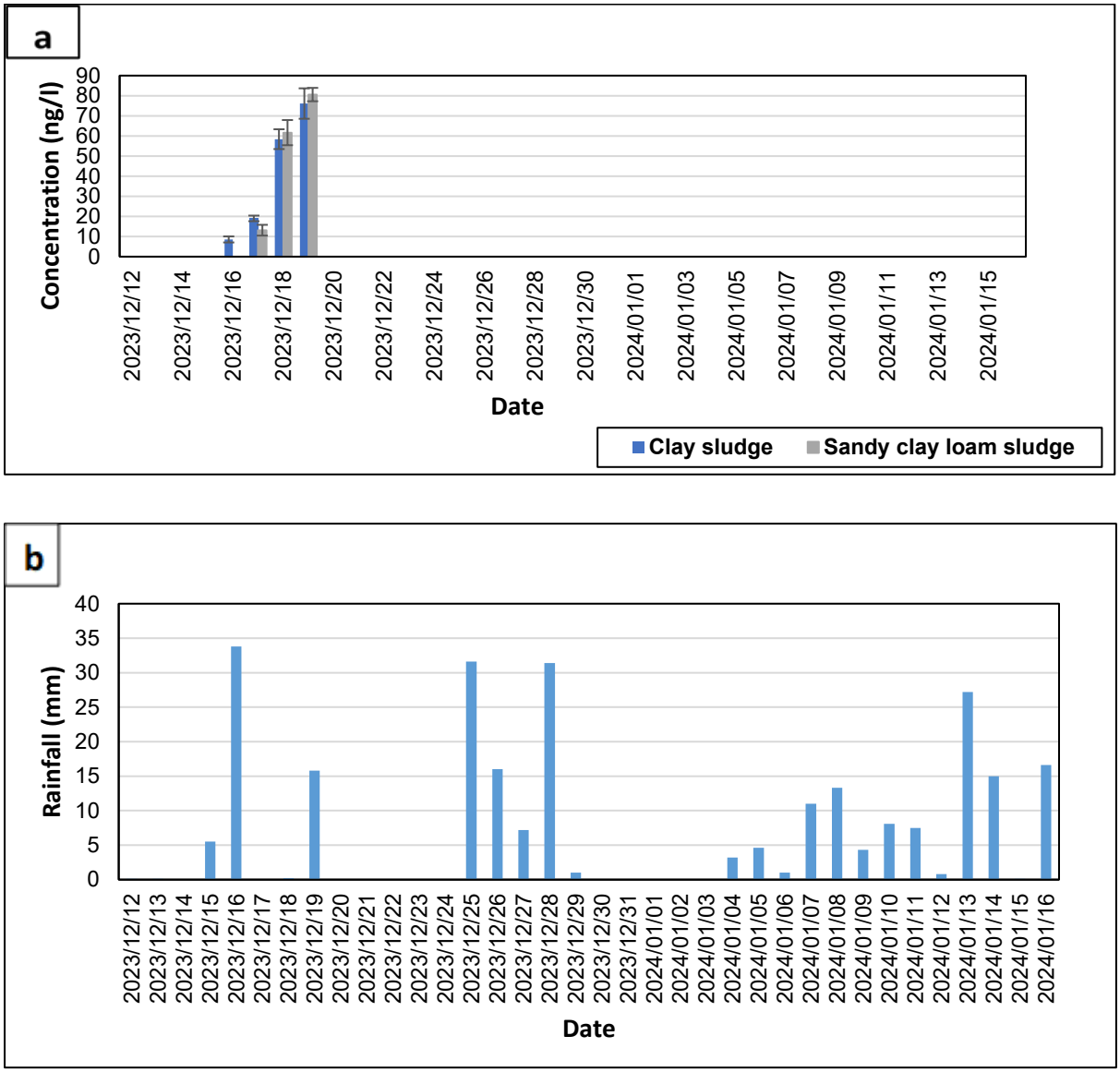


Figure 3.14: Concentration of N_4 acetylsulfamethoxazole in drainage water collected below the 70 cm maize root zone from clay and sandy clay loam soils amended with municipal sludge (a) and the amount of rainfall received throughout the planting season (b)

3.2.1.2.6 Carbamazepine-10,11-epoxide (CBZ-E)

In contrast to its parent compound (CBZ), CBZ-E exhibits poor sorption (Log Kow = 1.97) (Paz et al. 2016) and higher water solubility (1340 mg/L at 25 OC) (Paz et al. 2016). Consequently, it is anticipated that CBZ-E would undergo 1) rapid degradation in the soil, 2) high absorption in the plant roots, and 3) significant leaching. The presence of CBZ-E was found in the stems and leaves of maize plants grown in clay soil, as shown in Figure 3.15. In sandy clay loam soils, CBZ-E was only detected in maize stems (Figure 3.15). Interestingly, it was not detected in the maize grains of the same crop in either soil type (Figure 3.15). Limited research exists on the behavior of CBZ metabolites in the soil-plant-water system. Notable among such studies is the work of Mordechay et al. (2018), who examined the presence of CBZ-E in tomato plants (leaves and fruit) after applying municipal sludge to the soil. The results of Mordechay et al. (2018) align with our current study, showing that CBZ-E was not found in fruits or grains. The absence of CBZ-E in maize grains in our study may be attributed to the low translocation of CBZ-E to maize grains and the rapid conversion of CBZ-E to cis-DioH-CBZ in maize grains.

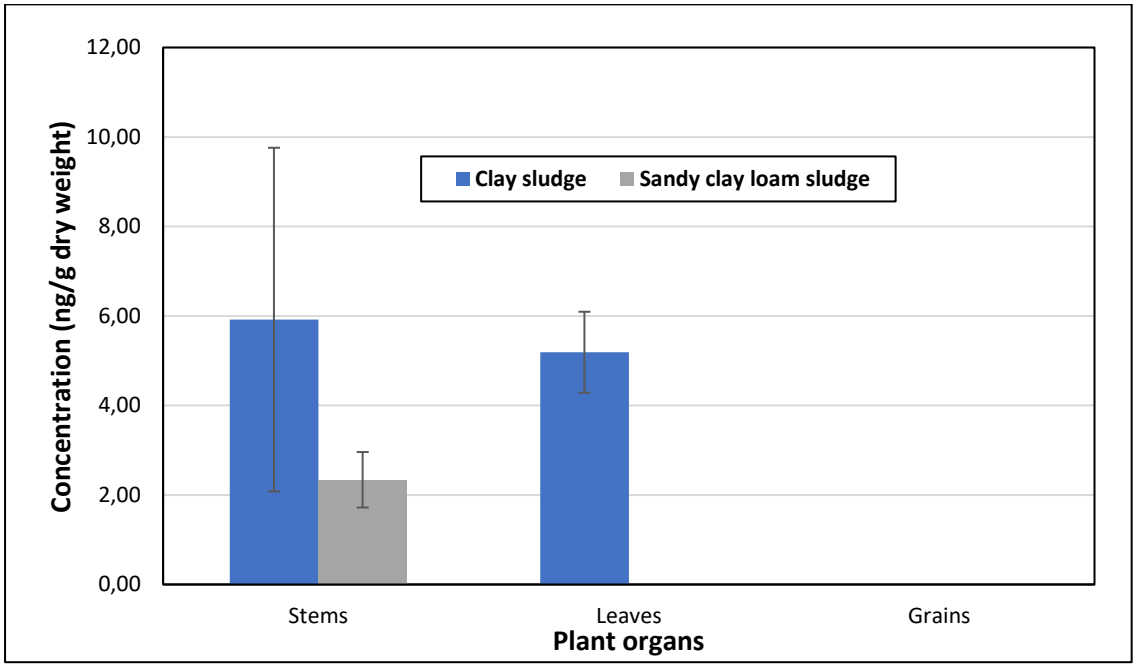


Figure 3.15: Concentration of carbamazepine-10,11 epoxide in stems, leaves, and grains of maize planted to clay and sandy clay loam soils amended with municipal sludge

After the maize crop harvest, the presence of CBZ-E was found only in the 40 - 70 cm layers of both clay and sandy clay loam soils that had been amended with municipal sludge (Figure 3.16). This indicates that CBZ-E exhibited similar behaviour in both types of soil. Additionally, the concentration of CBZ-E was higher in clay soils (3.26 ng/g dry weight) compared to sandy clay loam soils (1.74 ng/g dry weight) (Figure 3.16). Currently, there is no available information regarding the translocation of CBZ-E in the soil subsequent to municipal sludge application. Nevertheless, Mordechay et al. (2018) conducted a study that detected CBZ-E in a single soil layer (0 - 20 cm) at concentration levels below 0.68 and 0.49 ng/g dry weight during tomato and lettuce farming, respectively.

