OCCURRENCES, SEASONAL VARIATIONS, AND SOLID-LIQUID PARTITIONING OF PHARMACEUTICAL AND PERSONAL CARE PRODUCTS IN URBAN WASTEWATER SYSTEMS: WITH EMPHASIS ON ADSORPTION, AND ROOT ZONE BASED TREATMENTS

Thesis submitted to the
UPES

For the Award of
Doctor of Philosophy
in
Engineering

by
Rahul Silori

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August 2023

Dedicated

to

My Parents,

My Supervisors,

My Friends

&

All my well-wishers

DECLARATION

I declare that the thesis entitled **"Occurrences, seasonal variations, and solid-liquid partitioning of Pharmaceutical and Personal Care Products in urban wastewater systems: With emphasis on Adsorption, and Root Zone based Treatments"** has been prepared by me under the guidance of Prof. S. M. Tauseef, Department of HSE & Civil Engineering, UPES and Prof. Manish Kumar, Department of HSE & Civil Engineering, UPES. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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CERTIFICATE

I certify that **Rahul Silori** has prepared his thesis entitled **"*Occurrences, seasonal variations, and solid-liquid partitioning of Pharmaceutical and Personal Care Products in urban wastewater systems: With emphasis on Adsorption, and Root Zone based Treatments*"**, for the award of Ph.D. degree of the UPES, under my guidance. He has carried out the work at **the Department of HSE & Civil Engineering,** School of Engineering, UPES.

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ABSTRACT

Pharmaceutical and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) are one of the critical emerging contaminants (ECs) and frequently detected anthropogenic contaminants in the environment. Lately, there has been a significant global increase in the production and consumption of PPCPs and EDCs and this surge can be attributed to improved living standards and advancements in healthcare systems. As a result, these compounds have become ubiquitous in various aquatic environmental compartments. These compounds have the potential to cause adverse effects on both ecological systems and human health, thereby PPCPs and EDCs contamination have garnered significant concern and became a subject of discussion among scientific proponents. Out of the varied sources, municipal wastewater treatment plants (WWTPs) are one of the primary sources of these compounds intrusion into the environment. Henceforth, monitoring assessment of WWTPs in an area is required to evaluate the extent of PPCPs and EDCs contamination and conclude the remedial measures/suggestions.

Over time, there has been a significant focus on effectively removing PPCPs from wastewater matrices worldwide. Due to the limitations of conventional biological processes in WWTPs in their removal, various processes, comprising physical, chemical, and biological methods, have been evolved and studied. Although these methods demonstrated satisfactory removal performance, they possess certain constraints, primarily related to their economic and environmental sustainability. Henceforth, there is a growing need to comprehensively investigate sustainable and economical adsorptive-based and hybrid treatment systems to infer the most suitable and efficient techniques for removing PPCPs from water environments.

Given the concerns posed above, the present work is aligned towards the following three objectives:

1. To examine the **occurrence, seasonal variation, and removal of PPCPs and EDCs in municipal wastewater treatment plants** of Dehradun, Uttarakhand.
2. To determine **PPCPs** removal efficacy of *in-situ* **root zone treatment (RZT)/constructed wetland (CW)** hybrid system.
3. To investigate the various **waste materials-based biochar** suitability for **PPCPs** removal in aqueous solutions.

The thesis is structured through three major chapters to achieve these objectives, which are briefly summarized in the following sections.

Chapter 4: Occurrence, seasonal variation, and removal of PPCPs and EDCs in the municipal wastewater treatment plants of Dehradun city

This chapter quantified the occurrence, seasonal variation, and removal of the nine target compounds including PPCPs and EDCs at the four major WWTPs of Dehradun city, Uttarakhand, India. Diclofenac and caffeine occurred in all influent samples of the WWTPs indicating substantial consumption in the vicinity., Estrone, caffeine, and acetaminophen were detected in higher concentrations in influent among the WWTPs. A whopping concentration of 123.9 μgL^{-1} was recorded for the estrone (EDC) in the influent, which is to date the highest ever-recorded, globally. Estrone is a natural steroid hormone secreted by the ovary, placenta, and adrenal cortex in both human beings and animals, and excreted along with their urine and feces, which gets ultimately released into the environment. Such high hormonal concentration might be primarily attributed to the presence of its inactive glucuronides and sulfate conjugates, or free forms sourced from human excretion (urine and feces) in wastewater. In addition, the city resides in the hilly terrain, so based on drainage the movement and accumulation of EDCs from various potential non-point sources (landfill waste, sludge from WWTPs, and livestock excrement) in the area to the low-lying treatment facilities are prevalent through surface runoff. The total PPCPs concentration in influent and effluent ranged from 1849 to 74187 ngL^{-1} and 22 to 64275 ngL^{-1}, respectively in the WWTPs. Seasonal variations in the occurrence of the target compounds in the studied WWTPs were investigated. The mean total PPCPs concentrations were observed higher during the spring, followed by monsoon and summer seasons in influent water. The highest PPCP concentration detected was that of caffeine (71653 ngL^{-1}) during monsoon and ciprofloxacin (16931 ngL^{-1}) in the spring season. The highest EDC concentration detected was of estrone (123.9 μgL^{-1}) in the monsoon season. Among the PPCPs, acetaminophen was strongly correlated with diclofenac (r=+0.77) and ketoprofen (r=+0.62), whereas diclofenac was profoundly linked with ketoprofen (r=+0.89). Interestingly, ciprofloxacin was positively correlated with carbamazepine (r=+0.65). The tests for distribution showed a non-normal data distribution (p>0.05) for all wastewater PPCPs samples except for caffeine influents. PPCP samples showed a greater statistically significant variation between the influent and effluent samples (p<<<0.001), which shows highly decisive evidence for unequal means. Statistical data treatment indicated EDCs concentration with a bi-modal distribution that was confirmed with Anderson-Darling, Jarque-Bera, Lilliefors, and Shapiro-

Wilk tests elucidating a non-normal distribution for the EDCs sample data. Statistically significant difference (F=8.46; p<0.0001) in the seasonal data for the abundance of the target EDCs at the WWTPs has been observed. Highest and significantly different average EDCs concentrations were recorded during the monsoon, compared to the spring (p=0.025) and summer (p=0.0004) seasons in the influent waters. The PPCPs and EDCs removal in the WWTPs were observed in the ranges of -293% to 100%, whereas only PPCPs removals in the WWTPs were observed in the ranges of -68% to 100%. The maximum negative removal of 293% was observed for estrone in the WWTPs. In terms of total PPCPs, average removal efficiencies of WWTPs were recorded in the ranges of 41-71%. The maximum removals were observed for acetaminophen, ketoprofen, and triclosan, whereas negative removals for ciprofloxacin, caffeine, carbamazepine, and estrone in the WWTPs.

Chapter 5: Screening and removal of PPCPs along *in-situ* RZT-based wastewater treatment system

In this chapter, the RZT/CW hybrid system was investigated for PPCPs removal from the wastewater environment. RZTs/CWs are sophisticated hybrid systems comprised of plants, substrates, and microorganisms with physical, chemical, and biological processes occurring in them. Wastewater flows through the root zone either horizontally or vertically, where plants create favorable conditions for the growth of bacteria in the root system. Organic contaminants are decomposed biochemically in the rhizosphere of root plants by the bacteria in these systems. These work through the combined processes of plants, substrates, and microorganisms for PPCPs removal. For the same, we investigate an *in-situ* RZT system for the removal of PPCPs from domestic wastewater. The occurrence of more than a dozen PPCPs was detected in an academic institution WWTP at three specific locations i.e., influent, root treatment zone, and effluent. The comparisons of observed compounds detected at various stages of the WWTP suggest that the presence of PPCPs, like homatropine, cytisine, carbenoxolone, 4,2′,4′,6 - tetrahydroxychalcone, norpromazine, norethynodrel, fexofenadine, indinavir, dextroamphetamine, 3-hydroxymorphinan, phytosphingosine, octadecanedioic acid, meradimate, 1-hexadecanoyl-sn-glycerol, and 1-hexadecylamine, are unusual than the usual reported PPCPs in the WWTPs. In general, carbamazepine, ibuprofen, acetaminophen, trimethoprim, sulfamethoxazole, caffeine, triclocarban, and triclosan are often reported in wastewater systems. The normalized abundances of PPCPs range between 0.037-0.012, 0.108-0.009, and 0.208-0.005 in the main influent, root zone effluent, and main effluent, respectively

of the WWTP. In addition, the removals of PPCPs were observed from -200% to ~100% at the RZT phase in the plant. Interestingly, we observed several PPCPs at later stages of treatment which were not detected in the influent of the WWTP. This is probably owing to the presence of conjugated metabolites of various PPCPs present in the influent, which subsequently got deconjugated to reform the parent compounds during the biological wastewater treatment. In addition, we suspect the potential release of earlier absorbed PPCPs in the system, which were absent on that particular day of sampling but have been part of earlier influents. In essence, RZT-based WWTP was found to be effective in removing the PPCPs and other organic contaminants in the study which stresses the need for further comprehensive research on RZT system to conclude the exact removal efficacy and fate of PPCPs during treatment in the system

Chapter 6: Investigation of various waste materials-based biochar for removal of PPCPs in aqueous solution

This chapter focuses on another remediation approach, where biochars were produced from the pyrolysis of sawdust and co-pyrolysis of sawdust and plastic waste, and intended to remove PPCPs from aqueous solution. Sawdust-based biochar showed far better removal of the PPCPs from aqueous solution as compared to plastic-cum-biomass based biochars. This might be attributed to the more alkaline and amorphous nature of the sawdust biochar. Sawdust biochar reported ~95% and >95% removal efficiency for ciprofloxacin and sulfamethoxazole, respectively. Adsorption mechanisms involved were hydrogen bonding, electrostatic, and π–π electron donor-acceptor interactions. Adsorption kinetics of both the PPCPs onto biochars in aqueous solution primarily followed the pseudo-second-order model, implying that adsorption was dominated by chemisorption via electron sharing or transfer. These results delineate the potential for waste materials-based biochar to serve as an economical additional treatment for reducing PPCPs in wastewater effluents.

Finally, this thesis critically highlights the limitation of the WWTPs in the treatment, degradation, and assimilation of PPCPs and EDCs leading to their hyperaccumulation at WWTP effluents, thereby posing a substantial threat to nearby aquatic ecosystems, human health and hygiene, and the very ecological balance of the region. Out of all the treatment systems, aeration and fluidized media oxidation-based system showed efficient PPCPs removal capability from wastewater. As a current research gap, the current study recommended RZT to be appraised for PPCPs *in-situ* remediation from landfill leachates, an underestimated source

of PPCPs intrusion in the environment. In addition, based on the adsorptive-based remediation study, the present work also recommended saw dust biochar could be incorporated as a filter media in the WWTPs for enhanced removal of such emerging contaminants from the wastewater.

Keywords: Pharmaceuticals and personal care products (PPCPs); Endocrine disrupting chemicals (EDCs); occurrence; wastewater treatment plants (WWTPs); remediation; Root zone treatment (RZT); biochar; removal.

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ABBREVIATIONS

AI	Academic institution
AOPs	Advanced oxidation processes
AMR	Antimicrobial resistance
CFX	Ciprofloxacin
CWs	Constructed wetlands
ECs	Emerging contaminants
EDA	Electron donor-acceptor
EDCs	Endocrine disrupting chemicals
HPLC-MS	High-performance liquid chromatography-mass spectrometry
NSAIDs	Nonsteroidal anti-inflammatory drugs
PCPs	Personal care products
PPCPs	Pharmaceutical and personal care products
PSO	Pseudo-second-order
RZT	Root zone treatment
SB	Sawdust biochar
SPB	Sawdust-plastic biochar
SPE	Solid phase extraction
SMX	Sulfamethoxazole
Triclosan	TCS
WWTPs	Wastewater treatment plants

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CHAPTER 1: INTRODUCTION

1.1 Overview and Background

Emerging contaminants (ECs) encompass various compounds, such as pharmaceutical and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), pesticides, industrial chemicals, synthetic hormones, and surfactants, and their concentrations in the environment generally range in trace levels (μgL^{-1} to ngL^{-1}) (Rigueto et al., 2020; Silori & Tauseef, 2022). PPCPs are one of the critical ECs and belong to the class of most frequently detected anthropogenic contaminants in the environment (Kim & Zoh, 2016). They comprise a broad group of organic compounds, including pharmaceuticals and a combination of personal care products (PCPs), such as soaps, toothpaste, lotions, sunscreens, etc., which are used in high quantities in daily life across the globe (Silori et al., 2022). In recent times, for ensuring a better health system and modern living standards PPCPs production and consumption has been rapidly elevated (Daughton & Ternes, 1999; Khan et al., 2022; Mohapatra et al., 2016). As a result, PPCPs have shown their ubiquitous presence in the various aquatic environmental compartments (Biswas & Vellanki, 2021) and recently, this issue had gained a momentous concern due to their potential adverse ecological and human health effects, and should be taken at uttermost basis (Al-Odaini et al., 2010; Kosma et al., 2014). Similarly, EDCs are exogenous chemicals that have the potential to meddle with humans and animals endocrine systems and may even adversely affect future generations (Chen et al., 2022; Kasonga et al., 2021). Due to these reasons, these two chemical compounds (PPCPs and EDCs) have become a topic of discussion among scientific proponents.

PPCPs/EDCs are discharged into the environment as parental compounds or transformation products (metabolite) primarily through municipal and industrial wastewater treatment plants (WWTPs), landfill dumping sites, animal farming, urban runoffs, etc. (Singh & Suthar, 2021a; Zhang et al., 2016). Majorly, WWTPs are the dominant source of intrusion into the aquatic environment (Anumol et al., 2016; Daughton & Ternes, 1999; Gao et al., 2012), as the conventional treatment processes in these facilities have limitations on significant removal of these biorecalcitrant compounds (Bhagat et al., 2020; Mohapatra et al., 2016; Subedi et al., 2017). As a result, effluent from the WWTPs culminates in contaminating most of the surface to subsurface water sources, which are used for potable purposes in many developing countries (Ebele et al., 2017). In the same context, various literature have delineated PPCPs occurrence

in wastewater (Carballa et al., 2004; Palli et al., 2019) and aquatic environments globally in trace concentrations i.e. ngL^{-1} to µgL^{-1} (Ebele et al., 2020; He et al., 2018; Kibuye et al., 2019a; Lin et al., 2015; Wu et al., 2015). Several of these compounds are potential EDCs, enhance the antimicrobial resistance (AMR) risk and their bio-accumulation in non-target organisms in the environment (Frédéric & Yves, 2014; Kumar et al., 2019; Silori et al., 2022; Vasquez et al., 2014; Wee et al., 2019). Such as steroid estrogens (pharmaceutical drugs) are in the class of most potent EDCs and are capable of affecting aquatic organisms even at minute concentrations (Desbrow et al., 1998; Johnson & Sumpter, 2001). Similarly, several studies have reported the ubiquitous presence of EDCs in WWTPs; however, the concern is their incessant inflow into WWTPs. Some common EDCs that are found in WWTPs are phthalates, Bisphenol A (BPA), dioxins, perfluoroalkyl substances, triclosan (TCS), polyfluorinated biphenyl, estrogens, etc (Cao et al., 2014; Kitamura et al., 2005; Van Zijl et al., 2017; Warner & Flaws, 2018). Out of these, phthalates and BPA are utilized in plastic products, while TCS, dioxins, and polyfluoroalkyl substances are widely used in consumer products, food industries, and household products which opens up their easy pathway toward human exposure (Adegoke et al., 2021). A study by Van Zijl et al. (2017) classified that EDCs were detected almost 93% time in the WWTP effluents in the South African town of Cape Town with a considerable concentration of 5.1 µgL^{-1}. Significant concentrations of 3.6 µgL^{-1} and 1.1 µgL^{-1} of EDCs were recorded in the influent and effluents of a WWTP in Shanghai, China (Xu et al., 2016). Estrone, a prominent EDC was detected at a concentration of 18.8 ngL^{-1} in the WWTPs in Tehran, with a removal efficiency of merely 61%. Numerous other studies confirmed the presence of EDCs not just in WWTPs, but in various other aqueous environments. Heavy concentrations such as 45.5 µgL^{-1} in the river in South Africa (Olatunji et al., 2017), 28 µgL^{-1} in well water in India (Wee & Aris, 2019), 4.8 µgL^{-1} in the estuaries of Ave river in Portugal (Rocha et al., 2019), 450 ngL^{-1} in the coastal water of China (Lu et al., 2020) and 170 ngL^{-1} in drinking water in the U.S.A. (Benotti et al., 2009) were recorded for the EDCs. These studies are sufficient to highlight that PPCPs and EDCs are a global concern and not limited to a small region.