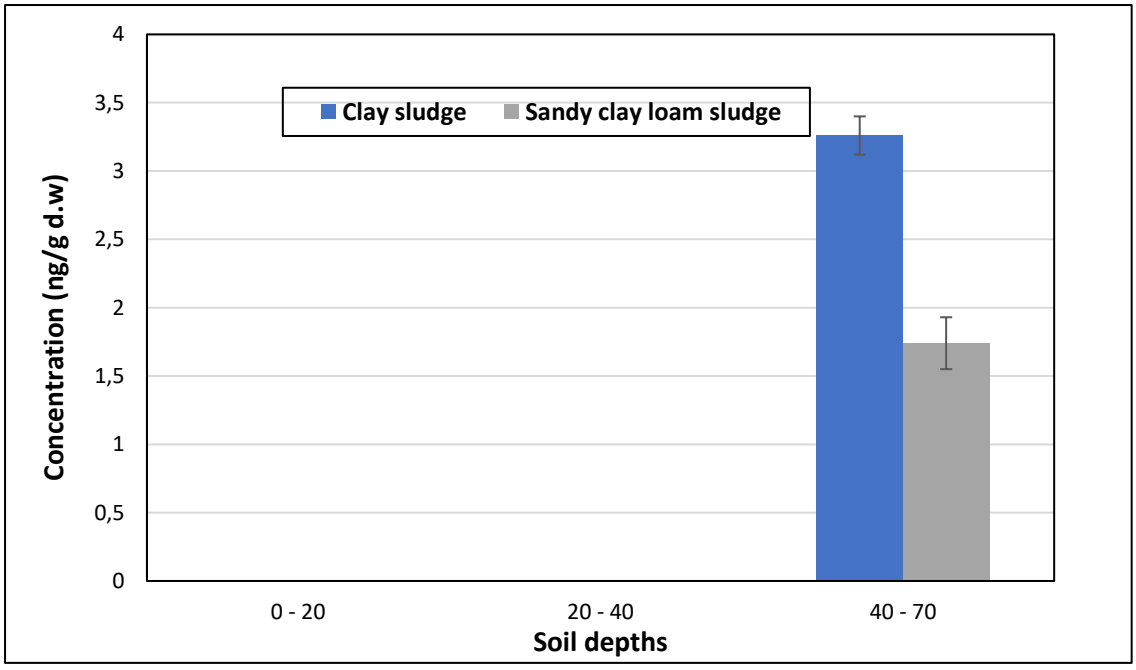


Figure 3.16: Concentration of carbamazepine-10,11 epoxide in clay and sandy clay loam soils amended with municipal sludge

Carbamazepine-10,11 epoxide was detected in drainage water collected from both clay and sandy clay loam soils that had been treated with municipal sludge (Figure 3.17a). The presence of Carbamazepine-10,11 epoxide in the drainage water was only observed a few days after the application of sludge and planting, following heavy rainfall events (Figure 3.17b). There were no further instances of CBZ-E observed after this initial period (Figure 3.17a). This timeframe aligned with the early stage of maize crop growth, when the roots are not yet fully established. Currently, there is no available information regarding the transportation of CBZ-E in soil subsequent to the application of municipal sludge. Previous studies have primarily examined

the transportation of CBZ-E in soils that are irrigated with treated wastewater (Malchin et al. 2012; Paz et al. 2016; Fenet et al. 2012). Within these studies, Fenet et al. (2012) observed the presence of CBZ-E in groundwater beneath soils that are subjected to wastewater irrigation, indicating the potential migration of CBZ-E below the soil's root zone.

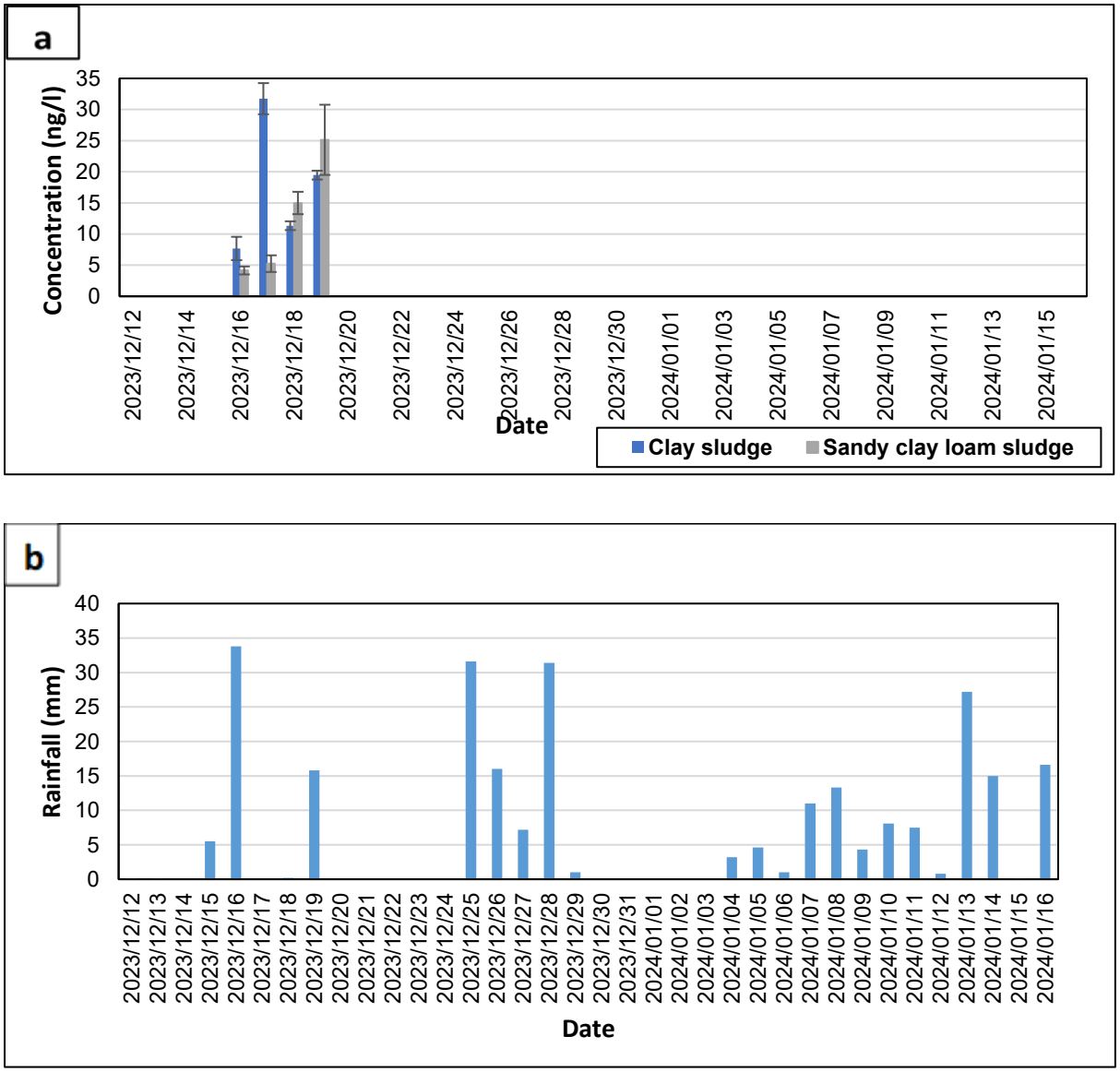


Figure 3.17: Concentration of Carbamazepine-10,11-epoxid in drainage water collected below the 70 cm maize root zone from clay and sandy clay loam soils amended with municipal sludge (a) and the amount of rainfall received through the planting season (b)

3.2.1.2.7 cis-10,11-dihydro-10,11-dihydrocabamazepine (cis-DiOH-CBZ)

The compound cis-10,11-dihydro-10,11-dihydrocabamazepine exhibits low sorption (Log Kow = 0.81) and high-water solubility (1800 mg/L at 25°C) (Paz et al. 2016). Consequently, it is anticipated that cis-DiOH-CBZ will 1) degrade more rapidly in the soil, 2) be readily absorbed by plants, and 3) leach into lower soil layers. The compound cis-DiOH-CBZ was detected in the stems and grains of maize planted in sandy clay loam soils, but was not present in the leaves of the same crop (Figure 3.18). Furthermore, cis-DioH-CBZ was detected in the grains of maize plants grown in clay soils but was not found in the stems and leaves of the same crop (Figure 3.18). The results differ from those of Mordechay et al. (2018), who did not detect cis-DioH-CBZ in lettuce, wheat, and tomato (leaves, fruits, and ears) planted in biosolids-amended soils.