Apart from their transformation in organisms as metabolites, transformation products can also be formed in the environment i.e., during wastewater treatment and due to several other processes, such as hydrolysis, photodegradation, biodegradation, etc., occurring in natural water systems/bodies (Deeb et al., 2017; Nikolaou, 2013). These transformation products are found to be more toxic than the parent compounds, hence they are significant to be considered

(Richardson & Ternes, 2018). Several recent literatures have concentrated on their potential ecotoxicity and but largely their fate and transport remain indecisive (Ankley et al., 2007; Ying et al., 2004). So far, regulations for some of the PPCPs have been regulated in few countries but WWTPs for PPCPs are not subjected to stringent emission guidelines in many countries, specifically in developing countries (Kim & Zoh, 2016). In the same context, United States Environmental Protection Agency has listed a few of these PPCPs as priority pollutants (Anand et al., 2022). In addition, despite potential adverse health effects, PPCPs are also not regulated in drinking water in any country (Bexfield et al., 2019). One of the reasons for rising attention to the fate of PPCPs in the environment across the world is the advancement in analytical technologies. In recent years, progress in analytical techniques has enabled the scientific community to determine the concentration of these compounds in the environment at trace levels. Several chromatographic analytical techniques for the detection of PPCPs in the water environment have been used by researchers worldwide, comprising from the principle Gas chromatography-mass spectrometry (GC-MS) method to the advanced techniques like Ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-tandem-MS) (Galindo-Miranda et al., 2019).

PPCPs are detected in bioactive forms in wastewater, and their removal in WWTPs mainly depends on the PPCPs inlet load, wastewater treatment mechanisms, and various other environmental factors (Duan et al., 2021; Guardian et al., 2021; Singh & Suthar, 2021a; Xiang et al., 2021). In recent times, PPCPs have been detected as common compounds in treated wastewater effluents in Indian urban cities (Akiba et al., 2015; Mutiyar & Mittal, 2013, 2014; Singh & Suthar, 2021b; Subedi et al., 2015). This is mainly due to the majority of WWTPs in urban areas in India work on conventional treatment processes, which have constraints on the removal of PPCPs (Mutiyar & Mittal, 2014). One of the comprehensive review stated that ibuprofen and acetaminophen (analgesics), carbamazepine (anticonvulsant), atenolol (antihypertensive), trimethoprim and sulfamethoxazole (antibacterial), caffeine (stimulant) and triclocarban and triclosan (antimicrobials) are the most commonly PPCPs detected at elevated concentrations in Indian WWTPs, predominantly treating domestic sewage (Balakrishna et al., 2017). Central Pollution Control Board (CPCB) reported that 72,368 million liters per day (MLD) of wastewater is generated in India whereas only 20,235 MLD wastewater gets treated by WWTPs installed for the treatment i.e., around 28% of the wastewater produced per day and the remaining untreated wastewater is discharged to local freshwater environment in urban areas (Down to Earth, 2021). Likewise, in Uttarakhand wastewater generation was estimated

as 495 MLD, whereas only 152.9 MLD (30%) has installed treatment capacity and remaining wastewater (70%) is being dumped in river Ganges, its tributaries, and other local freshwater bodies (Singh & Suthar, 2021b). Henceforth, WWTPs role in PPCPs/EDCs mass loading contribution to the aquatic environment system (majorly river systems) in major Indian urban cities needs to be explored utterly.

Over time, wide attention has been paid to the efficient removal of PPCPs from wastewater matrices worldwide. Subsequently, many processes, consisting physical, chemical, and biological, have been evolved to remove the PPCPs during wastewater treatment in WWTPs due to the limitations of conventional biological processes (activated sludge system) in their removal (Wang & Wang, 2016). The physical methods involve the principle of adsorption with the use of carbon-based adsorptive materials, including primarily activated carbon, graphene, graphene oxide, and carbon nanotubes. Adsorption is one of the better PPCPs removal approaches owing to its wide adaptability, insensitivity to toxic materials, readily available, low cost, effectiveness, not producing secondary pollutants, easily operational, and easy regeneration (Adegoke et al., 2017; Ahmad et al., 2020; Danish et al., 2017). Literature have confirmed various adsorbents but some of them such as activated carbon is cost-intensive and scarce (Adegoke et al., 2022).

Pure cultures and mixed cultures are the biological degradation methods found to be effective in the removal of a few such compounds (Wang & Wang, 2016). Low abundance and lack of degraders are found to be the limitations of biological methods. Additionally, the method was found to be unsatisfactory for some persistent PPCPs (Wang & Wang, 2016). On the other hand, chemical methods involve the principle of oxidation of such compounds, and the various processes include ozonation and other advanced oxidation processes (AOPs), including UV/H_2O_2, O_3/UV, Fenton and Fenton-like oxidation, gamma radiolysis, sonolysis, and electrochemical oxidation (Wang & Xu, 2012). AOPs are found to be the best-suited advanced methods for the removal of PPCPs, but high operational cost and resistant intermediates formation are the shortcomings associated with such techniques (Wang & Wang, 2016). Due to the limitations of single biological and single AOPs, attention has been paid more to the combination of AOPs and biological methods (He et al., 2014), and other cost-effective and hybrid ecofriendly methods in recent years. Henceforth, sustainable and economical adsorptive-based treatments (biochar) and hybrid systems need to be investigated

comprehensively for concluding the pertinent remediation techniques for PPCPs removal from the water environment.

1.2 Rationality of Problem

The usage of PPCPs and EDCs has substantially increased globally in recent years to enhance healthcare systems and elevate living standards. Consequently, they get released in wastewater in active forms/metabolites, and WWTPs constraints in removal have led to their pervasiveness in various aquatic environments. Therefore, WWTPs in a city could be a focal point for the appraisal of PPCPs/EDCs in the nearby environment and potential threats. The limited scientific investigation and literature concerning the PPCPs/EDCs monitoring assessment in Northern Indian cities have triggered the need for further investigations. Dehradun, the capital and major populous town in Uttarakhand is facing unregulated rapid urbanization and development, leading to consider it as a study area for our investigation. Furthermore, owing to limitations of the conventional treatment methods in WWTPs for the removal of these compounds, certain economical and sustainable remediation approaches are in critical exploration for PPCPs removal from water matrices. Henceforth, comprehensive investigation is imperative to address these issues, given their significant implications for the nation's health, economy, and future progress.

It becomes inquisitive and essential to ask the following pressing questions considering the stated problem:

Question 1: Can we evaluate the levels of PPCPs/EDCs contamination and their correlation in the WWTPs of Dehradun city?

Question 2: Can we delineate and collate the PPCPs/EDCs fate and removal in the various conventional treatment processes at the WWTPs of the city?

Question 3: Does the *in-situ* RZT (root zone treatment) can show better results for PPCPs removal from wastewater?

Question 4: Does the waste materials derived biochar can lead to the efficient removal of PPCPs from the aqueous solution?

Question 5: Does the hybrid biochar (produced from agglomerate of waste feedstocks) have the potential to show better removal results?

Working Hypothesis: Quantification of contaminants in wastewater portrays the picture of potential contamination in the nearby aquatic environment of an area. The hypothesis behind this study was that substantial PPCPs/EDCs levels can be found in the WWTPs of Dehradun city. This could be helpful in assessing the extent of PPCPs and EDCs contribution to the local environment by these treatment facilities and possible environmental threats. In addition, the hypothesis was that RZT and waste-derived biochar remediation approaches can effectively remove persistent PPCPs from wastewater effluents. It was hypothesized that RZT will prove to be an economical and sustainable treatment solution, whereas usage of such materials for biochar development will address waste disposal concerns, provide waste management solutions, and contribute to accomplishing sustainable development goals (SDGs).

1.3 Significance of Study

Limited literature has reported on PPCPs/EDCs occurrence, variation, fate, and removal in wastewater treatment facilities in Indian towns despite their high production and consumption, shortage in demand and supply for wastewater treatment in the country (Anumol et al., 2016; Balakrishna et al., 2017). However, few literature documented occurrence, fate, and removal of these compounds at WWTPs for some of the sites in India, spreading from southern Indian states (Anumol et al., 2016; Prabhasankar et al., 2016; Subedi et al., 2015, 2017) to only a few sites in northern Indian states (Mutiyar & Mittal, 2013, 2014; Singh & Suthar, 2021b). So as per the available published literature, it has been perceived that especially occurrence and removal pattern of PPCPs/EDCs in WWTPs of northern Indian cities, and their fate in the nearby environment are less explored and needs more attention.

Lately, RZT/CWs have been reported to show satisfactory PPCPs removal performance from the water environment. These are sophisticated hybrid systems comprised of plants, substrates, and microorganisms with physical, chemical, and biological processes occurring in them (Hu et al., 2021). Wastewater flows through the root zone either horizontally or vertically, where plants create favorable conditions for the growth of bacteria in the root system. Organic contaminants are decomposed biochemically in the rhizosphere of root plants by the bacteria in these systems. RZT/CWs work through the combined processes of plants, substrates, and microorganisms for removal; in which the direct and indirect roles of wetland plants in PPCP removal are found to be more significant (Hu et al.,2021). Henceforth, the investigation of *in-situ* RZT system for PPCPs removal needs more attention. In addition, literature have

confirmed various adsorbents for PPCPs removal, however, some of them are cost-intensive and scarce. Henceforth, lately, the conversion of waste materials to adsorptive materials (biochar) for PPCPs removal is under critical investigation and needs more emphasis to solve waste disposal problems and contribute to waste management systems.

1.4 Objectives of Study

The present thesis is based on three distinct objectives focusing on the monitoring assessment of PPCPs/EDCs in urban wastewater treatment systems, and exploration of sustainable and economical adsorptive-based and hybrid treatment systems. The summary of three distinct objectives is stated below –

Objective 1:

Based on the literature survey of previous studies conducted in the wastewater treatment facilities, it is evident that the wastewater effluents from these facilities contribute to PPCPs/EDCs contamination in the nearby environment and accelerates potential ecosystem threats. In northern Indian cities, monitoring and fate assessment of these compounds in WWTPs was rarely explored and had less information. Therefore, a detailed investigation is needed on a local scale to quantify these contaminants and their fate in treatment facilities. Hence, this chapter focuses on the occurrence, seasonal variation, and removal of PPCPs/EDC in four (two major municipals, and two academic institutions) WWTPs located in the Himalayan foothills. This study represents the first examination of the monitoring of these specific compounds in the wastewater treatment plants (WWTPs) of the most populous, major metropolitan, and capital city in the Indian state of Uttarakhand i.e., Dehradun. The compounds selected for investigation were based on their significant usage, known limited removal by conventional wastewater treatments, and prolonged persistence in the aquatic ecosystem. Statistical data treatment was performed to test the distribution of the obtained PPCPs and EDCs data (Anderson-Darling, Jarque-Bera, Lilliefors, and Shapiro-Wilk tests), and the significant difference between the mean of the wastewater sample population (ANOVA: F statistics, p values, Mann-Whitney test, Tukey's and Dunn's post hoc analysis). Statistical tests were used for linking trends and measurement of the strengths in relationships between the PPCPs/EDCs in wastewater matrices.

Sub-objectives of this chapter are as follows:

- Quantification of the PPCPs/EDCs in the major WWTPs of Dehradun city
- Evaluation of the seasonal variation of these compounds in influents and effluent at the WWTPs
- Comparison of the removal efficiencies of the WWTPs based on statistical data treatment.
- Gauging the distribution of these compounds concentration data across seasons and WWTPs.
- Appraisal of correlation/strength relationship between the compounds in the wastewater matrices.

Objective 2:

Over the years, significant focus has been directed toward effectively eliminating PPCPs from wastewater across the globe. Consequently, various techniques encompassing physical, chemical, and biological approaches have been devised to tackle the removal of PPCPs during wastewater treatment in WWTPs. However, economical and sustainable remediation techniques are still under exploration and a burning issue. Lately, RZT systems have shown promising results in effectively removing PPCPs from water environments, as they are hybrid systems consisting of plants, substrates, and microorganisms, incorporating physical, chemical, and biological processes. However, previous literature have primarily examined the lab/pilot scale RZT systems for PPCPs removal, and to date, no detailed investigation study has been conducted on *in-situ* RZT system for PPCPs removal from real-world wastewater matrices. Henceforth, the present chapter investigates the PPCPs removal efficacy of an *in-situ* RZT hybrid system-based WWTP at an academic institution in Gujarat, India. Screening of PPCPs along a wastewater treatment system accoutered with a root zone system was done and quantification of PPCPs at various treatment stages in terms of normalized abundance was delineated. Removal efficiency of the *in-situ* RZT system was characterized and paired sample *t*-test, a statistical procedure was used between influent and effluent (pre and post treatment) at various stages to conclude the effectiveness of abundance variations (at a $p < 0.05$ significance level).

Sub-objectives of this chapter are as follows:

- Tracing of organic contaminants (majorly PPCPs) in the wastewater at various stages/processes of the RZT-based WWTP.

- Quantification of organic contaminants/PPCPs in terms of abundances at various stages of the plant.
- Characterization of removal efficiency for PPCPs at various stages of the plant.

Objective 3:

As stated earlier, efficient removal of PPCPs from water matrices has been an evolving issue worldwide. Out of the varied approaches (physical, chemical, and biological), the physical methods involve the principle of adsorption with the use of carbon-based adsorptive materials. Adsorption is considered one of the superior approaches for removing PPCPs due to its ready availability, ease of operation, wide adaptability, low cost, insensitivity to toxic materials, effectiveness, absence of secondary pollutants generation, and easy regeneration. The literature has confirmed the effectiveness of various adsorbents; however, some, such as activated carbon, are cost-intensive and scarce. Therefore, in recent times, there has been a critical investigation into the utilization of waste materials such as biochar as adsorbents for the removal of PPCPs. This approach provides solutions to waste disposal issues, offers waste management solutions, and synergistically contributes to the attainment of SDGs. Henceforth, this chapter aims to investigate various waste materials-based biochar suitability for PPCPs removal in aqueous solutions. Sawdust and sawdust-plastic waste agglomerate-derived biochar was prepared through the pyrolysis process and were studied as potential adsorbents for PPCPs removal. Ciprofloxacin (CFX) and sulfamethoxazole (SMX) were chosen as the targeted PPCPs (adsorbates), owing to their widespread usage and potential negative environmental effects. Literature have confirmed various adsorption-based studies, however, to date, these combinations of adsorbents and adsorbates have not been investigated. Various techniques were employed to evaluate important adsorption-related properties of the biochar including crystallographic structure, functionality, pH. Subsequently, batch adsorption tests were conducted to assess the capacity of the biochar to remove PPCPs from aqueous solutions. The kinetics and adsorption processes controlling the synergy between PPCPs and biochar were clarified.