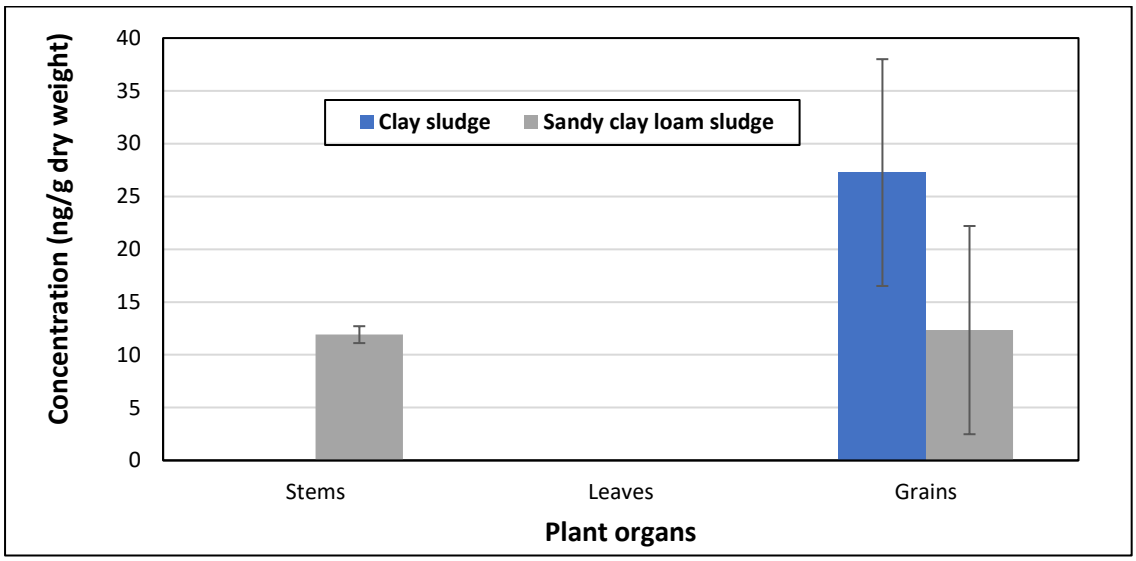


Figure 3.18: Concentration of cis-10,11-dihydro-10,11-dihydrocarbamazepine in stems, leaves, and grains of maize planted to clay and sandy clay loam soils amended with municipal sludge

cis-10,11-dihydro-10,11-dihydrocarbamazepine was found only in the top 20 cm soil layer of both clay and sandy clay loam soils amended with municipal sludge, suggesting limited leaching of these compounds under both medium and heavy textured soils. Consequently, cis-DioH-CBZ was not detected in the drainage water collected from both the clay and sandy clay loam soils. The concentration of cis-DioH-CBZ in the top 20 cm layer of both soils was, however, below the method limit of quantification (10.27 ng/g dry weight; see supplementary

data). In a study conducted by Paz et al. (2016), cis-DioH-CBZ was found distributed throughout the soil profile up to a depth of 100 cm. However, it is important to note that the study utilized irrigation wastewater as a source of cis-DioH-CBZ, and this may have contributed to its migration to deeper soil layers. Comparing concentration levels under sludge-amended soils is not possible due to a lack of available information.

3.2.2. Experiment 2: Macro-lysimeter study

The subsequent sections outline the results regarding the presence of specific pharmaceuticals and personal care products (PPCPs) in municipal sludge, their buildup in the soil profile and maize plants after application of municipal sludge and commercial inorganic fertilizers, and the movement of these substances below the plant root zone.

3.2.2.1 Dynamics of targeted PPCPs in municipal sludge and commercial inorganic fertilizer amended soils

The movement of the eight targeted compounds in the plant-soil-water system of sludge and commercial inorganic fertilizer-amended sandy clay loam soils planted with maize is outlined below. Diclofenac (DCF), sulfamethoxazole (SMX), sulfamethoxazole-N_1 glucuronide (SMX-N_1-glu), N4 acetylsulfamethoxazole (AcSMX), carbamazepine-10,11 epoxide (CBZ-E), and cis-10,11-dihydro-10,11-dihydrocarbamazepine (cis-DiOH-CBZ) were not found in the soil, plants, or leachates, despite their presence in the applied municipal sludge. Carbamazepine was the only compound detected in the soil profile of sludge-amended soils. Therefore, it is the only compound discussed in the following subsection.

None of the PPCPs were detected in the soil, leachate, and plant organs of the maize crop in the commercial inorganic fertilizer amended macro lysimeter soils.

3.2.2.1 Carbamazepine (CBZ)

Carbamazepine was detected in both the 0 - 30 cm and 30 - 60 cm layers of soils that received municipal sludge and were irrigated (Figure 3.19). In the 0 - 30 cm layer, the concentration of CBZ under this treatment was 7.10 ng g-1, while in the 30 - 60 cm layer, it was 2.34 ng g-1 based on dry weight (Figure 3.19). The concentration decreased with depth, indicating limited mobility of the compound. Additionally, CBZ was detected in soils that received municipal sludge without irrigation water, as well as in the stems, leaves, and grains of maize planted in

sludge-treated soils under both rainfall and supplemented rainfall with irrigation, albeit below the quantification limit of 2.07 ng g-1 dry weight (Table S.2). Similar findings were reported in a study conducted in Canada by Gottschall et al. (2012), CBZ was detected in the top 30 cm soil layer at a concentration level of 30 ng/g dry weight one year after sludge application, but was higher than the levels found in the current investigation. Furthermore, similar to the current investigation, CBZ was not detected in wheat grains at harvest in the study by Gottschall et al. (2012). In a separate study, Mordechay et al. (2018) reported CBZ concentrations of up to 0.68 ng/g dry weight in the soil following sludge application, which was lower than that observed in the current investigation.

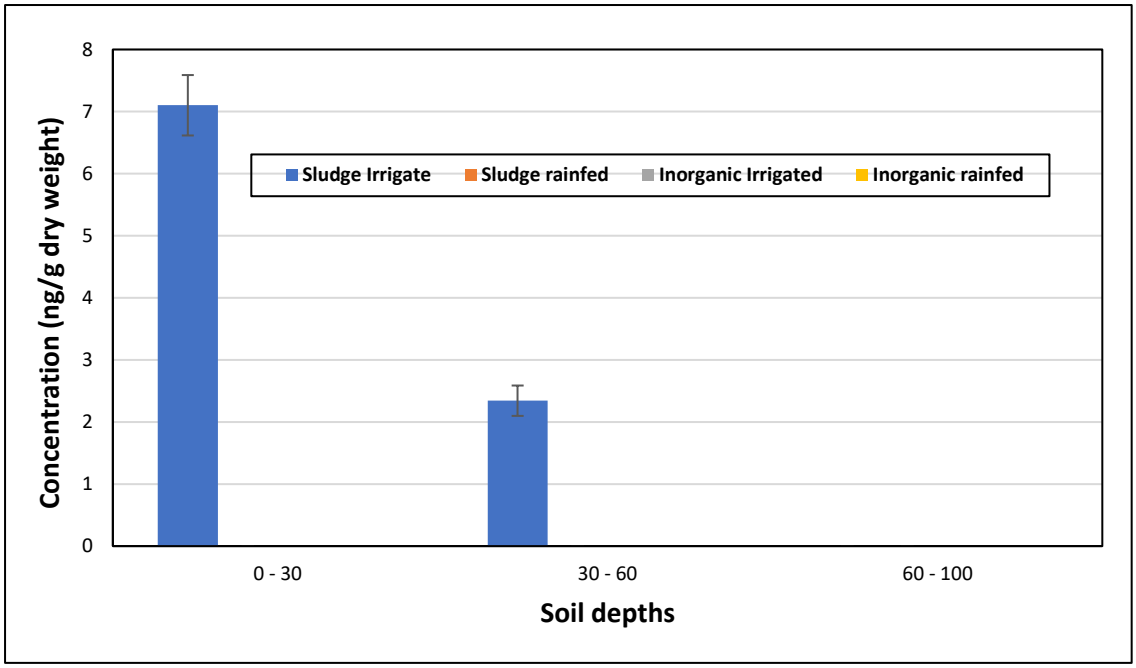


Figure 3.19: Concentration of carbamazepine in the soil profile under sludge irrigated, sludge rainfed, inorganic fertilizer irrigated, and inorganic fertilizer rainfed treatments.

The absence of PPCPs in the leachate, as well as the soil profiles in the macro lysimeter, is most probably attributed to the low sludge application rates on the macro lysimeters compared with the micro lysimeters. This is mainly due to the sludge model, which provides the recommendation rates based on existing nutrient contents in the soil as well as the history of previous sludge applications. The macro lysimeter has been receiving sludge according to the crop nutrient requirements for the past five years, and therefore, it has a nutrient carry-over effect for the existing year, which the model takes into account in order to estimate how much

sludge should be added. Considering the previous five years of sludge application on the macro lysimeter, it would be expected to find more of the PPCPs. However, this was not the case, indicating the short half-life of the majority of the PPCPs.

3.3 Conclusion

Seven out of the eight target PPCPs were found in the sludge used in both macro and micro lysimeters, with their concentration ranges falling within global reported ranges. Diclofenac, however, was present in the sludge but was not detected in the plants, leachate, and soil in both types of lysimeters. Carbamazepine was detected in the soil after the crop harvest in both types of lysimeters, but it was below the limit of detection in the micro lysimeters. None of the other five PPCPs were detected in the leachate, plants, and soils of the macro lysimeters. In contrast, caffeine, N4 acetyl sulfamethoxazole, and carbamazepine-10,11-epoxide were found in drainage water below the root zone, and caffeine, carbamazepine-10,11 epoxide, and cis-10,11-dihydro-10,11-dihydrocarbamazepine were detected in maize crop organs in the micro lysimeters. This suggests that the movement of PPCPs in the soil-plant-water continuum depends on soil type and depth.

CHAPTER 4: MODELLING THE LEACHING OF SELECTED EMERGING CONTAMINANTS FROM SLUDGE-AMENDED AGRICULTURAL SOILS ACROSS VARIOUS SOUTH AFRICAN AGRO-ECOLOGICAL ZONES

4.1 Materials and methods

4.1.1 Experimental site

Detailed information on the study site, experimental layout, treatments, lysimeter construction, all agronomic activities, and soil water plant sampling for emerging contaminant determination used for model calibration and validation can be found in Chapter 3, subheading 3.1.

Scenario simulations for contaminant leaching from sludge amended at 10 tons per hectare per year were carried out at representative sites in four of the six South African agro-ecological zones. The representative sites include Bloemfontein for the semi-arid zone, Johannesburg for the sub-humid zone, Durban for the humid zone, and Nelspruit for the super-humid zone. The simulation for each agro-ecological zone was conducted for two soil types: sandy clay loam and clay.

4.1.2 Selection of studied compounds

The present study has chosen to focus on the anticonvulsant drug carbamazepine and its main metabolite, carbamazepine-10,11 epoxide, for the purposes of model calibration, validation, and scenario simulation regarding contaminant dynamics across various agro-ecological zones in South Africa. This decision was influenced by the frequent occurrences of these substances in biowastes, soils, and groundwaters in the Gauteng region. Additionally, these compounds have been found in soil and leachate samples obtained from a field lysimeter experiment conducted as part of the current project.

4.1.3 Analytical procedures

Detailed information on analytical procedures and quantification and method validation for contaminants could be found in Chapter 3, subheading 3.1.

4.1.4 Model description

The HYDRUS model is a widely used numerical model for simulating water flow, solute transport, and heat transfer under both steady and transient conditions (Šimůnek et al., 2016). The latest version of the HYDRUS model (version 5.03) incorporates a modified version of the dynamic plant uptake (DPU) multi-compartment model proposed by Trapp (2007), which considers multiple differentiated metabolization pathways in plant tissue (Brunetti et al., 2019).

4.1.5 Model parameterisation

4.1.5.1 Hydrus model

a. Initial conditions

The initial conditions were determined based on the volumetric moisture content measured at the start of the experiment, expressed as volume of water per volume of soil [cm^3 cm^{-3}]. Additionally, the concentration levels of the specified compounds in the entire soil profile were recorded at the beginning of the experiment and utilized as the initial conditions. These concentration levels were expressed as the mass of solutes per volume of soil [ng cm^{-3}].

b. Boundary conditions

The upper boundary conditions for water flow were defined as atmospheric conditions within the surface layer to facilitate interaction with model simulations and atmospheric factors such as solar radiation, temperature, wind speed, and humidity. The lower boundary conditions for water flow were set as free drainage, as the water table is located well below the soil domain. In the case of solute transport, concentration boundary conditions and concentration flux boundary conditions were respectively assigned to the upper and lower boundaries.

c. Soil hydraulic parameters

The soil hydraulic parameters were estimated using the pedotransfer functions integrated into the Hydrus-1D software. This estimation was performed based on the unimodal van Genuchten equation and the measured particle size distribution (Van Genuchten, 1980). The estimated soil hydraulic parameters for the two soils under investigation are presented in Table 4.1.

Table 4. 1: Selected hydraulic parameters for the two soils

Soil layer [cm]	**Θ**s [cm^3/cm^3]	**Θ**r [cm^3/cm^3]	Alpha [1/cm]	n [-]	Ks [cm/day]
Sandy clay loam					
0 - 20	0.3839	0.0715	0.0271	1.2718	12.88
20 - 40	0.4043	0.0814	0.0284	1.2231	14.73
40 - 70	0.4048	0.0821	0.0287	1.2159	15.67
Clay					
0 - 20	0.4549	0.0920	0.0230	1.2272	12.55
20 - 40	0.4809	0.0967	0.0221	1.1983	16.50
40 - 70	0.4757	0.0959	0.0225	1.2022	16.15

Θs means saturated moisture content; Θr means residual moisture content; Ks is the saturated hydraulic conductivity

d. Solute transport and reaction parameters

The model requires the input of the compound's molecular diffusion coefficients in both the liquid phase (Dw) and air (Da) as specific transport parameters. The Dw value was taken from Brunetti et al. (2019), and the Da value was assumed to be zero due to the non-volatile nature of the targeted compounds. Additionally, the model also requires the input of the adsorption isotherm coefficient (K_d), solute degradation rate in the liquid phase (SinkL1), and solute degradation rate in the solid phase (SinkS1) as solute reaction parameters. The solute degradation rates in both liquid and solid phases were also obtained from Brunetti et al. (2019). The K_d value was calculated using the equation provided by Filipović et al. (2020):

$$K_d = Koc \times Foc \quad (3)$$

where Koc is the soil organic carbon-water partitioning coefficient, and Foc is the fraction of the soil organic carbon. The Koc values for a similar soil were taken from the literature (Paz et al., 2016) and used to calculate K_d by multiplying with the fraction of soil organic carbon.

e. Root growth parameters

The model also relies on data about the depth of the plant roots throughout the simulation period to calculate the uptake of water and nutrients by the roots. We used the daily root depth data provided by the SWB-Sci model as input parameters.

4.1.5.2. Dynamic plant uptake model

a. General information

The model requires general information, including the proportion of solute adsorbed on particles, particle deposition velocity, average relative air humidity, and average air temperature. Given the non-lipophilic nature of the compounds of interest, the proportion of solute adsorbed on particles and the particle deposition velocity were both set to zero. The average relative air humidity and temperature were sourced from an automatic weather station located in the study site.

b. Plant information

The dynamic plant uptake model requires input parameters such as plant tissue water content, lipid content, initial mass, maximum mass, growth rate coefficient, plant-specific area, and plant density for each compartment. Water content was determined by measuring the difference between the fresh and oven-dry biomass of samples collected at harvest. Maximum mass was derived from the fresh plant biomass collected at harvest. Initial mass was assumed to be zero since there were no roots, leaves, stems, or fruits at the beginning of the experiment. Plant-specific area was calculated by dividing the compartment area by the dry biomass weight, as outlined by Brunetti et al. (2019). Growth rate coefficients and lipid contents for each compartment were taken from Trapp (2007).

c. Solute parameters and metabolization matrix

The candidate compounds' air-water partitioning coefficients (Kaw) were sourced from Brunetti et al. (2019), while the octanol-water partitioning coefficients (Kow) were obtained from Paz et al. (2016). Due to the non-volatile nature of the targeted compounds, the concentration of the studied solutes in the air (Ca) was set to zero. Molar masses of the studied solutes were acquired from Paz et al. (2016). Metabolization rates were extracted from Brunetti et al. (2019) and adjusted for a maize crop.

4.1.5.3 Model calibration and validation

The HYDRUS-2D model was calibrated using data collected from a sludge-amended sandy clay loam soil planted with maize during the 2023/24 growing season in micro-lysimeters. Following this calibration, the model was validated using an independent data set collected from sludge-amended clay soil planted with maize during the same growing season. The

calibration and validation aimed to establish the model's reliability for assessing contaminant leaching. To evaluate the model's performance, the simulated results were compared to measured values using statistical parameters such as coefficient of determination (R2), Wilmott index of agreement (D), and mean absolute error (MAE) as recommended by de Jager (1994), as shown in Table 4.2.

Table 4. 2: Statistical parameters for validation

Statistical parameter	Value
D	> 0.8
MAE (%)	< 20
R^2	> 0.8

4.1.5.4 Scenario simulation

The validated model was used to simulate the leaching potential of carbamazepine and its metabolite from two types of soil (sandy clay loam and clay) across four South African agroecological zones (Semi-arid, sub-humid, humid, and super-humid) following the application of sludge at a rate of 10 tons per hectare. This rate aligns with the maximum allowable sludge application rate as per the current South African sludge guideline. The model simulation spanned the duration of a maize crop growth season, consistent with the customary practice in South Africa, where sludge is applied every season.

4.2 Results and Discussion

4.2.1 Model calibration and validation

The HYDURS-2D model was calibrated successfully for simulating the leaching of carbamazepine and its metabolite, carbamazepine-10,11-epoxide, using data collected from the sludge-amended sandy clay loam soil planted with maize during the 2023/2024 growing

season. The values for the three statistical parameters, as described by de Jager (1994), fell within the acceptable ranges as specified in Table 4.3 (column 2).

The HYDRUS-2D model was successfully validated for simulating the leaching of carbamazepine and its metabolite (carbamazepine-10,11-epoxide) using data collected during the 2023/24 growing season from a sludge-amended clay soil. All the statistical indicators (R^2 = 0.93, D = 0.82, and MAE = 9.56) fell within acceptable ranges as prescribed by de Jager (1994).

Table 4. 3: Statistical parameters for HYDRUS-2D model calibration and validation

Statistical parameters	Recommendations by de Jager (1994)	Calibration values	Validation values
Coefficient of determination (R^2)	> 0.8	0.99	0.93
Willmott index of agreement (D)	> 0.8	0.89	0.82
Mean absolute error (MAE) (%)	< 20	6.69	9.56

After successful model calibration, the model was validated using the data collected from the clay soils during the same 2023/2024 season. Similar to model calibration, all statistical parameters were within an acceptable range, according to de Jager (1994) (Table 4.3).