Sub-objectives of this chapter are as follows:
- Investigation of the PPCPs removal efficiency of sawdust-derived biochar and hybrid biochar.

- Understanding the role of absorbent properties on their PPCPs adsorption behavior in aqueous solution.
- Investigation of the kinetics and adsorption mechanisms controlling the interaction between PPCPs and biochar.

1.5 Thesis Workflow and Integration

The present thesis is divided into seven chapters, out of which three main chapters (Chapter 4, Chapter 5, and Chapter 6) are made based on three distinct objectives. The detailed framework/workflow of the thesis is effectively represented in Figure **1.1.** The present thesis work is aimed toward monitoring assessment of PPCPs/EDCs in major municipal WWTPs of Dehradun city, Uttarakhand, India. In addition, root zone and adsorption-based (biochar) treatments were evaluated for their PPCPs removal efficiency as a sustainable and economic remediation approaches. To carry out the assessment, wastewater sampling is conducted at the municipal and RZT-based WWTPs, followed by sample analysis. Waste material-derived biochars were produced under controlled conditions and tested for adsorption studies. Diverse techniques have been employed during the investigation to accomplish the research objectives outlined in various chapters. Finally, the overall occurrence and prevalence pattern of PPCPs/EDCs along with their fate in WWTPs of Dehradun city is explained. Additionally, the PPCPs removal characteristics of the *in-situ* RZT and biochar systems are elucidated along with controlling mechanisms and kinetics. The illustrative diagram representing the integration of the various objective-focused chapters of the research work is shown in Figure **1.2.**
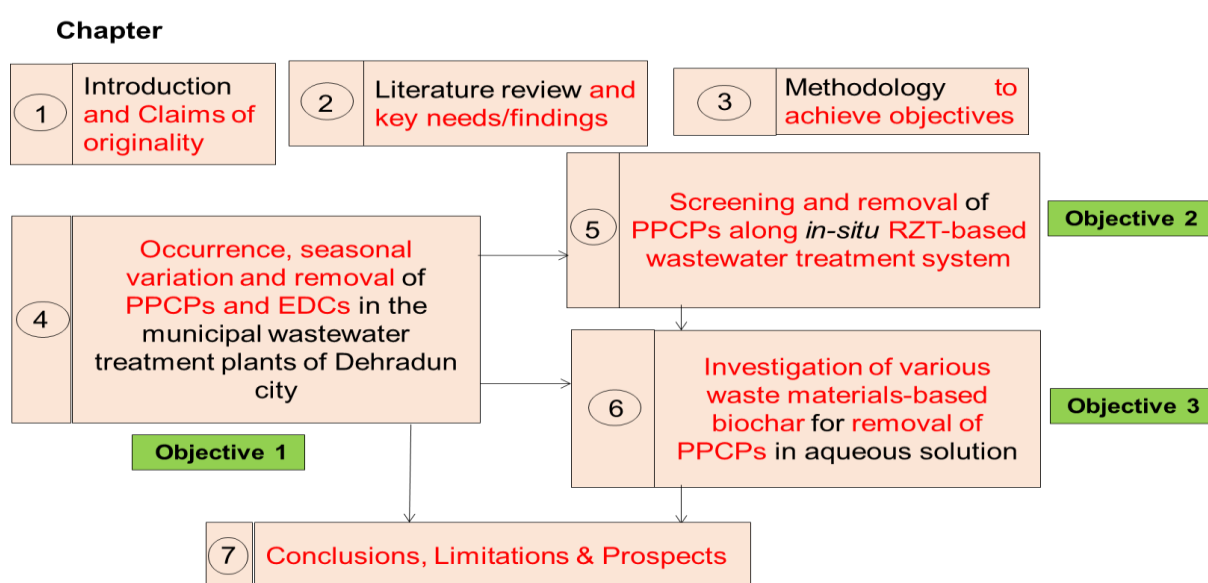
Figure 1.1 Chapter design and workflow of the thesis.
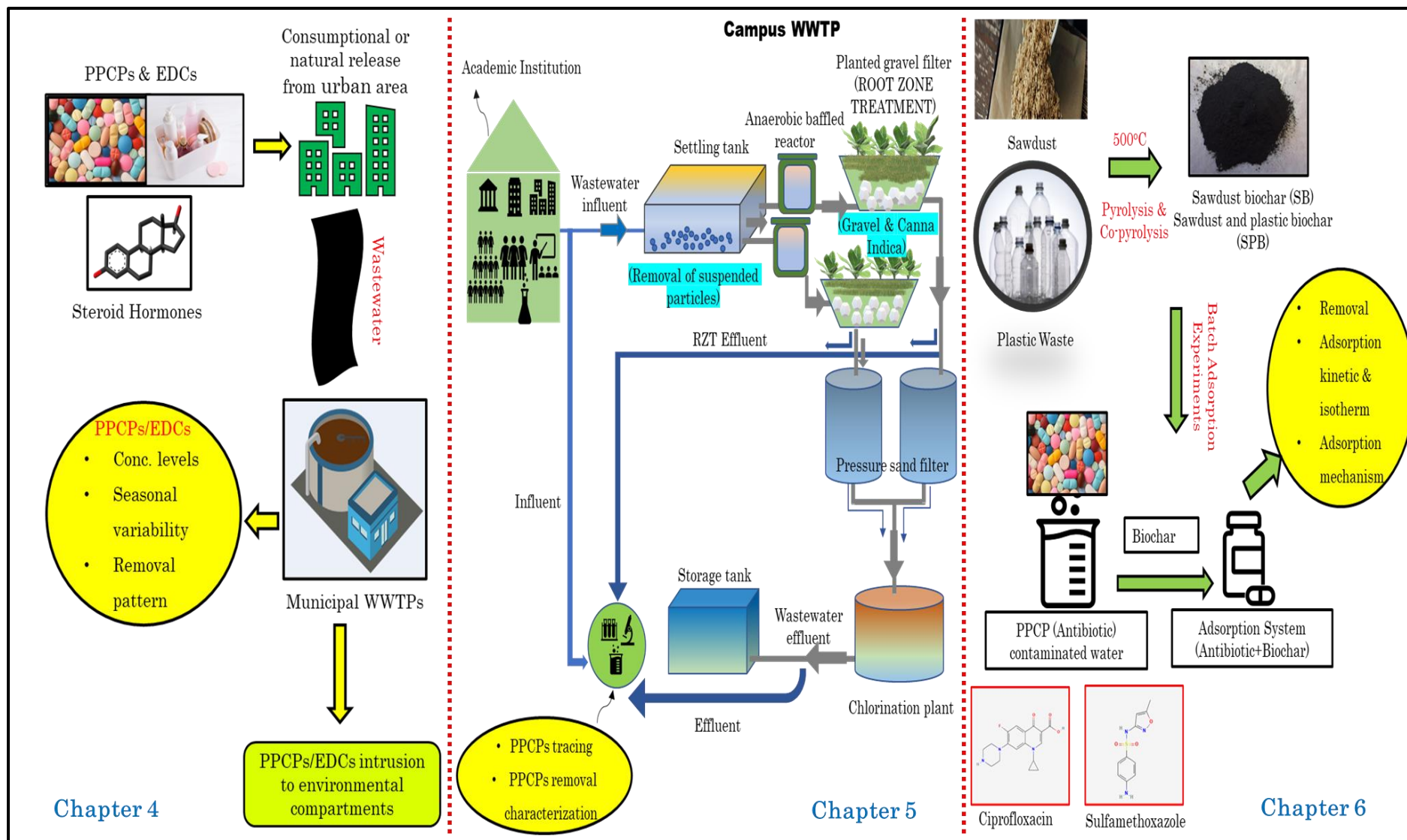
Figure 1.2. Conceptual figure delineating the integration of the various objective-focused chapters of the research work.

1.6 Highlights of Study

- This study represented the first reporting of PPCPs and EDCs in the urban wastewater systems of the most populous, major metropolitan, and capital city in the Indian state of Uttarakhand situated in Himalyan foothills.

- An astounding concentration of 123.9 μgL^{-1} was recorded for the estrone (EDC) in the wastewater influent, which is to date the highest ever recorded, globally. In addition, estrone enrichment in effluents was observed during the treatment, which might be attributed to the steroidal interconversion and is an emerging threat.

- High EDCs concentrations in influents of WWTPs were observed during monsoon, indicating significant runoff component from various potential sources (landfill waste, sludge from WWTPs, and livestock excrement) in the studied hilly region.

- The work delineated the detailed investigation on screening and removal of PPCPs along *in-situ* RZT system from wastewater matrices, which has been rarely reported to date.

- The RZT-based WWTP founds to be effective in the removal of majority of PPCPs with ~100% removal rate, however, further comprehensive research on RZT-based system could be performed to conclude the exact removal efficacy and fate of PPCPs during treatment in this particular system.

- Adsorptive-based approach was also found to be a pertinent remediation solution, where sawdust biochar showed higher antibiotics removal compared to the hybrid one (sawdust and plastic waste) in aqueous solution.

- The current work recommended RZT to be appraised for PPCPs in-situ remediation from landfill leachates, and sawdust-derived biochar could be incorporated as a filter media in the WWTPs for enhanced removal of such emerging contaminants from wastewater.

- This study could be used as a footprint/base for future studies pertaining to monitoring of PPCPs and other such emerging contaminants, and sustainable remediation approaches for their removals, especially in hilly terrains.

CHAPTER 2: LITERATURE REVIEW

2.1 PPCPs Sources in the Environment

High consumption of pharmaceutical drugs is reported across the world. Due to the complete or incomplete metabolism of these drugs, they get excreted in unchanged form or metabolites and are present in sufficient concentrations in wastewater (Chander et al., 2016). Treated and untreated effluent discharge by pharmaceutical industries in open lands and surface water contaminates the aquatic and soil environment (Chander et al., 2014). Improper disposal of expired or unused drugs is also one of the sources of PPCPs in the environment (Glassmeyer et al., 2005; Wu et al., 2009). Wastewater discharge from hospitals is one of the significant sources of pharmaceutical compounds.

Usage in aquaculture, livestock, field application of manure from livestock, and subsequent runoff are the primary sources of the entrance of veterinary pharmaceutical compounds into the environment (Fent et al., 2006; Johnson et al., 2006; Kay et al., 2005). PPCPs may enter into a) surface water through wastewater treatment plants and surface runoff (comprising sludge from WWTPs, livestock excretion, and landfill waste), b) in the soil through excretion from livestock and human beings, landfill dumping, and sludge application and c) in groundwater through leaching from waste dumped on soil (Zhang et al., 2016). The various sources of PPCPs discharge in the aquatic environment are shown in Figure **2.1**.

2.2 Impact of PPCPs Pollution on Health

PPCPs are reported as potential EDCs, their release into the environment may cause endocrine-related diseases in living organisms, and their exposure may also be responsible for a change in the reproductive health of human beings, including declining male fertility, birth defects, breast and testicular cancer (Nikolaou et al., 2007). Steroid estrogens drugs are in the group of most potent EDCs, which affect aquatic organisms even in very low concentrations (Desbrow et al., 1998; Johnson & Sumpter, 2001).

It has also been reported that the accumulation of PPCPs in the environment also causes negative effects ranging from near elimination of entire species of fishes to their feminization and the spread of antimicrobial resistance (AMR) (Nordea, 2016). AMR is the potential of a

microorganism (like bacteria, viruses, etc.) to cease an antimicrobial (such as antibiotics, antivirals, etc.) from working against it. This leads to the ineffectiveness of standard treatments, infection persistence, and the spread of the same to others. AMR is a situation prevailing right now across the world, and the effectiveness of pharmaceutical compounds in treating common infections in the community and hospitals is at risk (WHO, 2014). The use of water (polluted with pharmaceutical industry untreated effluent) for irrigation indirectly lowers the productivity of agricultural land and alters the agricultural infrastructure (Cherukupalli & Dhara, 2010).
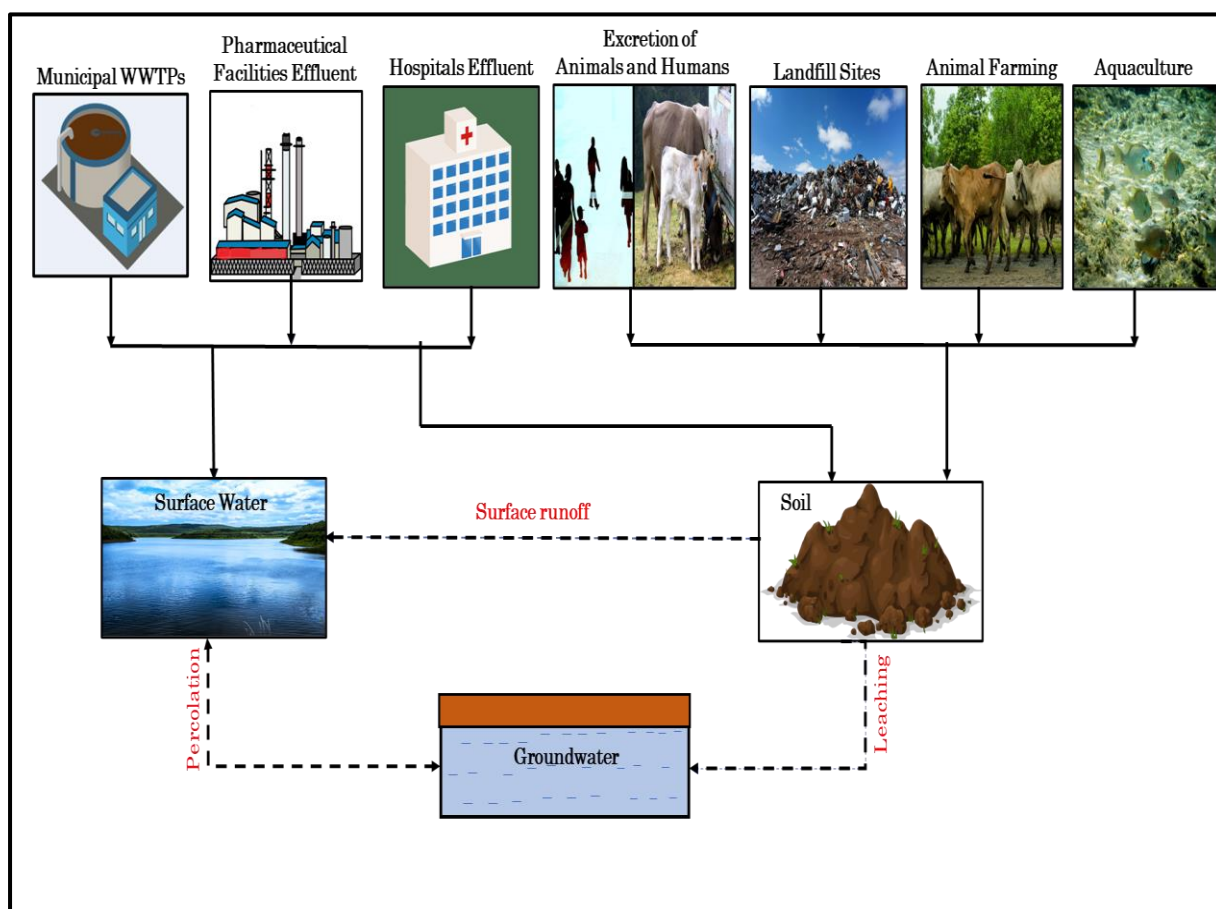
Figure 2.1. Different origins of PPCPs discharge in the aquatic environment.