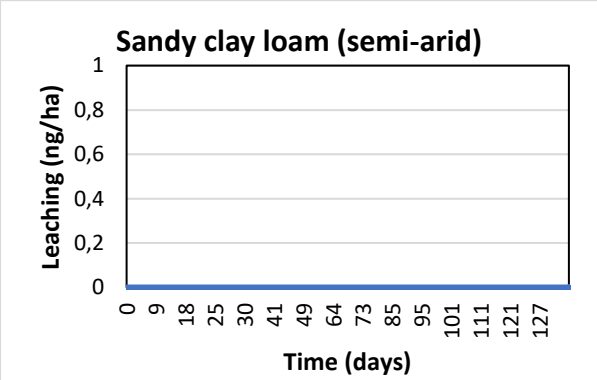
4.2.2 Model simulations on leaching potentials of carbamazepine and carbamazepine 10,11 epoxide from two soil types in four South African agroecological zones

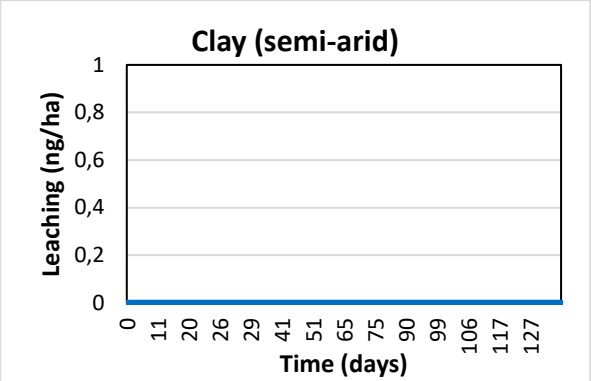
4.2.2.1 Time series leaching potential of carbamazepine and its metabolite

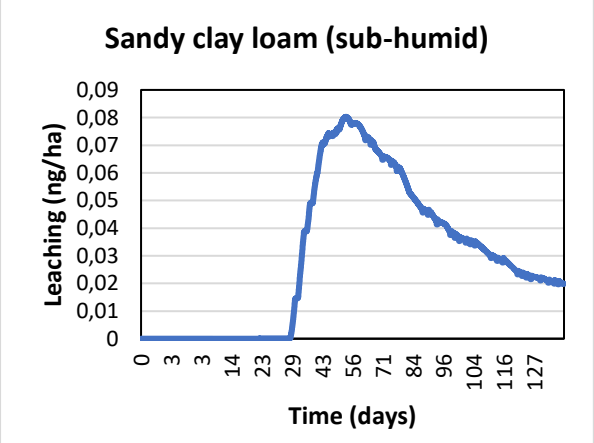
The following results present the outcomes of scenario simulations conducted using the HYDRUS model to assess the leaching potential of carbamazepine and its metabolite, carbamazepine 10,11 epoxide, from two soil types amended with sludge at a rate of 10 t ha^{-1}

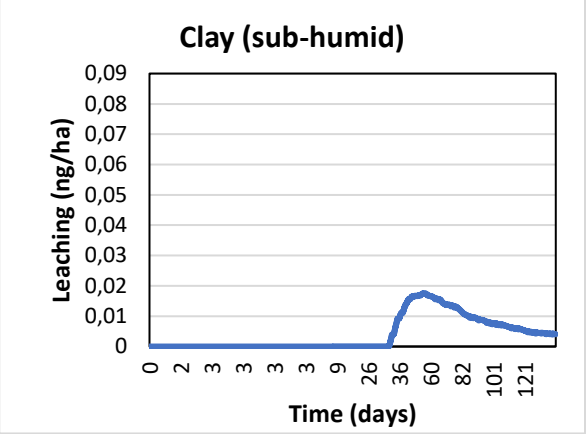
and planted with maize in four distinct South African agroecological zones (semi-arid, sub-humid, humid, and super-humid).

The results from the time series model simulations show that both carbamazepine (Fig 4.1) and its metabolite carbamazepine-10,11-epoxide (Fig 4.2) leached earlier from sandy clay loam soils compared to clay soils in all agro-ecological zones. This can be attributed to the higher infiltration rates of sandy clay loam soil. Most of the leaching occurred during the early growth stage of the plant while it was still young and consuming less water, which resulted in higher soil water availability for leaching out the contaminants below the root zone.









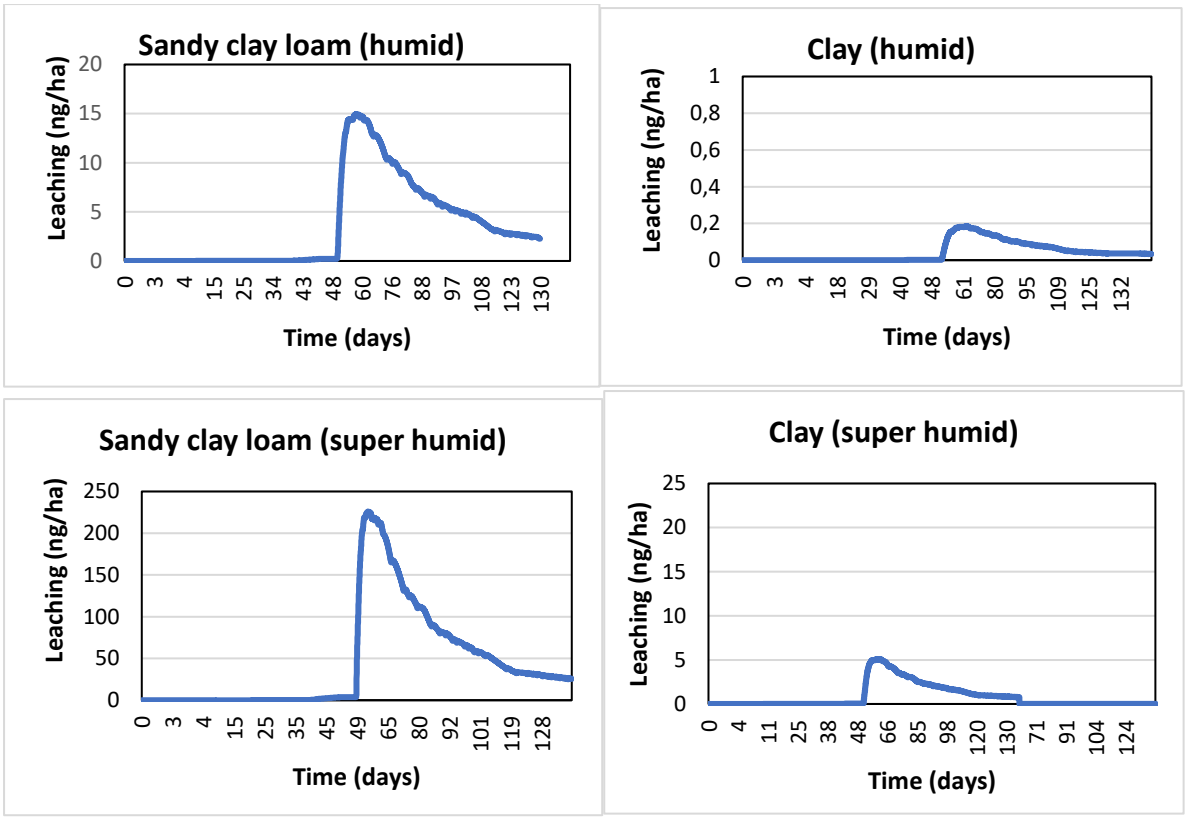
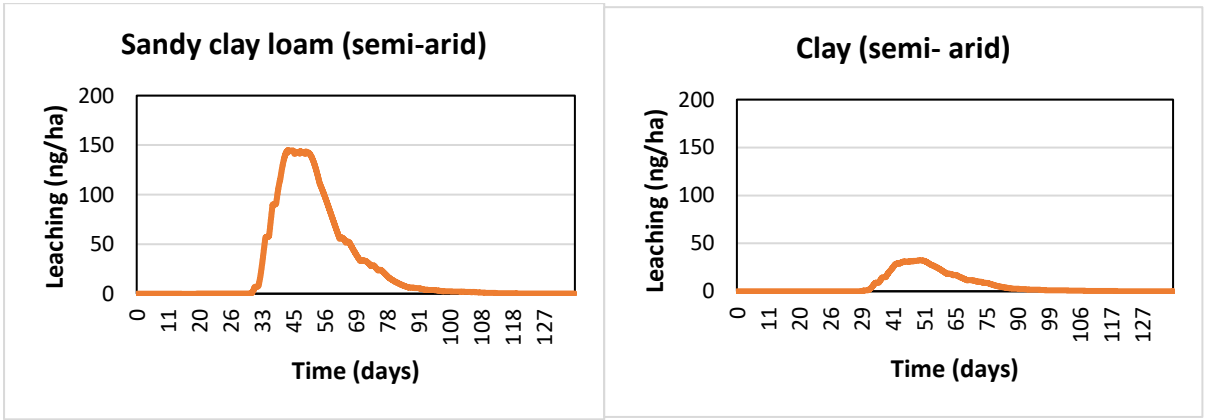


Figure 4. 1: Time series of carbamazepine leaching in two soil types across four agro-ecological zones