2.3 Occurrence of PPCPs in Various Environmental Matrices

2.3.1 Occurrence of PPCPs in treated wastewater environment

Conventional treatment processes (activated sludge process/trickling filters) are the most widely used methods for treatment in WWTPs. But these methods have limitations in the removal of certain PPCPs (Luo et al., 2014; Santos et al., 2007). Some PPCPs, such as

acetaminophen and ibuprofen, are removed to the extent of 99.9% and 87-98.2%, respectively, using conventional treatment methods, whereas others, such as metoprolol, sulfamethazine, and carbamazepine, have a lesser removal rate of 23%, 13.1%, and 7–23.1% respectively (Ratola et al., 2012). As a result, various PPCPs were reported in WWTPs effluents by studies across the world (Chiffre et al., 2016; Deeb et al., 2017; Gurke et al., 2015; Hofman-Caris et al., 2019; Lacey et al., 2012; Mijangos et al., 2018; Mohapatra et al., 2016)

Municipal WWTPs (process domestic sewage or predominantly domestic sewage) were found to have lower levels (ngL^{-1} to µgL^{-1}) of PPCPs in wastewater effluents (Chiffre et al., 2016; Kosma et al., 2010; Lacey et al., 2012; Mijangos et al., 2018; Mohapatra et al., 2016), whereas higher levels (mgL^{-1}) of PPCPs were detected in effluents of WWTPs that primarily process wastewater from the pharmaceuticals production units (Fick et al., 2009; Larsson et al., 2007; Li et al., 2008a; Lin & Tsai, 2009; Phillips et al., 2010; Sim et al., 2011a).

A study conducted by Larsson et al. (2007) at a Patancheru Enviro Tech Ltd. WWTP (receiving wastewater primarily from about 90 bulk drug producers) situated near Hyderabad, India, reported 11 pharmaceutical drugs with concentrations levels greater than 100 µgL^{-1} in the effluent. These were the highest recorded concentrations in any effluent from anywhere else in the world. Ciprofloxacin (fluoroquinolone antibiotics) was the most abundant drug detected in the effluent with a maximum concentration of 31 mgL^{-1}, which is approximately 6568 times higher than the concentration (4.72 µgL^{-1}) reported (Mijangos et al., 2018) for ciprofloxacin in the WWTP effluent in Basque. Fick et al. (2009) revisited the Patancheru Enviro Tech Ltd. WTWP and detected the same eleven pharmaceutical compounds in the effluent as reported (Larsson et al., 2007), but their concentrations were found to be considerably lower, except for cetirizine. Ciprofloxacin and cetirizine were present in very high concentrations with maximum values of 14 mgL^{-1} and 2.1 mgL^{-1}, respectively, in the effluent.

Diclofenac (NSAID), carbamazepine (an antiepileptic drug), and caffeine (stimulant) were the most frequently detected pharmaceutical compounds in municipal WWTP effluents across the world. Diclofenac was observed in the highest concentrations of 228.5 µgL^{-1} in Taiwan (Lin & Tsai, 2009) and 19.2 µgL^{-1} in Korea (Sim et al., 2011a) in treated effluents from pharmaceutical production facilities. In municipal WWTPs, concentrations of 2.95 µgL^{-1} in Ireland (Lacey et al., 2012), 2.67 µgL^{-1} in Greece (Papageorgiou et al., 2016), 4.2 µgL^{-1} in Portugal (Gaffney et

al., 2017), and 4.88 µgL^{-1} in Italy (Palli et al., 2019) were observed for diclofenac in the effluents.

Sim et al. (2011a) detected carbamazepine in the effluent from pharmaceutical manufacture WWTPs in Korea with a maximum concentration of 150 µgL^{-1}. Studies by Santos et al. (2009) in Spain, Sim et al. (2011a) in Korea, Lacey et al. (2012) in Ireland, Deeb et al. (2017) in Germany, and Paíga et al. (2019) in Portugal reported concentrations of carbamazepine as 1.55 µgL^{-1}, 21 µgL^{-1}, 6.5 µgL^{-1}, 4.61 µgL^{-1} and 1.06 µgL^{-1} respectively in the wastewater effluents from municipal WWTPs. Caffeine was detected in highest concentrations of 13.9 µgL^{-1} in Greece (Kosma et al., 2010), 2.7 µgL^{-1} in Ireland (Lacey et al., 2012), 5.4 µgL^{-1} in India (Anumol et al., 2016), 11.45 µgL^{-1} in Sweden (Gros et al., 2017) and 65.99 µgL^{-1} in Basque (Mijangos et al., 2018) in municipal WWTPs effluents.

Due to the limited pharmaceutical removal efficiency of conventional wastewater treatment processes, pharmaceutical compounds/residues are predominantly present in the treated wastewater environment. The highest measured concentrations (above 1 µgL^{-1}) of various PPCPs in WWTPs effluents are mentioned in Table **2.1**.

Table 2.1. Maximum concentrations of various PPCPs measured worldwide in treated wastewater effluents.

PPCP	Max. Conc. (µgL^{-1})	Country	Reference
Analgesic/Antipyretic/ NSAID			
Acetaminophen	417.5[a]	Taiwan	(Lin & Tsai, 2009)
	1.7	Greece	(Kosma et al., 2010)
	7.4[b]	Greece	(Kosma et al., 2010)
	11.73	United Kingdom	(Petrie et al., 2015)
	2.14	Portugal	(Paíga et al., 2017)
	5.46	Basque	(Mijangos et al., 2018)
Diclofenac	228.5[a]	Taiwan	(Lin & Tsai, 2009)
	2.6	Greece	(Kosma et al., 2010)
	6.5[b]	Greece	(Kosma et al., 2010)
	1.76	Korea	(Sim et al., 2011a)
	19.2[a]	Korea	(Sim et al., 2011a)
	2.95	Ireland	(Lacey et al., 2012)
	7	Greece	(Stasinakis et al., 2012)
	1.31	Greece	(Stasinakis et al., 2013)
	2.3	India	(Anumol et al., 2016)
	2.67	Greece	(Papageorgiou et al., 2016)

	>2	Finland	(Lindholm-Lehto et al., 2016)
	2.48	France	(Chiffre et al., 2016)
	2.71	Algeria	(Kermia et al., 2016)
	2.24	Spain	(Afonso-Olivares et al., 2017)
	4.2	Portugal	(Gaffney et al., 2017)
	23.5	South Africa	(Madikizela & Chimuka, 2017)
	2.83	United Kingdom	(Kay et al., 2017)
	4	Germany	(Schmidt et al., 2018)
	1.93	Basque	(Mijangos et al., 2018)
	4.88	Italy	(Palli et al., 2019)
	1.93	Portugal	(Paíga et al., 2019)
Ibuprofen	55	Spain	(Santos et al., 2009)
	1500[a]	Taiwan	(Lin & Tsai, 2009)
	2.6	Greece	(Kosma et al., 2010)
	21.7	Spain	(Afonso-Olivares et al., 2017)
	9.2	Sweden	(Gros et al., 2017)
	4.62	United Kingdom	(Kay et al., 2017)
	1.3	South Korea	(Park et al., 2020)
Naproxen	5.09	Spain	(Santos et al., 2009)
	1.05[a]	Taiwan	(Lin & Tsai, 2009)
	39.3[a]	Korea	(Sim et al., 2011a)
	1.724 ± 0.007	United States	(Mohapatra et al., 2016)
	14.4	South Africa	(Madikizela & Chimuka, 2017)
Ketprofen	3.92	Spain	(Santos et al., 2009)
	1.57	Greece	(Stasinakis et al., 2012)
	5.25	United States	(Oliveira et al., 2015)
	1.03	Algeria	(Kermia et al., 2016)
	1.17	Spain	(Afonso-Olivares et al., 2017)
Metamizole	3.81	Spain	(Afonso-Olivares et al., 2017)
Codeine	5.41	Australia	(Yadav et al., 2019)
Aspirin	12.1	Korea	(Sim et al., 2011a)
	47.6[a]	Korea	(Sim et al., 2011a)
Salicylic acid	10.1	Greece	(Kosma et al., 2010)
	14.6[b]	Greece	(Kosma et al., 2010)
Mefenamic acid	1.73	Ireland	(Lacey et al., 2012)
Nimesulide	9.73	Greece	(Papageorgiou et al., 2016)
Oxycodone	1700[a]	United States	(Phillips et al., 2010)
Tramadol	59.05	United Kingdom	(Petrie et al., 2015)
	>1	Netherland	(Hofman-Caris et al., 2019)
	Antibiotic		
Ciprofloxacin	31000[a]	India	(Larsson et al., 2007)
	14000[a]	India	(Fick et al., 2009)
	2.05	Korea	(Sim et al., 2011a)
	2.95[a]	Korea	(Sim et al., 2011a)

	2.79	India	(Mohapatra et al., 2016)
	1.4	Portugal	(Gaffney et al., 2017)
	4.72	Basquse	(Mijangos et al., 2018)
Erythromycin	7.84[a]	Taiwan	(Lin & Tsai, 2009)
	2.78	Portugal	(Gaffney et al., 2017)
	1.86	United Kingdom	(Kay et al., 2017)
Lincomycin	21.28	South Korea	(Behera et al., 2011)
	45.7	Korea	(Sim et al., 2011a)
	43909[a]	Korea	(Sim et al., 2011a)
Sulfamethoxazole	1340[a]	Taiwan	(Lin & Tsai, 2009)
	29.8[a]	Korea	(Sim et al., 2011a)
	1.38	France	(Chiffre et al., 2016)
	4.145 ± 0.390	United States	(Mohapatra et al., 2016)
	2.01	India	(Mohapatra et al., 2016)
	3.34	Kenya	(Ngumba et al., 2016)
	1.52	Spain	(Afonso-Olivares et al., 2017)
	2	Portugal	(Gaffney et al., 2017)
	8.96	Basque	(Mijangos et al., 2018)
Sulfamethazine	> 400[a]	Croatia	(Babić et al., 2007)
	3.41[a]	Taiwan	(Lin & Tsai, 2009)
Sulfaguanidine	>1100[a]	Croatia	(Babić et al., 2007)
Sulfathiazole	2.77	Korea	(Sim et al., 2011a)
	3.96[a]	Korea	(Sim et al., 2011a)
Sulfapyridine	1.5	Portugal	(Gaffney et al., 2017)
Sulfadiazine	5.48	Basque	(Mijangos et al., 2018)
Trimethoprim	2	Korea	(Sim et al., 2011a)
	10.1[a]	Korea	(Sim et al., 2011a)
	5.84	Basque	(Mijangos et al., 2018)
Amoxicillin	7.69	Italy	(Palli et al., 2019)
Enrofloxacin	900[a]	India	(Larsson et al., 2007)
	210[a]	India	(Fick et al., 2009)
Ofloxacin	160[a]	India	(Larsson et al., 2007)
	55[a]	India	(Fick et al., 2009)
Enoxacin	300[a]	India	(Larsson et al., 2007)
Norfloxacin	420[a]	India	(Larsson et al., 2007)
	25[a]	India	(Fick et al., 2009)
Cephalexin	5.624 ± 0.376	United States	(Mohapatra et al., 2016)
	5.07	Germany	(Deeb et al., 2017)
Oxytetracycline	19.5 ± 2.9[a,c]	China	(Li et al., 2008a)
	7.44[a]	Taiwan	(Lin & Tsai, 2009)
Penicillin G	1.68 ± 0.48[a]	China	(Li et al., 2008b)
Beta-Blocker			
Metoprolol	950[a]	India	(Larsson et al., 2007)
	4[a]	India	(Fick et al., 2009)

	4.34	Ireland	(Lacey et al., 2012)
	5.76	Germany	(Gurke et al., 2015)
	>2	Netherland	(Hofman-Caris et al., 2019)
Atenolol	5.91	South Korea	(Behera et al., 2011)
	1.6	India	(Anumol et al., 2016)
	1.87	Greece	(Papageorgiou et al., 2016)
	1.035 ± 0.008	United States	(Mohapatra et al., 2016)
	2.87	Germany	(Deeb et al., 2017)
Sotalol	3.33	Australia	(Roberts et al., 2016)
	2	Netherland	(Hofman-Caris et al., 2019)
Lipid Regulator			
Gemfibrozil	13[a]	Taiwan	(Lin & Tsai, 2009)
	1.3	Greece	(Kosma et al., 2010)
	1.7[b]	Greece	(Kosma et al., 2010)
	20.1	Spain	(Afonso-Olivares et al., 2017)
	2	Netherland	(Hofman-Caris et al., 2019)
Simvastatin	1.74	Greece	(Papageorgiou et al., 2016)
Bezafibrate	3.12	Sweden	(Gros et al., 2017)
Antiepileptics			
Carbamazepine	1.55	Spain	(Santos et al., 2009)
	1.1	Greece	(Kosma et al., 2010)
	1.9[b]	Greece	(Kosma et al., 2010)
	21	Korea	(Sim et al., 2011a)
	150[a]	Korea	(Sim et al., 2011a)
	6.5	Ireland	(Lacey et al., 2012)
	1[a]	Israel	(Lester et al., 2013)
	1.01	France	(Chiffre et al., 2016)
	1.77	Spain	(Afonso-Olivares et al., 2017)
	1.6	Portugal	(Gaffney et al., 2017)
	4.61	Germany	(Deeb et al., 2017)
	1.06	Portugal	(Paíga et al., 2019)
	1	Netherland	(Hofman-Caris et al., 2019)
Gabapentin	79.86	United States	(Oliveira et al., 2015)
Phenytoin	2.37	Basque	(Mijangos et al., 2018)
Antidepressant			
Citalopram	840[a]	India	(Larsson et al., 2007)
	430[a]	India	(Fick et al., 2009)
Venlafaxine	11.2	Israel	(Gasser et al., 2012)
	200[a]	Israel	(Lester et al., 2013)
	2.66	Spain	(Collado et al., 2014)
	5.5	Australia	(Roberts et al., 2016)
Antihistamine			
Cetrizine	1400[a]	India	(Larsson et al., 2007)
	2100[a]	India	(Fick et al., 2009)

	1.24	Greece	(Papageorgiou et al., 2016)
Fexofenadine	1.61	South Africa	(Archer et al., 2017)
Stimulant			
Caffeine	5.65	Spain	(Santos et al., 2009)
	13.9	Greece	(Kosma et al., 2010)
	10.6[b]	Greece	(Kosma et al., 2010)
	3.18	Korea	(Sim et al., 2011a)
	9.38[a]	Korea	(Sim et al., 2011a)
	2.7	Ireland	(Lacey et al., 2012)
	5.4	India	(Anumol et al., 2016)
	~1	Greece	(Papageorgiou et al., 2016)
	3.26	Spain	(Afonso-Olivares et al., 2017)
	2.9	Portugal	(Gaffney et al., 2017)
	11.45	Sweden	(Gros et al., 2017)
	65.99	Basque	(Mijangos et al., 2018)
Diuretics			
Furosemide	2.28	Ireland	(Lacey et al., 2012)
	9.96	Greece	(Papageorgiou et al., 2016)
Hydrochlorothiazide	1.04	Spain	(Collado et al., 2014)
Antagonist			
Valsartan	28.22	Germany	(Gurke et al., 2015)
	9.48	Basque	(Mijangos et al., 2018)
Irbesartan	17.9	Sweden	(Kårelid et al., 2017)
	1.27	Basque	(Mijangos et al., 2018)
Cimetidine	2.1	South Korea	(Park et al., 2020)
Muscle Relaxant			
Metaxalone	3800[a]	United States	(Phillips et al., 2010)
Antifungal			
Clotrimazole	8.65	Ireland	(Lacey et al., 2012)
Antiretroviral			
Lamivudine	3.98	Kenya	(Ngumba et al., 2016)
	55.76 ± 5.48	Zambia	(Ngumba, 2018)
Efavirenz	34 ± 2.8	South Africa	(Abafe et al., 2018)
Darunavir	17 ± 0.55	South Africa	(Abafe et al., 2018)
Lopinavir	3.8 ± 0.35	South Africa	(Abafe et al., 2018)
Nevirapine	1.9 ± 0.68	South Africa	(Abafe et al., 2018)
Ritonavir	1.50 ± 0.053	South Africa	(Abafe et al., 2018)
Zidovudine	37.14 ± 2.56	Zambia	(Ngumba, 2018)
Biguanide			
Metformin	58	Portugal	(Gaffney et al., 2017)
	10.35	Switzerland	(Das et al., 2017)
	>5	Netherland	(Hofman-Caris et al., 2019)
Metabolite/Degradation Product			
Penilloic Acid (Penicillin G degradation product)	44.5 ± 2.5[a,c]	China	(Li et al., 2008b)

O-desmethylvenlafaxine (Venlafaxine metabolite)	2.49	Israel	(Gasser et al., 2012)
	2.01	Portugal	(Paíga et al., 2019)
N-acetyl-4-aminoantipyrine (Metamizole metabolite)	25.03	Germany	(Evgenidou et al., 2015)
4′-Hydroxy diclofenac (Diclofenac metabolite)	7.02	Spain	(García-Galán et al., 2016)
O-Desmethyltramadol (Tramadol metabolite)	1.47	South Africa	(Archer et al., 2017)
Guanylurea (Metformin metabolite)	40	Netherland	(Hofman-Caris et al., 2019)
Hydroxy ibuprofen (Ibuprofen metabolite)	>1	Netherland	(Hofman-Caris et al., 2019)
10,11-trans-diol-carbamazepine (Carbamazepine metabolite)	>2	Netherland	(Hofman-Caris et al., 2019)

[a]Concentrations in treated effluent from pharmaceutical production facilities,
[b]Concentrations in treated effluent from hospitals
[c]Maximum concentrations in mgL^{-1}

2.3.2 Occurrence of PPCPs in surface water environment

PPCPs are discharged into the surface water environment by wastewater treatment plants and surface runoff, encompassing sludge from WWTPs, livestock excretion, and landfill solid waste (Zhang et al., 2016). But, treated wastewater from WWTPs is the main source for the presence of emerging contaminants such as PPCPs in the surface waters (Petrie et al., 2015). In surface waters, pharmaceutical compounds get diluted, absorbed on soil/sediments, and encounter photochemical and/or biological transformations (Onesios et al., 2009). PPCPs concentrations are usually detected in the range from a few μgL^{-1} to a few ngL^{-1} in surface waters (Grujić et al., 2009; Kibuye et al., 2019a; Yang et al., 2013), but concentrations as high as mgL^{-1} are reported in surface waters receiving effluent from point sources such as pharmaceutical production and manufacturing units WWTPs (Fick et al., 2009; Li et al., 2008b).

In China, Li et al. (2008b) reported the dominant presence of penilloic acid (a metabolite of Penicillin G pharmaceutical) in Wangyang River receiving effluent from the penicillin production WWTP. The maximum mean concentration of penilloic acid was detected as 10.54 mgL^{-1} along the stretch of the river. Fick et al. (2009) detected the presence of 12 pharmaceuticals in the Isakavagu-Nakkavagu rivers, which receive effluent from the Patancheru Enviro Tech Ltd. WWTP near Hyderabad, India (process wastewater from

approximately 90 pharmaceutical production facilities). Ciprofloxacin was the leading dominant pharmaceutical detected in the river, with the highest concentration of 2.5 mgL^{-1}.

Acetaminophen (analgesics and antipyretics), Diclofenac (NSAID), Ibuprofen (NSAID), Naproxen (NSAID), Ciprofloxacin (fluoroquinolone antibiotics), Sulfamethoxazole (sulfonamide antibiotic), Carbamazepine (an antiepileptic drug), and Caffeine (stimulant) were the most frequently detected pharmaceutical compounds in different surface water sources across the world. Acetaminophen was reported in the highest concentrations of 610 ngL^{-1} in the Sava River in Serbia (Grujić et al., 2009), 13126 ngL^{-1} in surface water in Costa Rica (Spongberg et al., 2011), 339 ngL^{-1} in Shijing River in China (Yang et al., 2013), 200 ngL^{-1} in Allier River in France (Celle-Jeanton et al., 2014), 4460 ngL^{-1} in Apatlaco River in Mexico (Rivera-Jaimes et al., 2018), 400 ngL^{-1} in Susquehanna River in Unites States/USA (Kibuye et al., 2019a) and 12430 ngL^{-1} in Rivers, Canals and Lagoons in Nigeria (Ebele et al., 2020).

Studies by Zhao et al. (2009) on Shijing River in China, Spongberg et al. (2011) on surface waters in Costa Rica, Carmona et al. (2014) on Turia River in Spain, Kay et al. (2017) on River Aire and Calder Catchments in the United Kingdom and Rivera-Jaimes et al. (2018) on Apatlaco River in Mexico detected maximum concentrations of diclofenac as 150 ngL^{-1}, 266 ngL^{-1}, 3462 ngL^{-1}, 2991 ngL^{-1}, and 1398 ngL^{-1} respectively. Other NSAIDs, such as Ibuprofen and Naproxen, were also reported in higher concentrations (in μgL^{-1}) by previous literature. Ibuprofen was observed in the highest concentrations of 36.79 μgL^{-1} in surface water in Costa Rica (Spongberg et al., 2011), 65.93 μgL^{-1} in Turia River in Spain (Carmona et al., 2014), 4.84 μgL^{-1} in River Aire and Calder Catchments in the United Kingdom (Kay et al., 2017), 2.74 μgL^{-1} in Rivers, Canals and Lagoons in Nigeria (Ebele et al., 2020). In contrast, Naproxen was observed in the highest concentrations of 7.19 μgL^{-1} in Turia River in Spain (Carmona et al., 2014), 4.82 μgL^{-1} in Apatlaco River in Mexico (Rivera-Jaimes et al., 2018), 2.12 μgL^{-1} in Rivers, Canals, and Lagoons in Nigeria (Ebele et al., 2020).

Antibiotics, such as ciprofloxacin and sulfamethoxazole are reported in different surface waters by various authors worldwide. Concentration as high as 6.5 mgL^{-1} was detected for ciprofloxacin in lakes in India by Fick et al. (2009), whereas other highest reported concentrations were 0.74 μgL^{-1} in surface water in Costa Rica (Spongberg et al., 2011), 0.51 μgL^{-1} in the Nairobi River watershed in Kenya (Ngumba et al., 2016) and 1.17 μgL^{-1} in Wiwi

and Oda Rivers in Ghana (Azanu et al., 2018). On the other hand, sulfamethoxazole was observed in maximum concentrations of 2.7 µgL^{-1} in Ravi River in Pakistan (Khan et al., 2013), 13.76 µgL^{-1} in the Nairobi River watershed in Kenya (Ngumba et al., 2016) and 3.18 µgL^{-1} in Rivers, Canals, and Lagoons in Nigeria (Ebele et al., 2020).

Carbamazepine is usually detected at concentrations in ngL^{-1} in surface waters across the world. Studies by Kim et al. (2009) on Mankyung river in South Korea, Loos et al. (2010a) on tributaries of Danube River in Europe, Nannou et al. (2015) on Pamvotis Lake and Kalamas River in Greece, and Ebele et al. (2020) on Rivers, Canals and Lagoons in Nigeria reported maximum concentrations of carbamazepine as 595±14 ngL^{-1}, 945 ngL^{-1}, 406 ngL^{-1}, and 342 ngL^{-1}, respectively. Caffeine was detected in the highest concentrations of 6.8 µgL^{-1} in tributaries of Danube River in Europe (Loos et al., 2010a), 1121.45 µgL^{-1} in surface water in Costa Rica (Spongberg et al., 2011), 18.83 µgL^{-1} in surface water in Brazil (Machado et al., 2016), and 4.5 µgL^{-1} in Susquehanna River in the USA (Kibuye et al., 2019a).

The highest measured concentrations (above one ngL^{-1}) of various PPCPs in different surface waters are listed in Table **2.2.**

Table 2.2. Maximum concentrations of various PPCPs measured worldwide in different surface waters.

PPCP	Max. Conc. (ngL^{-1})	Surface water source	Country	Reference
Analgesic/Antipyretic/NSAID				
Acetaminophen	73	Han River, Nakdong River and Youngsan River	South Korea	(Kim et al., 2007)
	127	Han River	South Korea	(Choi et al., 2008)
	610	Sava River	Serbia	(Grujić et al., 2009)
	310	Tamis River	Serbia	(Grujić et al., 2009)
	13216	Surface water	Costa Rica	(Spongberg et al., 2011)
	243	Onyar River	Spain	(Gros et al., 2012)
	152	Beijiang River	China	(Yang et al., 2013)
	334	Zhujiang River	China	(Yang et al., 2013)
	339	Shijing River	China	(Yang et al., 2013)
	200	Allier River	France	(Celle-Jeanton et al., 2014)
	156	Pamvotis Lake and Kalamas River	Greece	(Nannou et al., 2015)

	4460	Apatlaco River	Mexico	(Rivera-Jaimes et al., 2018)
	13.7	Surface water	China	(He et al., 2018)
	400	Susquehanna River	United States	(Kibuye et al., 2019a)
	384	Surface water	China	(Lu et al., 2019)
	12430	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Diclofenac	72	Rivers of Spain, Belgium, Germany, and Slovenia	Europe	(Hernando et al., 2006)
	150	Shijing River	China	(Zhao et al., 2009)
	52	Danube River Tributaries - Arges, Timok, Rusenski Lom and Velika Morava	Romania, Bulgaria, and Serbia	(Loos et al., 2010a)
	266	Surface water	Costa Rica	(Spongberg et al., 2011)
	52	Onyar River	Spain	(Gros et al., 2012)
	71	Lyngbygaards River	Denmark	(Matamoros et al., 2012)
	3462	Turia River	Spain	(Carmona et al., 2014)
	457	Pamvotis Lake and Kalamas River	Greece	(Nannou et al., 2015)
	230.5	Dongting Lake	China	(Ma et al., 2016)
	260	Fyris River	Sweden	(Gago-Ferrero et al., 2017)
	2991	River Aire and Calder Catchments	United Kingdom	(Kay et al., 2017)
	1398	Apatlaco River	Mexico	(Rivera-Jaimes et al., 2018)
	20.2	Surface water	China	(He et al., 2018)
	68	Surface water	China	(Lu et al., 2019)
	200	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Ibuprofen	152	Rivers of Spain, Belgium, Germany, and Slovenia	Europe	(Hernando et al., 2006)
	38	Han River, Nakdong River and Youngsan River	South Korea	(Kim et al., 2007)
	17	Shijing River	China	(Zhao et al., 2009)
	414±13	Mankyung River	South Korea	(Kim et al., 2009)
	27	Danube River	Germany	(Loos et al., 2010a)

	718	Danube River Tributaries - Arges, Timok, Rusenski Lom and Velika Morava	Romania, Bulgaria, and Serbia	(Loos et al., 2010a)
	36788	Surface water	Costa Rica	(Spongberg et al., 2011)
	380	Onyar River	Spain	(Gros et al., 2012)
	723	Lima River	Portugal	(Paíga et al., 2013)
	65928	Turia River	Spain	(Carmona et al., 2014)
	1351	Pamvotis Lake and Kalamas River	Greece	(Nannou et al., 2015)
	1317	Lis River	Portugal	(Paíga et al., 2016)
	19.8	Dongting Lake	China	(Ma et al., 2016)
	2	Surface water	United States	(McEachran et al., 2016)
	4838	River Aire and Calder Catchments	United Kingdom	(Kay et al., 2017)
	1106	Apatlaco River	Mexico	(Rivera-Jaimes et al., 2018)
	14.3	Surface water	China	(He et al., 2018)
	116	Surface water	China	(Lu et al., 2019)
	2740	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Naproxen	70	Rivers of Spain, Belgium, Germany, and Slovenia	Europe	(Hernando et al., 2006)
	125	Shijing River	China	(Zhao et al., 2009)
	32	Source waters of Drinking WTPs	United States	(Benotti et al., 2009)
	156	Onyar River	Spain	(Gros et al., 2012)
	36	Lyngbygaards River	Denmark	(Matamoros et al., 2012)
	7189	Turia River	Spain	(Carmona et al., 2014)
	114.04	Ebro River	Spain	(Osorio et al., 2016)
	12.21	Júcar River	Spain	(Osorio et al., 2016)
	6	Surface water	United States	(McEachran et al., 2016)
	4820	Apatlaco River	Mexico	(Rivera-Jaimes et al., 2018)
	24.1	Surface water	China	(Lu et al., 2019)
	2120	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Ketprofen	9808	Surface water	Costa Rica	(Spongberg et al., 2011)
	42.4	Surface water	China	(Lu et al., 2019)
Codeine	1780	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Salicylic acid	3001	Pamvotis Lake and Kalamas River	Greece	(Nannou et al., 2015)

Meclofenamic acid	2000	Rivers,Canals and Lagoons	Nigeria	(Ebele et al., 2020)
Tramadol	240	Fyris River	Sweden	(Gago-Ferrero et al., 2017)
	852	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Antibiotic				
Ciprofloxacin	2500000	Isakavagu-Nakkavagu Rivers	India	(Fick et al., 2009)
	6500000	Lakes	India	(Fick et al., 2009)
	740	Surface water	Costa Rica	(Spongberg et al., 2011)
	60.3	Baiyangdian Lake	China	(Li et al., 2012)
	23	Onyar River	Spain	(Gros et al., 2012)
	101	Beijiang River	China	(Yang et al., 2013)
	96	Zhujiang River	China	(Yang et al., 2013)
	304	Shijing River	China	(Yang et al., 2013)
	16.34	Ebro River	Spain	(Osorio et al., 2016)
	20	Llobregat River	Spain	(Osorio et al., 2016)
	509	Nairobi River Basin	Kenya	(Ngumba et al., 2016)
	1168	Wiwi and Oda Rivers	Ghana	(Azanu et al., 2018)
Erythromycin	18.58	Ebro River	Spain	(Osorio et al., 2016)
	12.66	Llobregat River	Spain	(Osorio et al., 2016)
	1378	River Aire and Calder Catchments	United Kingdom	(Kay et al., 2017)
	1149	Wiwi and Oda Rivers	Ghana	(Azanu et al., 2018)
	7.3	Surface water	China	(He et al., 2018)
	45.6	Surface water	China	(Lu et al., 2019)
	275	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Lincomycin	10.1	Surface water	China	(He et al., 2018)
Sulfamethoxazole	300	Rio Grande River	United States	(Brown et al., 2006)
	36	Han River, Nakdong River and Youngsan River	South Korea	(Kim et al., 2007)
	82	Han River	South Korea	(Choi et al., 2008)
	110	Source waters of Drinking WTPs	United States	(Benotti et al., 2009)
	28	Danube River	Germany	(Loos et al., 2010a)
	204	Danube River Tributaries - Arges, Timok, Rusenski Lom and Velika Morava	Romania, Bulgaria, and Serbia	(Loos et al., 2010a)
	56	Surface water	Costa Rica	(Spongberg et al., 2011)
	79	Onyar River	Spain	(Gros et al., 2012)