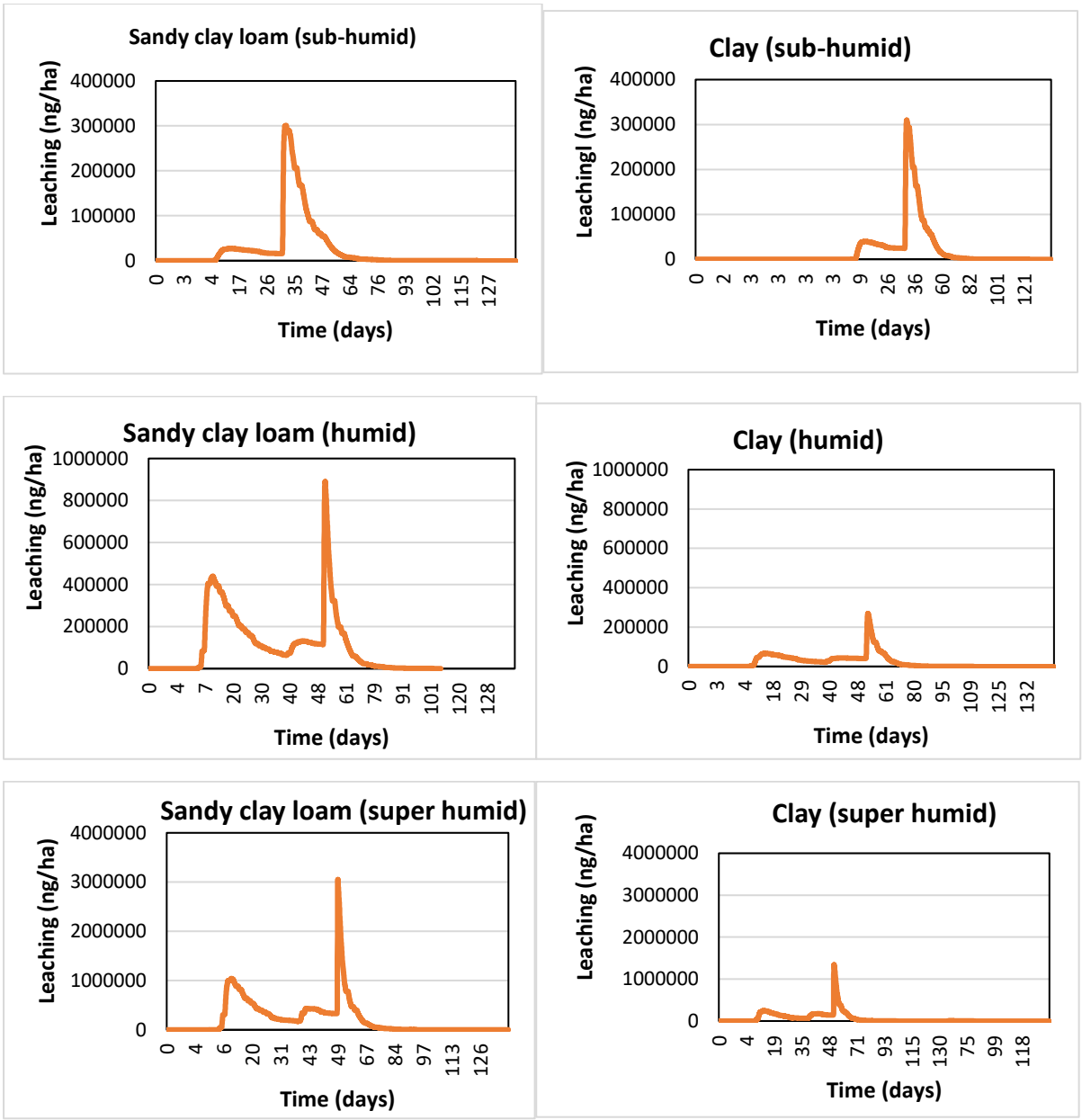


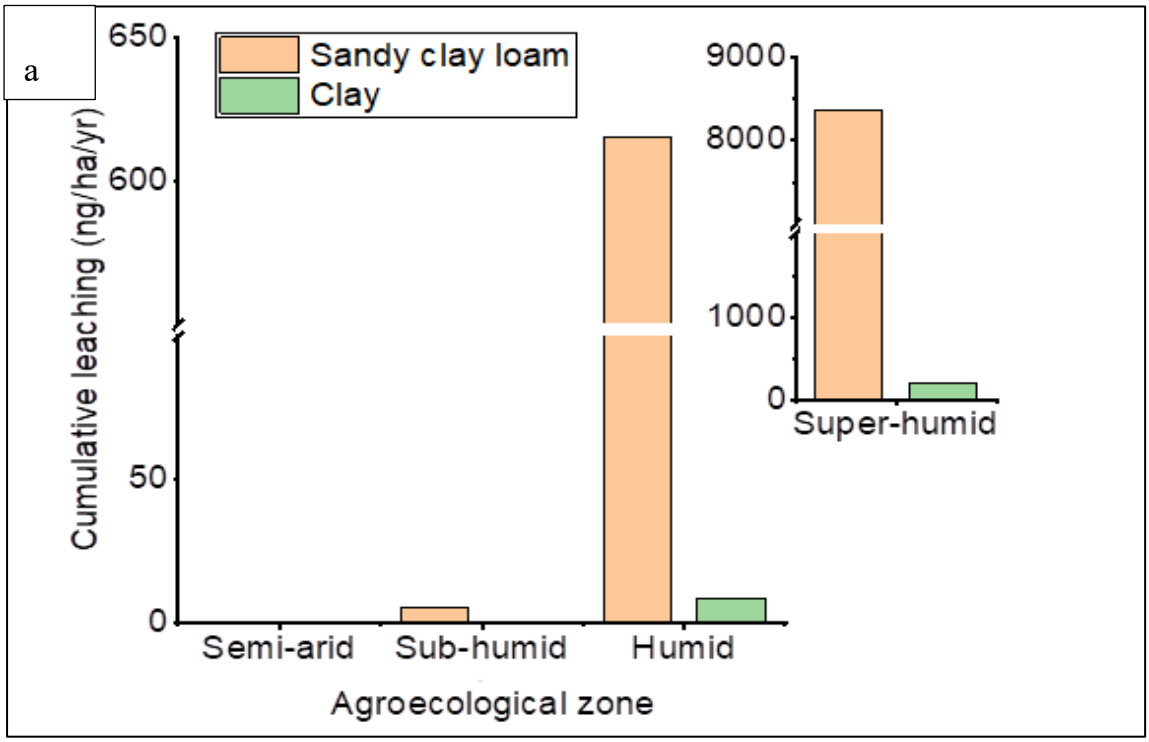
Figure 4. 2: Time series of the metabolite carbamazepine 10,11-epoxide leaching in two soil types across four agro-ecological zone

The concentration levels of contaminants in the leachate were generally higher in sandy clay loam compared to clay, attributed to the higher adsorption capacity of clay than sandy clay loam. No leaching of carbamazepine was detected in either soil type within the semi-arid agroecological zone (Figure. 4.1). This is mainly due to the lower amount of rainfall in the semi-arid area, as well as the lower water solubility (125 mg/L vs. 1340 mg/L at 25°C) and higher absorbability of the compound relative to its metabolite, which leached in both soils under the same agro-ecological zone during the same period. Similarly, the concentration of

carbamazepine leachate was several magnitudes lower than that of its metabolite carbamazepine-10,11-epoxide in all agro-ecological zones and soil types, mainly due to the relatively higher contents of the metabolite in the sludge relative to the carbamazepine, as well as the higher solubility of the metabolite.

4.2.2.2 Cumulative seasonal leaching of carbamazepine and its metabolite carbamazepine-10,11-epoxide

The cumulative seasonal leaching of carbamazepine (Figure 4.3a) and its metabolite (carbamazepine-10,11-epoxide) (Figure 4.3b) was observed to be higher in sandy clay loam soils compared to clay soils. Furthermore, it was noted that the cumulative leaching of carbamazepine and its metabolite increased with higher rainfall across different agro-ecological zones (semi-arid<sub-humid<humid<super-humid). This suggests that regions with greater rainfall or supplemented with irrigation, along with areas featuring light-textured soils and shallow groundwater, are more susceptible to contaminant leaching, posing a higher risk of potential groundwater contamination.