	39	Beijiang River	China	(Yang et al., 2013)
	50	Zhujiang River	China	(Yang et al., 2013)
	65	Shijing River	China	(Yang et al., 2013)
	2700	Ravi River	Pakistan	(Khan et al., 2013)
	190	Pamvotis Lake and Kalamas River	Greece	(Nannou et al., 2015)
	2	Surface water	United States	(McEachran et al., 2016)
	13765	Nairobi River Basin	Kenya	(Ngumba et al., 2016)
	17.4	Surface water	China	(He et al., 2018)
	500	Susquehanna River	United States	(Kibuye et al., 2019a)
	16.4	Surface water	China	(Lu et al., 2019)
	3180	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Sulfamethazine	1626	Surface water	Costa Rica	(Spongberg et al., 2011)
Trimethoprim	4000	Isakavagu-Nakkavagu Rivers	India	(Fick et al., 2009)
	12	Beijiang River	China	(Yang et al., 2013)
	17	Zhujiang River	China	(Yang et al., 2013)
	14	Shijing River	China	(Yang et al., 2013)
	20	Surface water	United States	(McEachran et al., 2016)
	2650	Nairobi River Basin	Kenya	(Ngumba et al., 2016)
	500	Susquehanna River	United States	(Kibuye et al., 2019a)
	17.4	Surface water	China	(Lu et al., 2019)
Amoxicillin	12.3	Surface water	China	(He et al., 2018)
	272150	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Ofloxacin	10000	Isakavagu-Nakkavagu Rivers	India	(Fick et al., 2009)
	11000	Lakes	India	(Fick et al., 2009)
	335	Surface water	Costa Rica	(Spongberg et al., 2011)
	8	Surface water	China	(He et al., 2018)
	1500	Susquehanna River	United States	(Kibuye et al., 2019a)
	17.8	Surface water	China	(Lu et al., 2019)
Enoxacin	66000	Isakavagu-Nakkavagu Rivers	India	(Fick et al., 2009)
	160000	Lakes	India	(Fick et al., 2009)
Norfloxacin	4700	Isakavagu-Nakkavagu Rivers	India	(Fick et al., 2009)
	520000	Lakes	India	(Fick et al., 2009)
	1744	Surface water	Costa Rica	(Spongberg et al., 2011)
	14.6	Surface water	China	(Lu et al., 2019)
Oxytetracycline	712 ± 95[a]	Xiao River	China	(Li et al., 2008a)
Doxycycline	73722	Surface water	Costa Rica	(Spongberg et al., 2011)

	32.9	Surface water	China	(He et al., 2018)
		Beta-Blocker		
Metoprolol	240	Isakavagu-Nakkavagu Rivers	India	(Fick et al., 2009)
	7000	Lakes	India	(Fick et al., 2009)
	380	Llobregat river	Spain	(Huerta-Fontela et al., 2011)
	105.5	Pearl River	China	(Yu et al., 2011)
	47.6	Surface water	China	(Lu et al., 2019)
	168	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Atenolol	36	Source waters of Drinking WTPs	United States	(Benotti et al., 2009)
	690±26	Mankyung River	South Korea	(Kim et al., 2009)
	900	Llobregat river	Spain	(Huerta-Fontela et al., 2011)
	26	Onyar River	Spain	(Gros et al., 2012)
	13	Allier River	France	(Celle-Jeanton et al., 2014)
Propanolol	270	Llobregat river	Spain	(Huerta-Fontela et al., 2011)
Sotalol	160	Llobregat river	Spain	(Huerta-Fontela et al., 2011)
		Lipid Regulator		
Gemfibrozil	685	Shijing River	China	(Zhao et al., 2009)
	24	Source waters of Drinking WTPs	United States	(Benotti et al., 2009)
	17036	Surface water	Costa Rica	(Spongberg et al., 2011)
	284	Onyar River	Spain	(Gros et al., 2012)
	3735	Turia River	Spain	(Carmona et al., 2014)
	602	Pamvotis Lake and Kalamas River	Greece	(Nannou et al., 2015)
	552	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
	9.8	Surface water	China	(Lu et al., 2019)
		Antiepileptic		
Carbamazepine	61	Han River, Nakdong River and Youngsan River	South Korea	(Kim et al., 2007)
	36	Han River	South Korea	(Choi et al., 2008)
	51	Source waters of Drinking WTPs	United States	(Benotti et al., 2009)
	595±14	Mankyung River	South Korea	(Kim et al., 2009)
	66	Danube River	Germany	(Loos et al., 2010a)
	945	Danube River Tributaries - Arges, Timok,	Romania, Bulgaria, and Serbia	(Loos et al., 2010a)

		Rusenski Lom and Velika Morava		
	94.1	Pearl River	China	(Yu et al., 2011)
	82	Surface water	Costa Rica	(Spongberg et al., 2011)
	41	Onyar River	Spain	(Gros et al., 2012)
	63.36	Llobregat River	Spain	(Osorio et al., 2012)
	38	Lyngbygaards River	Denmark	(Matamoros et al., 2012)
	62	Lake Geneva	Switzerland	(Chèvre, 2014)
	5.8	Allier River	France	(Celle-Jeanton et al., 2014)
	406	Pamvotis Lake and Kalamas River	Greece	(Nannou et al., 2015)
	214	Lis River	Portugal	(Paíga et al., 2016)
	6.4	Dongting Lake	China	(Ma et al., 2016)
	2	Surface water	United States	(McEachran et al., 2016)
	17.7	Surface water	China	(Lu et al., 2019)
	342	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Gabapentin	11200	South Platte River and its tributaries	United States	(Bai et al., 2018)
	67	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Lamotrigine	530	Fyris River	Sweden	(Gago-Ferrero et al., 2017)
Phenytoin	29	Source waters of Drinking WTPs	United States	(Benotti et al., 2009)
Antidepressant				
Citalopram	76000	Isakavagu-Nakkavagu Rivers	India	(Fick et al., 2009)
	8000	Lakes	India	(Fick et al., 2009)
Desvenlafaxine	260	Fyris River	Sweden	(Gago-Ferrero et al., 2017)
Fluoxetine	40.2	Dongting Lake	China	(Ma et al., 2016)
Antihistamine				
Cetrizine	530000	Isakavagu-Nakkavagu Rivers	India	(Fick et al., 2009)
	1200000	Lakes	India	(Fick et al., 2009)
Stimulant				
Caffeine	194	Han River, Nakdong River and Youngsan River	South Korea	(Kim et al., 2007)
	373	Han River	South Korea	(Choi et al., 2008)
	1467	Danube River	Germany	(Loos et al., 2010a)
	6798	Danube River Tributaries - Arges, Timok,	Romania, Bulgaria, and Serbia	(Loos et al., 2010a)

		Rusenski Lom and Velika Morava		
	1121446	Surface water	Costa Rica	(Spongberg et al., 2011)
	382	Lyngbygaards River	Denmark	(Matamoros et al., 2012)
	356	Beijiang River	China	(Yang et al., 2013)
	454	Zhujiang River	China	(Yang et al., 2013)
	865	Shijing River	China	(Yang et al., 2013)
	81	Allier River	France	(Celle-Jeanton et al., 2014)
	3508	Pamvotis Lake and Kalamas River	Greece	(Nannou et al., 2015)
	18828	Surface water	Brazil	(Machado et al., 2016)
	174.4	Dongting Lake	China	(Ma et al., 2016)
	7	Surface water	United States	(McEachran et al., 2016)
	340	Fyris River	Sweden	(Gago-Ferrero et al., 2017)
	26.3	Surface water	China	(He et al., 2018)
	4500	Susquehanna River	United States	(Kibuye et al., 2019a)
	1080	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Estrogen				
17β-estradiol	4.8	Pearl River	China	(Yu et al., 2011)
Diuretic				
Hydrochlorothiazide	1900	Llobregat river	Spain	(Huerta-Fontela et al., 2011)
	220	Fyris River	Sweden	(Gago-Ferrero et al., 2017)
Antagonist				
Valsartan	1300	Llobregat river	Spain	(Huerta-Fontela et al., 2011)
	734	Onyar River	Spain	(Gros et al., 2012)
	230	Fyris River	Sweden	(Gago-Ferrero et al., 2017)
	3330	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Losartan	620	Llobregat river	Spain	(Huerta-Fontela et al., 2011)
Irbesartan	830	Llobregat river	Spain	(Huerta-Fontela et al., 2011)
Cimetidine	1338	Han River	South Korea	(Choi et al., 2008)
Muscle Relaxant				
Carisoprodol	87	Lake Geneva	Switzerland	(Chèvre, 2014)
Antifungal				
Clotrimazole	618	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)

Antiviral				
Lamivudine	5428	Nairobi River Basin	Kenya	(Ngumba et al., 2016)
Acyclovir	190	Erlenbach (tributary)	Germany	(Prasse et al., 2010)
Zidovudine	170	Bieber river	Germany	(Prasse et al., 2010)
	7684	Nairobi River Basin	Kenya	(Ngumba et al., 2016)
Biguanide				
Metformin	370	Lake Geneva	Switzerland	(Chèvre, 2014)
	7130	South Platte River and its tributaries	United States	(Bai et al., 2018)
	1760	Rivers, Canals, and Lagoons	Nigeria	(Ebele et al., 2020)
Tranquilizer				
Meprobamate	73	Source waters of drinking water treatment plants	United States	(Benotti et al., 2009)
Metabolite/Degradation Product				
Penilloic Acid (Penicillin G degradation product)	10540000	Wang yang River	China	(Li et al., 2008b)
10,11-Epoxy carbamazepine (Carbamazepine metabolite)	105	Onyar River	Spain	(Gros et al., 2012)
	46	Allier River	France	(Celle-Jeanton et al., 2014)
Clofibric acid (Clofibrate metabolite)	35	Rivers of Spain, Belgium, Germany and Sloveniain	Europe	(Hernando et al., 2006)
	18.3	Zhujiang River	China	(Zhao et al., 2009)

[a] Maximum concentration in μgL^{-1}

2.3.3 Occurrence of PPCPs in groundwater environment

PPCPs can enter groundwater environments through various anthropogenic sources and pathways, resulting in their concentrations ranging from a few μgL^{-1} to a few ngL^{-1}. Wastewater and contaminated surface water, solid landfill waste, livestock breeding, septic systems/onsite wastewater treatment systems, and sewer leakage are the different sources of pharmaceutical contamination in groundwater through soil (Sui et al., 2015). The fate of PPCPs during their movement through the soil to the groundwater is governed mainly by the three primary processes, which include adsorption, degradation, and migration (Sui et al., 2015).

In the USA, Kibuye et al. (2019a) reported high concentrations (μgL^{-1}) of several PPCPs in private groundwater sources (wells and springs) in Central Pennsylvania. Caffeine, Ofloxacin, and Sulfamethoxazole were observed in the highest concentrations of 13.1 μgL^{-1}, 122.7 μgL^{-1} and 32 μgL^{-1}, respectively (Kibuye et al., 2019a). Higher concentrations in μgL^{-1} for PPCPs were also observed in groundwater wells in villages near Hyderabad, India (Fick et al., 2009). Cetrizine and ciprofloxacin were the PPCPs detected in very high concentrations with maximum concentration values of 28 μgL^{-1} and 14 μgL^{-1}, respectively. Similarly, a research study by Tran et al. (2014) reported the highest concentration of 16.25 μgL^{-1} for caffeine in monitoring wells in an urban catchment area, Singapore and Jindal et al. (2015) reported the highest concentration of 48.1 $ngmL^{-1}$ for diclofenac in bore wells/tube wells of villages in Punjab, India.

Diclofenac (NSAID), Ibuprofen (NSAID), Sulfamethoxazole (sulfonamide antibiotic), Carbamazepine (an antiepileptic drug), and Caffeine (stimulant) were the most frequently detected pharmaceutical compounds in groundwater worldwide. Diclofenac was reported in the highest concentrations of 477 ngL^{-1} in monitoring wells (Llobregat deep aquifer) in Spain (Teijon et al., 2010), 380 ngL^{-1} in pumping wells and observation piezometers in Spain (López-Serna et al., 2013), 2770 ngL^{-1} in monitoring wells from landfills in Poland (Kapelewska et al., 2018), and 518 ngL^{-1} in boreholes, wells and springs in Cameroon (Branchet et al., 2019). Studies by Barnes et al. (2008) in the USA, López-Serna et al. (2013) in Spain, Lin et al. (2015) in Taiwan, and Ebele et al. (2020) in Nigeria detected maximum concentrations of ibuprofen as 3110 ngL^{-1} in wells, springs and sumps, 988 ngL^{-1} in pumping wells and observation piezometers, 836.7 ngL^{-1} in shallow wells and 2250 ngL^{-1} in wells and boreholes respectively.

Sulfamethoxazole and carbamazepine were observed in groundwater at concentrations ranging from ngL^{-1} to low μgL^{-1} by previous literature. Some of the highest reported concentrations for sulfamethoxazole were 1.11 μgL^{-1} in wells, springs, and sumps in the USA (Barnes et al., 2008), 1.82 μgL^{-1} in shallow wells in Taiwan (Lin et al., 2015) and 1.28 μgL^{-1} in boreholes, wells, and springs in Cameroon (Branchet et al., 2019) whereas for carbamazepine were 3.6 μgL^{-1} in groundwater sources in the United Kingdom (Stuart et al., 2011) and 1 μgL^{-1} in wells in USA (Elliott et al., 2018). Similar to surface water, caffeine was also one of the predominantly found pharmaceuticals in groundwater across the world. In addition to higher concentrations reported in the groundwater of Singapore (Tran et al., 2014) and the USA (Kibuye et al., 2019a) (mentioned above), other highest reported concentrations for caffeine

were 930.7 ngL^{-1} in shallow wells in Taiwan (Lin et al., 2015) and 677 ngL^{-1} in wells and springs in the USA (Bexfield et al., 2019).

Worldwide, traces of these compounds have been found in the last one and half decades and the data is presented in Table **2.3**, which shows that no geographical zone of this planet is unaffected by the contamination of PPCPs in their groundwater. The highest measured concentrations (above one ngL^{-1}) of various PPCPs in groundwater are listed in Table **2.3.**

Table 2.3. Maximum concentrations of various PPCPs measured worldwide in groundwater.

PPCP	Max. Conc. (ngL^{-1})	Groundwater source	Country	Reference
		Analgesic/Antipyretic/NSAID		
Acetaminophen	380	Wells, springs, and sumps	United States	(Barnes et al., 2008)
	1890	Wells	United States	(Fram & Belitz, 2011)
	9	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	1036	Shallow wells	Taiwan	(Lin et al., 2015)
	2200	Private wells and springs	United States	(Kibuye et al., 2019a)
	17	Wells and Springs	United States	(Bexfield et al., 2019)
	111	Boreholes, wells, and springs	Cameroon	(Branchet et al., 2019)
	188	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Diclofenac	31.7	Wells	Canada	(Carrara et al., 2008)
	24	Groundwater monitoring stations	Europe	(Loos et al., 2010b)
	15.4	Karst Springs	Germany	(Einsiedl et al., 2010)
	477	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	55	Monitoring wells and Piezometers	Spain	(Cabeza et al., 2012)
	129	Monitoring wells	Germany	(Wolf et al., 2012)
	380	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	3	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	17	Monitoring wells	Singapore	(Tran et al., 2014)
	48.1[a]	Bore and tube wells	India	(Jindal et al., 2015)
	33.2	Shallow wells	Taiwan	(Lin et al., 2015)
	113.8	Monitoring wells	Taiwan	(Lu et al., 2016)
	18	Wells in the immediate vicinity	Serbia	(Kovačević et al., 2017)

		of Danube, Sava, Velika Morava, and Tisa Rivers		
	2770	Monitoring wells from landfills	Poland	(Kapelewska et al., 2018)
	>5	Private wells	China	(Yang et al., 2018)
	518	Boreholes, wells, and springs	Cameroon	(Branchet et al., 2019)
	42	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
	1390000	Borewells	India	(Velpandian et al., 2018)
Ibuprofen	3110	Wells, springs and sumps	United States	(Barnes et al., 2008)
	395	Groundwater monitoring stations	Europe	(Loos et al., 2010b)
	185	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	290	Groundwater	United Kingdom	(Stuart et al., 2011)
	104	Monitoring wells	Germany	(Wolf et al., 2012)
	988	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	57.9	Wells	China	(Peng et al., 2014)
	65	Springs and wells	Jordan	(Zemann et al., 2015)
	836.7	Shallow wells	Taiwan	(Lin et al., 2015)
	25.5	Monitoring wells	Taiwan	(Lu et al., 2016)
	2	Groundwater wells	United States	(McEachran et al., 2016)
	>10	Private wells	China	(Yang et al., 2018)
	276	Boreholes, wells, and springs	Cameroon	(Branchet et al., 2019)
	49.4	Hand pumps along Ganges River	India	(Sharma et al., 2019)
	2250	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Naproxen	98390	Wells	United States	(Kibuye et al., 2019b)
	263	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	12	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	5.59	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	86.9	Wells	China	(Peng et al., 2014)
	128	Shallow wells	Taiwan	(Lin et al., 2015)
	12	Groundwater wells	United States	(McEachran et al., 2016)
	17	Wells and Boreholes	Nigeria	(Ebele et al., 2020)

Ketprofen	8	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	290	Monitoring wells	Taiwan	(Lu et al., 2016)
	23.4	Hand pumps along Ganges River	India	(Sharma et al., 2019)
Codeine	348.3	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	214	Wells	United States	(Fram & Belitz, 2011)
	2440	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Salicylic acid	29	Wells	Canada	(Carrara et al., 2008)
	9.3	Monitoring wells and Piezometers	Spain	(Cabeza et al., 2012)
	620	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	1994	Monitoring wells	Singapore	(Tran et al., 2014)
	2015	Wells	China	(Peng et al., 2014)
	2.5	Private wells	Serbia	(Petrović et al., 2014)
Meclofenamic acid	43	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Tramadol	186	Wells	United States	(Elliott et al., 2018)
	883	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Antibiotic				
Ciprofloxacin	14000	Wells	India	(Fick et al., 2009)
	770	Wells	India	(Rutgersson et al., 2014)
Erythromycin	54.8	Shallow wells	Taiwan	(Lin et al., 2015)
	>10	Private wells	China	(Yang et al., 2018)
Lincomycin	320	Wells, springs, and sumps	United States	(Barnes et al., 2008)
Sulfamethoxazole	1110	Wells, springs, and sumps	United States	(Barnes et al., 2008)
	48	Groundwater	Switzerland	(Federal Office for the Environment (FOEN), 2009)
	38	Groundwater monitoring stations	Europe	(Loos et al., 2010b)
	117	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	170	Wells	United States	(Fram & Belitz, 2011)
	46	Monitoring wells and Piezometers	Spain	(Cabeza et al., 2012)
	65	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	17	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	124.5	Wells	China	(Peng et al., 2014)

	113	Public wells	United States	(Schaider et al., 2014)
	1820	Shallow wells	Taiwan	(Lin et al., 2015)
	21	Groundwater wells	United States	(McEachran et al., 2016)
	>10	Private wells	China	(Yang et al., 2018)
	965	Wells	United States	(Elliott et al., 2018)
	32000	Private wells and springs	United States	(Kibuye et al., 2019a)
	120	Wells and Springs	United States	(Bexfield et al., 2019)
	1285	Boreholes, wells, and springs	Cameroon	(Branchet et al., 2019)
	64	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Sulfamethazine	360	Wells, springs, and sumps	United States	(Barnes et al., 2008)
	446	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	83.9	Monitoring wells and Piezometers	Spain	(Cabeza et al., 2012)
	29.2	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	1.2	Boreholes	China	(Tong et al., 2014)
	28.9	Shallow wells	Taiwan	(Lin et al., 2015)
Trimethoprim	55	Wells	India	(Fick et al., 2009)
	18	Wells	United States	(Fram & Belitz, 2011)
	3	Monitoring wells and Piezometers	Spain	(Cabeza et al., 2012)
	3	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	9.41	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	5.2	Boreholes	China	(Tong et al., 2014)
	10.5	Wells	China	(Peng et al., 2014)
	17.8	Shallow wells	Taiwan	(Lin et al., 2015)
	2	Groundwater wells	United States	(McEachran et al., 2016)
	3200	Private wells and springs	United States	(Kibuye et al., 2019a)
	14.9	Wells and Springs	United States	(Bexfield et al., 2019)
Amoxicillin	6490	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Ampicillin	700	Private wells and springs	United States	(Kibuye et al., 2019a)
Ofloxacin	480	Wells	India	(Fick et al., 2009)
	48	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)

	367	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	7.6	Boreholes	China	(Tong et al., 2014)
	44.2	Wells	China	(Peng et al., 2014)
	9.4	Wells	India	(Rutgersson et al., 2014)
	11.8	Shallow wells	Taiwan	(Lin et al., 2015)
	114940	Wells	United States	(Kibuye et al., 2019b)
	122700	Private wells and springs	United States	(Kibuye et al., 2019a)
Enoxacin	1900	Wells	India	(Fick et al., 2009)
Norfloxacin	31	Wells	India	(Fick et al., 2009)
	2	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	462	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	47.1	Boreholes	China	(Tong et al., 2014)
	145	Wells	India	(Rutgersson et al., 2014)
	9.3	Shallow wells	Taiwan	(Lin et al., 2015)
Azithromycin	10	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	1620	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	68	Observation wells near Danube River and tributaries	Serbia	(Radović et al., 2015)
Beta-Blocker				
Metoprolol	90	Wells	India	(Fick et al., 2009)
	9	Karst Springs and Swallow hole	Switzerland	(Morasch, 2013)
	355	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	14	Wells in the immediate vicinity of Danube, Sava, Velika Morava, and Tisa Rivers	Serbia	(Kovačević et al., 2017)
	54	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Atenolol	106	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	3.6	Shallow wells	Taiwan	(Lin et al., 2015)
	8.7	Wells and Springs	United States	(Bexfield et al., 2019)
Propanolol	9.38	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	4.5	Private wells	Serbia	(Petrović et al., 2014)

		Lipid Regulator		
Gemfibrozil	574	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	23	Monitoring wells	Germany	(Wolf et al., 2012)
	751	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	17	Monitoring wells	Singapore	(Tran et al., 2014)
	1.2	Public wells	United States	(Schaider et al., 2014)
	172.3	Shallow wells	Taiwan	(Lin et al., 2015)
	730	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Bezafibrate	4.22	Monitoring wells and Piezometers	Spain	(Cabeza et al., 2012)
	19	Monitoring wells	Germany	(Wolf et al., 2012)
	25.8	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
		Antiepileptic		
Carbamazepine	45	Groundwater	Switzerland	(Federal Office for the Environment (FOEN), 2009)
	390	Groundwater monitoring stations	Europe	(Loos et al., 2010b)
	118	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	420	Wells	United States	(Fram & Belitz, 2011)
	3600	Groundwater	United Kingdom	(Stuart et al., 2011)
	62.4	Monitoring wells and Piezometers	Spain	(Cabeza et al., 2012)
	35	Monitoring wells	Germany	(Wolf et al., 2012)
	9.3	Monitoring wells	Singapore	(Tran et al., 2014)
	41	Observation wells near Danube River and tributaries	Serbia	(Radović et al., 2015)
	72	Public wells	United States	(Schaider et al., 2014)
	100	Springs and wells	Jordan	(Zemann et al., 2015)
	37.9	Shallow wells	Taiwan	(Lin et al., 2015)
	27	Monitoring wells	Taiwan	(Lu et al., 2016)
	11	Groundwater wells	United States	(McEachran et al., 2016)
	890	Wells	Czech Republic	(Rozman et al., 2017)
	57	Wells in the immediate vicinity of Danube, Sava, Velika Morava, and Tisa Rivers	Serbia	(Kovačević et al., 2017)
	>10	Private wells	China	(Yang et al., 2018)

	1000	Wells	United States	(Elliott et al., 2018)
	162	Wells and Springs	United States	(Bexfield et al., 2019)
	335	Boreholes, wells, and springs	Cameroon	(Branchet et al., 2019)
	27.2	Hand pumps along Ganges River	India	(Sharma et al., 2019)
	50	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Gabapentin	41	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Phenytoin	66	Public wells	United States	(Schaider et al., 2014)
	115	Wells	United States	(Elliott et al., 2018)
Antidepressant				
Citalopram	1400	Wells	India	(Fick et al., 2009)
	7.4	Wells and Springs	United States	(Bexfield et al., 2019)
Venlafaxine	134	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
Antihistamine				
Cetrizine	28000	Wells	India	(Fick et al., 2009)
Stimulant				
Caffeine	130	Wells, springs, and sumps	United States	(Barnes et al., 2008)
	189	Groundwater monitoring stations	Europe	(Loos et al., 2010b)
	290	Wells	United States	(Fram & Belitz, 2011)
	55.5	Monitoring wells and Piezometers	Spain	(Cabeza et al., 2012)
	16249	Monitoring wells	Singapore	(Tran et al., 2014)
	930.7	Shallow wells	Taiwan	(Lin et al., 2015)
	75	Monitoring wells	Taiwan	(Lu et al., 2016)
	25	Groundwater wells	United States	(McEachran et al., 2016)
	>10	Private wells	China	(Yang et al., 2018)
	50	Wells	United States	(Elliott et al., 2018)
	13100	Private wells and springs	United States	(Kibuye et al., 2019a)
	677	Wells and Springs	United States	(Bexfield et al., 2019)
	262	Hand pumps along Ganges River	India	(Sharma et al., 2019)
	166	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Amphetamine	68.3	Monitoring wells	Taiwan	(Lu et al., 2016)
Estrogen				
17α-Ethynylestradiol	1822.2	Shallow wells	Taiwan	(Lin et al., 2015)
Antagonist				
Valsartan	84	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Cimetidine	23.6	Wells and Springs	United States	(Bexfield et al., 2019)

Antifungal				
Clotrimazole	191	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Terbinafine	1800	Wells	India	(Fick et al., 2009)
Antiviral				
Acyclovir	5.7	Wells and Springs	United States	(Bexfield et al., 2019)
Biguanide				
Metformin	206	Wells	United States	(Elliott et al., 2018)
	38.7	Wells and Springs	United States	(Bexfield et al., 2019)
	349	Wells and Boreholes	Nigeria	(Ebele et al., 2020)
Tranquilizer				
Flunitrazepam	196	Monitoring wells	Taiwan	(Lu et al., 2016)
Metabolite				
Para-xanthine (Caffeine)	57	Wells, springs, and sumps	United States	(Barnes et al., 2008)
	120	Wells	United States	(Fram & Belitz, 2011)
	416	Wells and Springs	United States	(Bexfield et al., 2019)
N-formyl-4-amino-antipyrine (Metamizole)	275	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	150	Wells in the immediate vicinity of Danube, Sava, Velika Morava, and Tisa Rivers	Serbia	(Kovačević et al., 2017)
N-acetyl-4-amino-antipyrine (Metamizole)	362	Monitoring wells (Llobregat deep aquifer)	Spain	(Teijon et al., 2010)
	128	Wells in the immediate vicinity of Danube, Sava, Velika Morava, and Tisa Rivers	Serbia	(Kovačević et al., 2017)
Clofibric acid (Clofibrate)	1350	Monitoring wells	Germany	(Wolf et al., 2012)
	7.57	Pumping wells and observation piezometers	Spain	(López-Serna et al., 2013)
	18	Monitoring wells	Singapore	(Tran et al., 2014)
	73.9	Wells	China	(Peng et al., 2014)

[a] Maximum concentration in ngmL^{-1}

Furthermore, it is vital to understand the global distribution and occurrence of different therapeutic classes in groundwater. Henceforth, the maximum values of concentrations of PPCPs tabulated above for groundwater contamination worldwide are represented in the form

of box-plot in Figure **2.2**. The purpose of the box plot is to show the range/spectrum of maximum concentrations of these PPCPs of all the therapeutic classes reported in the literature. The concentration of those compounds showing abnormally high values with respect to others within their therapeutic class are presented as outlier points in the plot. As maximum concentrations for naproxen (NSAID) and ofloxacin (antibiotic) stand at 98390 ngL^{-1} (Kibuye et al., 2019b) and 122700 ngL^{-1} (Kibuye et al., 2019a) respectively in groundwater of United States, which represents anomalous values which are rare to be seen in other parts of the world. However, a very abnormal and high concentration has been detected for diclofenac (NSAID) in the aquifers of India, which peaked up to 1390000 ngL^{-1} due to the presence of a landfill site nearby to the groundwater sampling site (Velpandian et al., 2018).
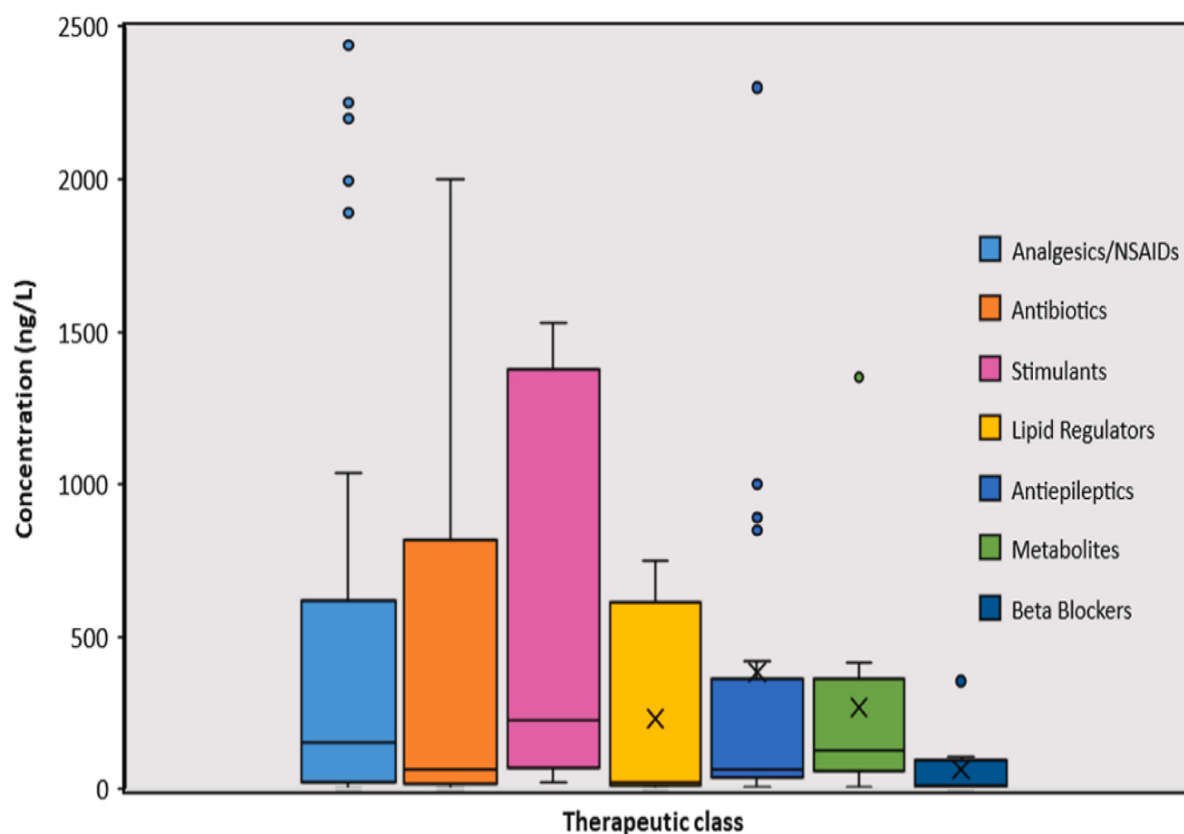
Figure 2.2. Box-plot of various PPCPs therapeutic classes with their maximum concentrations. Highest concentration for diclofenac (13,90,000 ngL^{-1}) of analgesics/NSAIDs class is not shown as an outlier in the boxplot as it is an extreme point, hard to display effectively in the plot.