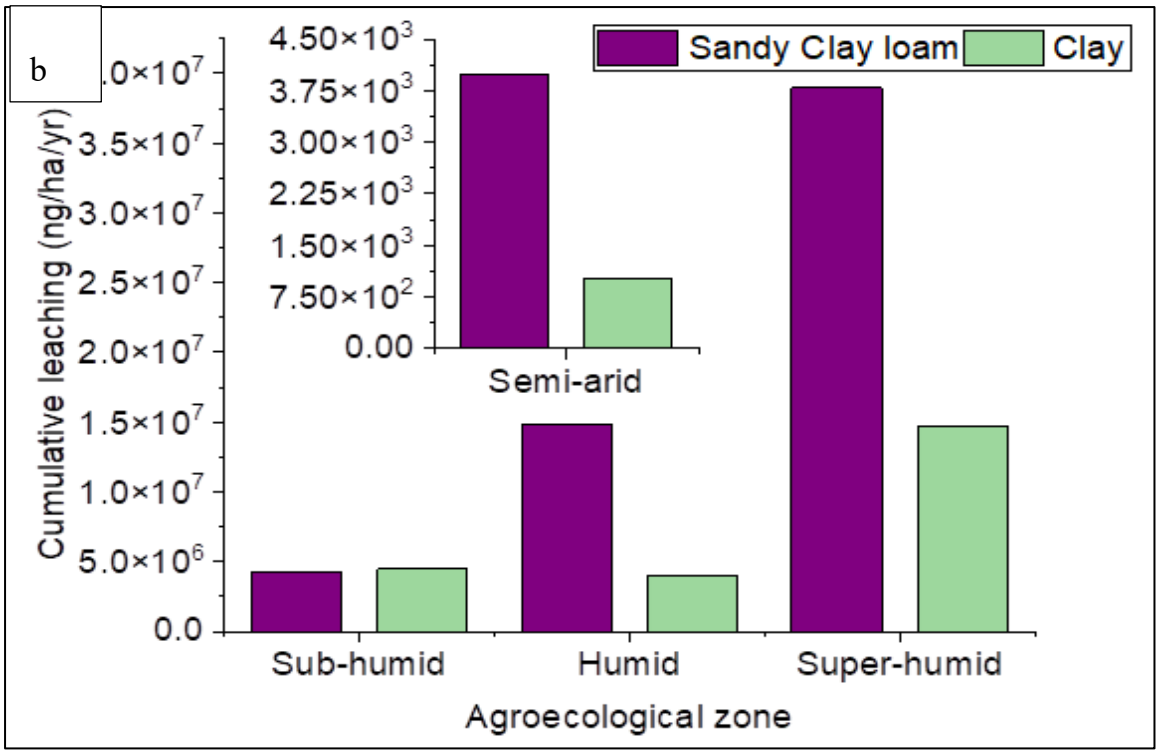


Figure 4.3: The cumulative leaching of carbamazepine (a) and carbamazepine-10,11-epoxide (b) from sludge added at a rate of 10 tons per hectare to soil planted with maize in semi-arid, sub-humid, humid, and super-humid agro-ecological zones of South Africa

4.2.2.3 Residual of carbamazepine and its metabolite carbamazepine-10,11-epoxide in the soil profile after crop harvest

The amount of residual carbamazepine in the soil profile decreased with depth after crop harvesting at the end of the growing season, particularly in the sandy clay loam and clay soils of semi-arid and sub-humid agro-ecological zones (see Figure 4.4). This suggests that a significant portion of the contaminant is concentrated in the top soil layer, likely due to low rainfall, which may have caused it to percolate down to the lower layers. In contrast, in humid and sub-humid zones, a substantial amount of carbamazepine was found in the middle (20-40cm) and lower (40-120cm) soil depths, indicating that the contaminant was transported by excess drained water.

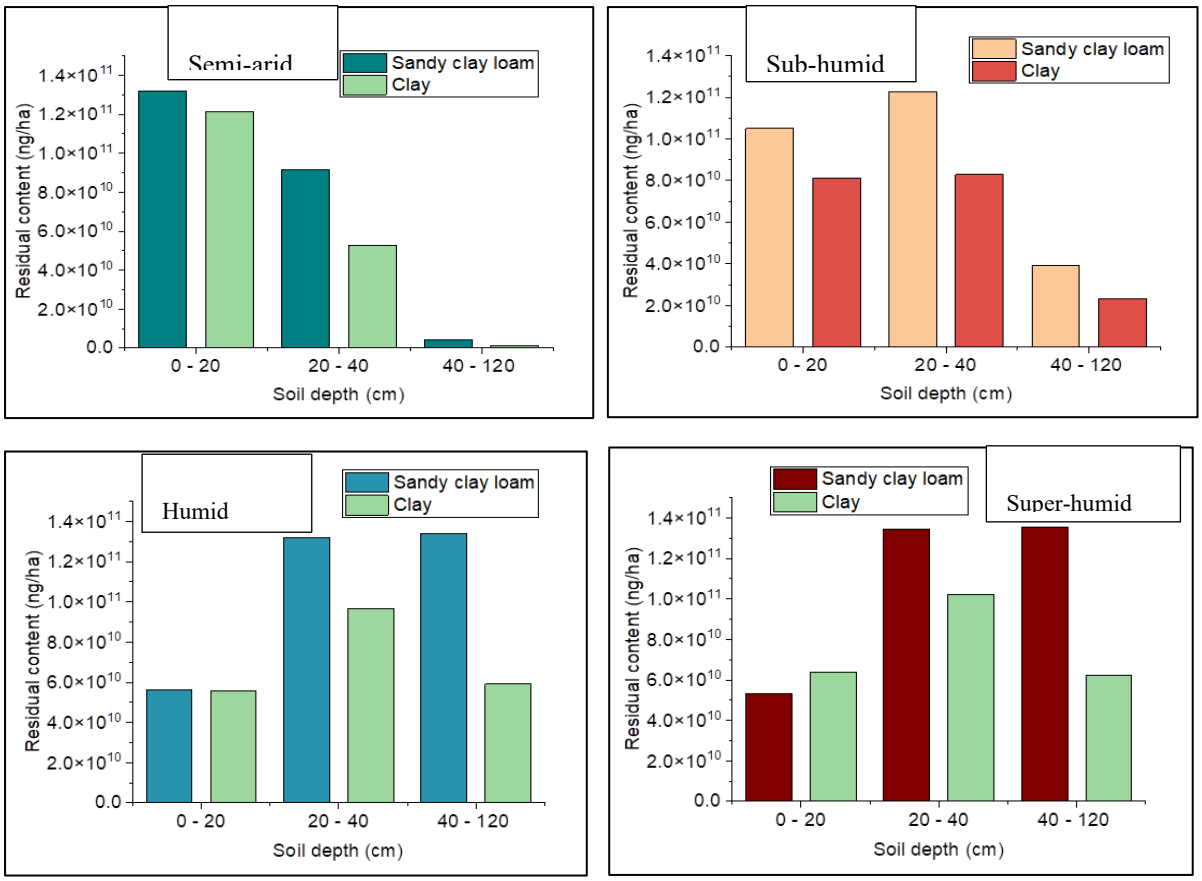


Figure 4.4: Residual content of carbamazepine in the profiles of both clay and sandy clay loam soil in the semi-arid, sub-humid, humid, and super-humid agroecological zones

The concentration of the residual metabolite carbamazepine-10,11-epoxide in the soil profile of the semi-arid agro-ecological zone decreased with depth, irrespective of the soil type, primarily due to low rainfall (Figure 4.5). However, in the sub-humid zone, the metabolite decreased with depth in clay soil, which has a higher adsorption capacity. It exhibited an increase in the 20-40 cm layer and then decreased in the 40-120 cm depth in the sandy clay loam soil. In the humid agro-ecological zone, the residual concentration of the metabolite increased with depth for both soil types, and for sandy clay loam in the super-humid zone. Conversely, it showed an increase in the 20-40 cm layer and then decrease in the 40-120 cm layer of the clay soil under the super-humid zone.

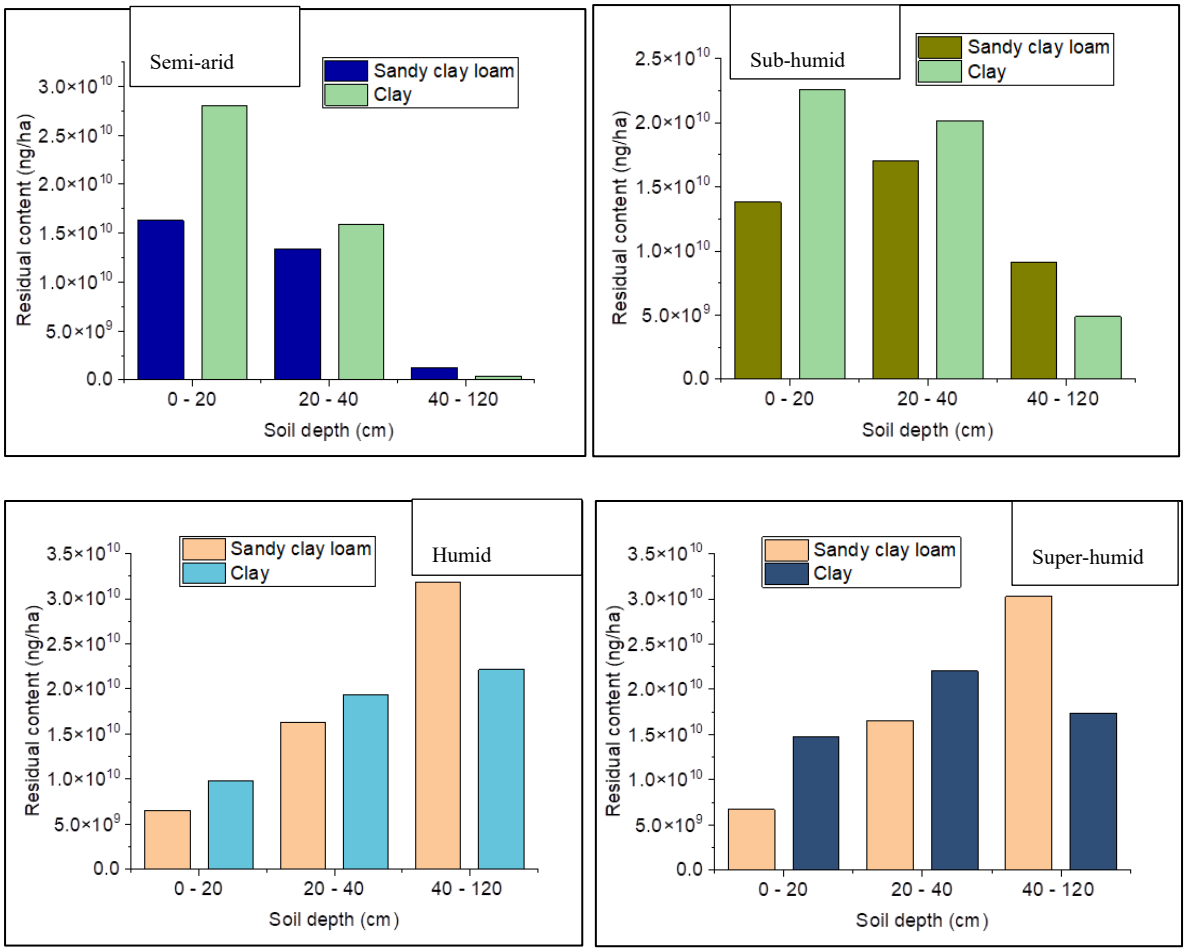


Figure 4.5: Residual content of the metabolite carbamazepine 10,11 epoxide in the profiles of both clay and sandy clay loam soils in the semi-arid, sub-humid, humid, and super-humid agroecological zones

Given the extended half-life of carbamazepine (355 – 1624 days (Yang et al., 2019)) and its metabolite in the soil, the model simulation suggests a high potential for long-term groundwater contamination. This aligns with the results of Chapter 2, which showed the presence of carbamazepine metabolites in 50 to 70% of the groundwater samples from different sites in Gauteng.

4.3 Conclusion

Both carbamazepine and its metabolite carbamazepine-10,11 epoxide were found to leach below the root zone at a depth of 1.2m in all agroecological zones, regardless of soil type. The annual leaching losses of both compounds increased with higher total annual rainfall at the

sites (Super-humid > humid > sub-humid > semi-arid). Notably, the leaching losses of the metabolite carbamazepine-10,11 epoxide below the root zone were significantly higher than the parent carbamazepine compound due to its higher water solubility and lower adsorbability. This emphasizes the need to establish baseline levels of emerging contaminants in South African groundwater and soils. It is crucial to integrate requirements for emerging contaminant levels into fertilizer guidelines encompassing commercial inorganic fertilizer, compost, and biosolids to ensure fertilizer quality registration. This process should start with determining the concentrations that could potentially lead to groundwater contamination through leaching and uptake by plants, thereby posing risks to human health.

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SUPPLEMENTARY INFORMATION

This section contains supplementary information for all the chapters contained in this report

Supplementary Table 1: Soil and treatment

	Soil							Fertilization system				
			%									
Farms	pH	EC (µS/cm)	Sand	Silt	Clay	Textural class	Soil depth (cm)	Type	Consecutive applications for the past years	Months since last application	Pesticides and herbicides	Tillage
A	5.06	23	78	6	16	Sandy loam	≥ 100	CIF and PM	2	12	Roundup, Guardian,	Mouldbord
B	4.93	21.1	82	4	14	Sandy loam	≥ 100	CIF and PM	2	12	Roundup, Guardian,	Mouldbord
C	4.09	91.4	78	10	12	Sandy loam	≥ 100	CIF and CKM	5	11	NA	Mouldbord
D	4.29	30.6	83	7	10	Loamy sand	≤ 60	CIF and CKM	2	3	NA	mouldbord
E	6.7	123.2	82	8	10	Loamy sand	≥ 100	CIF	5	12	NA	Mouldbord
F	4.85	35.6	87	5	8	Sand	≤ 40	CIF	5	12	Roundup	Mouldbord
G	4.85	25.7	88	4	8	Sand	≥ 100	CIF	5	12	Roundup	Mouldbord
H	5.54	31.3	81	9	10	Sandy loam	≤ 60	CIF and CTLM	10	3	Glysophyte, Agricyne	Mouldbord
I	4.43	30.2	60	16	24	Sandy clay loam	≥ 100	CIF and CTLM	10	12	Roundup	Mouldbord
J	5.11	71.6	68	2	30	Sandy clay loam	≤ 40	CIF and CTLM	8	6	Roundup	Mouldbord
K	5.44	55.4	59	17	24	Sandy clay loam	≥ 100	CIF	5	6	Roundup	Mouldbord
L	4.87	154.5	48	22	30	Loam	≥ 100	CIF and CKM	2	13	Supermatric	Hand plough and rotovator
M	5.03	44.9	47	23	30	Sandy clay loam	≤ 80	CIF	2	10	Karatizion, Chemix, stelastar	Mouldbord
N	3.77	49	78	8	14	Sandy loam	≥ 100	CIF	4	7	Chemix, Roundup	mouldbord and disc
O	4.09	28.9	78	10	12	Sandy loam	≤ 20	CIF	4	7	Chemix, Roundup	mouldbord and disc
P	4.51	52.6	64	16	20	Sandy loam	≤ 80	CIF and MS	31	6	Chemix, Roundup, 2.4-D	mouldbord and disc
Q	4.51	18.11	76	8	16	Sandy loam	≥ 100	CIF	3	12	Lamda, guardian, Roundup	mouldbord and disc
R	5.71	43	79	9	12	Sandy loam	≥ 100	CIF	3	6	Roundup, 2.4'D	mouldbord and disc
S	5.77	117.8	84	6	10	Loamy sand	≥ 100	CIF	2	6	Roundup, 2.4'D	mouldbord and disc
T	6.61	195.3	80	10	10	Sandy loam	≥ 100	CIF	3	12	Roundup, 2.4'D	mouldbord and disc
U	4.18	44.8	82	6	12	Loamy sand	≥ 100	CIF	3	12	Roundup, 2.4'D	mouldbord and disc

CIF Commercial inorganic fertilizer, PM Pig manure, CKM Chicken manure, CTLM Cattle manure.

Supplementary Table 2: Instrument parameters

Compound	Ionization mode	Retention time (min)	Quantification ion (m/z)
Bisphenol A	Negative	9.5	227
Caffeine	Positive	4.8	195
Carbamazepine	Positive	8.8	237
Carbamazepine-10,11-epoxide	Positive	7.5	253
Cis-10,11-Dihydroxyl-10,11-dihydrocarbamazepine	Positive	4.9	271
Diclofenac	Positive	6.4	215
Sulfamethoxazole	Positive	5.3	254
N4-Acetylsulfamethoxazole	Positive	6.3	296
Sulfamethoxazole-N1-beta-D-Glucoside	Positive	4.4	254

Supplementary Table 3: Linearity of the calibration curve

	Linearity			
Target compounds	**Range (ng/mL)**	**Number of points**	**Regression equation***	**R^2**
Caffeine	1 – 500	6	y = 1.09231x + 0.0618	0.991
Carbamazepine	1 – 500	6	y = 10592.7x - 69.5151	0.989
Diclofenac	1 – 500	6	y = 3216.31x - 28.1044	0.991
Sulfamethoxazole	1 – 500	6	y = 1.20676x - 0.0136747	0.993
Sulfamethoxazole N1 glucuronide	1 – 500	6	y = 1459.13x - 18.068	0.994
N4 Acetyl sulfamethoxazole	1 – 500	6	y = 25.9956x + 0.397317	0.977
Carbamazepine-10,11 epoxide	1 – 500	6	y = 1049.79x - 7.25038	0.993
cis-10,11-dihydro-10,11-dihydrocarbamazepine	1 – 500	6	y = 109.529x - 0.736874	0.993

*y = peak area of the target compound; x = concentration of the compound (ng/mL)

Supplementary Table 4: Limit of detections (LODs) and limit of quantifications (LOQs) for solid samples

Compound	LODs (ng/g dry weight)	LOQs (ng/g dry weight)
Caffeine	0.0152	0.0507
Carbamazepine	0.6233	2.077
Diclofenac	6.424	21.4133
Sulfamethoxazole	1.0166	3.3886
Sulfamethoxazole N1 glucuronide	1.9947	6.6489
N4 Acetyl sulfamethoxazole	1.0221	3.4072
Carbamazepine-10,11 epoxide	0.3056	1.0189
cis-10,11-dihydro-10,11-dihydrocarbamazepine	3.0801	10.2669

Supplementary Table 5: Limit of detections (LODs) and limit of quantifications (LOQs) for solid samples

Compound	LODs (ng/L)	LOQs (ng/L)
Caffeine	0.0304	0.1014
Carbamazepine	1.2466	4.1540
Diclofenac	12.8480	42.8260
Sulfamethoxazole	2.0332	6.7720
Sulfamethoxazole N1 glucuronide	3.9894	13.2978
N4 Acetyl sulfamethoxazole	2.0440	6.8143
Carbamazepine-10,11 epoxide	0.6112	2.0374
cis-10,11-dihydro-10,11-dihydrocarbamazepine	6.1602	20.5338