In addition, graphical comparisons (Figure **2.3**) have been made among developed and developing countries based on the maximum concentration of these pharmaceutical compounds found in their groundwater. This graph will help to set an understanding about a country using or discharging various therapeutic class drugs. Another depiction of the occurrence of PPCPs

in groundwater is represented in Figure **2.4** highlighting the range of the contaminants in the above included six developed and developing countries. The given figure demonstrates the minimum and maximum range of all the six therapeutic classes included along with the mention of sites where these classes were detected. It can be postulated that Spain and Switzerland displayed a diminutive level of concentration of all the therapeutic classes taken into consideration except for stimulants in Spain. On the other side, United States groundwater was severely infested with analgesics and antibiotics ranging from (0-98390 ngL^{-1}) and (0-122700 ngL^{-1}) respectively. The scenario of Indian groundwater shows a heavy prevalence of analgesics and antibiotics in its groundwater which could range from as low as 150 and 10 ngL^{-1} and could spike up to 1390000 and 14000 ngL^{-1}, respectively. For Nigeria, its wells and boreholes were infested with antibiotics (<1-6490 ngL^{-1}) while Taiwanese groundwater showed moderate presence of every therapeutic class.
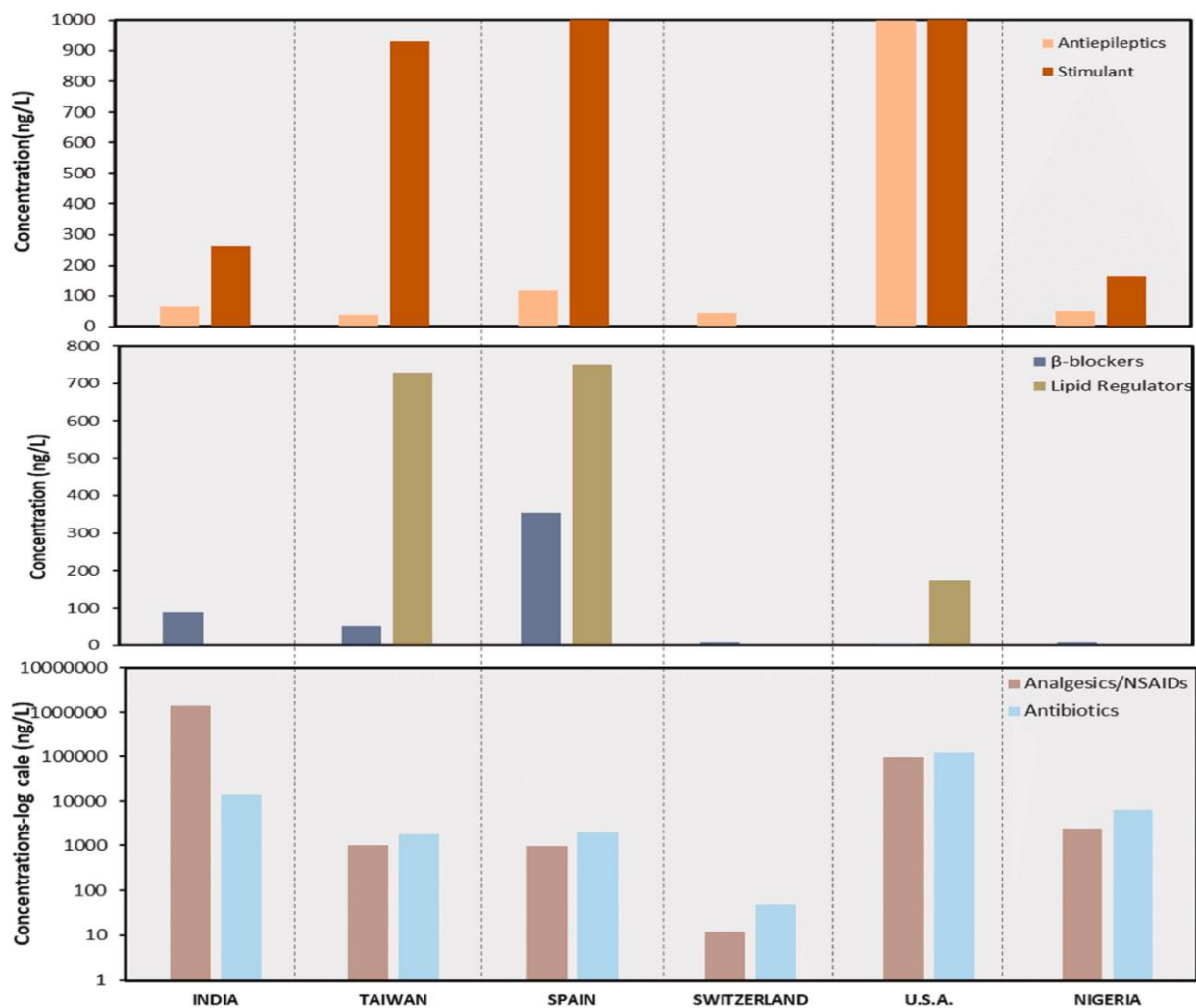
Figure 2.3. Graphs comparing PPCPs in ngL^{-1}, therapeutic classes (antiepileptics and stimulants), (β-blockers and lipid regulators) in ngL$^{-1,}$ and therapeutic classes (analgesics/NSAIDs and antibiotics) in ngL^{-1} in logarithmic scale.

Class	USA Range	USA Source	SPAIN Range	SPAIN Source	NIGERIA Range	NIGERIA Sources	SWITZERLAND Range	SWITZERLAND Sources	INDIA Range	INDIA Sources	TAIWAN Range	TAIWAN Sources
AG	0-98390	Wells	29.5-988	Wells & piezometers	<1-2440	Wells & boreholes	1-12	Springs & swallow hole	150-1390000	Borewells	0.9-1036	Shallow wells
AB	0-122700	Wells & springs	0.869-2000	Natural springs, Wells & piezometers	<1-6490	Wells & boreholes	0.3-48	Ground water	<10-140000	Wells	0.2-1820	Shallow wells
β-B	8.7*	Wells	18-355	Monitoring wells & piezometers	<1-54	Wells & boreholes	229	Springs & swallow hole	90*	Wells	3.6*	Shallow wells
AP	0-1000	Wells	2-118	Monitoring wells	<1-54	Wells & boreholes	45*	Ground water	<MDL-67	Public wells	<0.4-37.9	Shallow wells
LR	<5-1.2	Public wells	4.34-751	Wells & piezometers	<4-730	Wells & boreholes	-	-	-	-	0.1-172.3	Shallow wells
ST	6-141150	Wells	10-14770	Ground water	<4-166	Wells & boreholes	-	-	15-262	Hand pumps-pumps	1.2-930.7	Shallow wells

Figure 2.4. Range of PPCPs contamination of all the therapeutic classes (analgesics, antiepileptics, β-blockers, antibiotics, lipid regulators, and stimulants) in United States, Spain, Switzerland, Nigeria, India, and Taiwan. The information provided follows this sequence: Therapeutic class-(range) – maximum contamination detected site. (*)- Only maximum concentration of the given therapeutic class. AG, AB, β-B, AP. LR, ST stands for Analgesics, Antibiotics, β-blockers, Antiepileptics, Lipid regulators, and Stimulant classes, respectively.

CHAPTER 3: METHODOLOGY

This chapter provides an overview of the study area and presents a comprehensive description of the methodology employed in this thesis. The sampling, analysis strategies and statistical tools/approaches utilized for the investigation purposes have been thoroughly elucidated in this section.

3.1 Study Area

Dehradun serves as the capital and most populous city of the state of Uttarakhand, India, and is situated in the valley at the foothills of the Himalayas. Dehradun is located between latitudes 30°01' N and 31°02' N and longitudes 77°34' E and 78°18' E. The average elevation of the city is 450 m (1,480 ft) above sea level. The city has a diverse landscape comprising the Terai and Bhabar forests, alongside the Shivalik hills and the Lower Himalayan Range. It is nestled between the Himalayas on its northern side, the Rajaji Range of the Shivalik Hills on its southern side, the Song River, a tributary of the Ganga, on its eastern side, and the Asan River, a tributary of the Yamuna, on its western side, Notable hill stations like Mussoorie and Chakrata are nestled nearby to this city. Dehradun is one of the districts in the state of Uttarakhand, comprising six tehsils namely Dehradun, Rishikesh, Chakrata, Kalsi, Vikasnagar, and Tiuni. According to the 2011 census, the population of the city was reported to be 5,78,420 and the current estimated population in 2023 is 7,84,000.

The Dehradun city experiences a humid subtropical climate, which undergoes significant variations ranging from tropical to severe cold depending on the altitude of the area. In summers, moderate heat is experienced in the city, but for a few days the heat can be intense, with temperatures soaring up to 44 °C. Winters, on the other hand, experience temperatures dropping below freezing point, usually ranging between 1 and 20 °C. The region receives an average annual precipitation of 2,073 mm with the majority of it occurring during the months from June to September, with July and August being the rainiest. The monsoon season often brings heavy and prolonged rainfall in the area.

Wastewater sampling was done from March 2022 to August 2022 on a monthly frequency at the selected WWTPs in Dehradun city. Seasonal sampling covers the wastewater samples from

spring, summer, and monsoon seasons to assess the PPCPs and EDCs seasonal variation. In addition, wastewater samples were collected from three stages of an *in-situ* RZT-based WWTP located in Gandhinagar, Gujarat i.e., influent (point I), root zone treatment effluent (point II), and the main effluent (point III), and screening and removal of PPCPs along the wastewater treatment system equipped with RZT were studied. The location of the study area (Dehradun) and Gandhinagar (RZT plant location) are shown in the geographical map (Figure **3.1**), whereas detailed sampling locations (WWTPs) in Dehradun city and associated information are mentioned in Chapter 4.
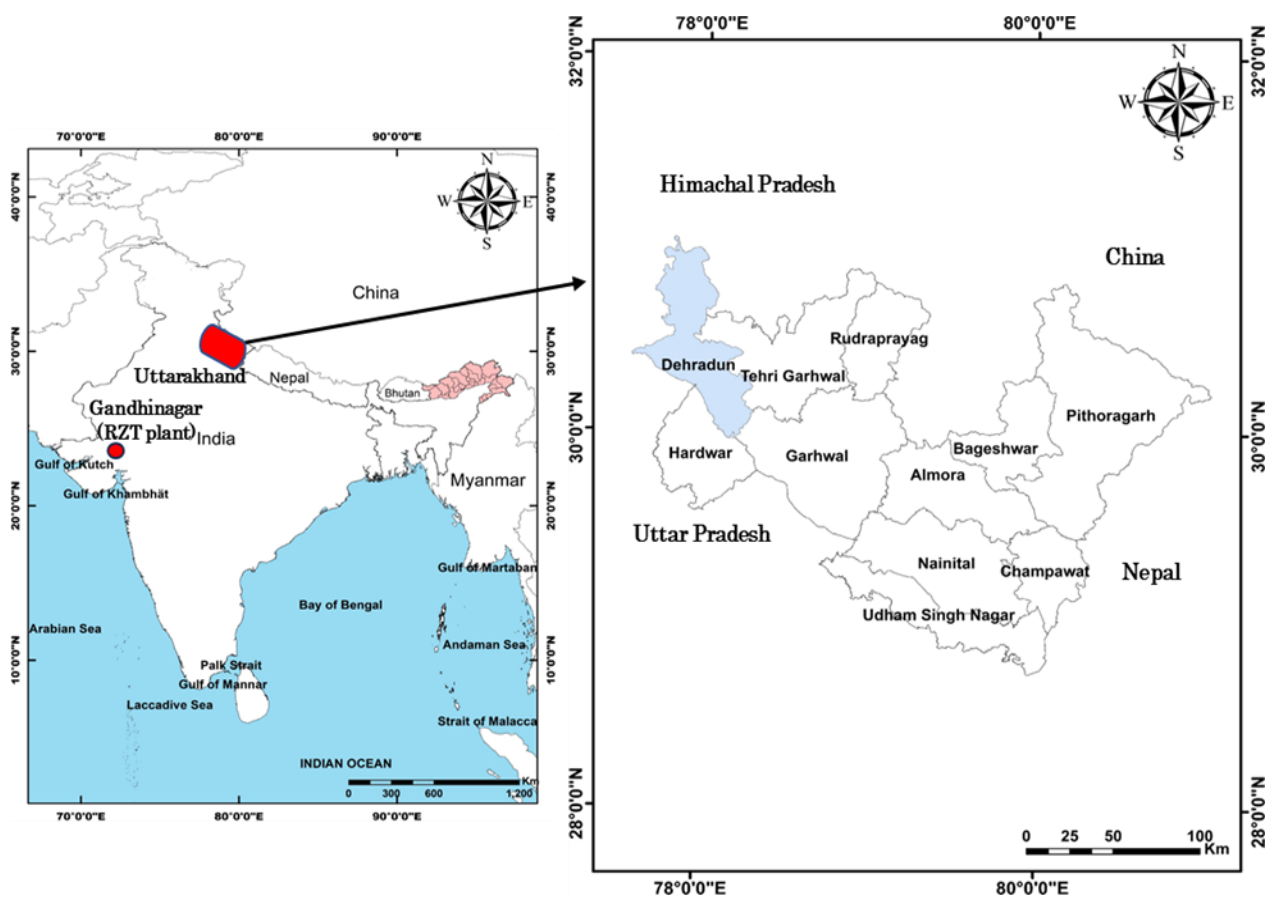
Figure 3.1. Location of the study area in the geographical map.

3.2 Sampling Strategy and Analysis

Wastewater samples were collected in 500 mL or 1 L amber colored glass bottles to protect the degradation of the targeted compounds from UV rays. The samples were kept in an ice box during transportation and brought immediately to the laboratory. Afterward, samples were filtered with 0.45-micron cellulose nitrate membrane filters and acidified by 2% H_2SO_4 to ensure the targeted compounds in the sample were intact prior to the solid phase extraction (SPE). SPE was conducted to load our target analytes into the cartridges. The extracted samples

were filtered with 0.2-micron filters and analysed by High-Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS) for determination of targeted PPCPs and EDCs. All laboratory analyses included duplicates and were carried out on the same day. HPLC-MS analysis results were analysed and PPCPs and EDCs occurrence, seasonal variation, and removal in the studied were reported. Similarly, PPCPs variations and removal were determined at various stages of RZT-based WWTP, eventually reporting the PPCPs removal efficiency of the RZT hybrid system. Statistical approaches were used to substantiate the results. *In-situ* analysis of physicochemical parameters namely pH, electrical conductivity (EC), total dissolved solids (TDS), and were carried out for influent and effluent samples by using the multi-parameter probe (Hanna Instruments, USA). Other general parameters such as total suspended solids (TSS), Biochemical oxygen demand (BOD), and Chemical Oxygen Demand (COD) were analysed as per the guidelines prescribed by APHA-AWWA (APHA, 2012). Nitrate (NO_3^-) was determined by UV–visible spectrophotometry technique.

Biochar production from various waste materials was performed in a small-scale batch-type reactor by the pyrolysis process at a temperature of 500^oC. Subsequently, batch adsorption experiments were conducted in the laboratory to evaluate the PPCPs removal efficiency of prepared biochar. Characterization (pH, crystallographic structure, and surface functional groups) of the prepared biochars was done. The pH, crystallographic structure, and surface functional groups of the prepared biochars were determined through potentiometric, X-Ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR) analyses, respectively. High-Performance Liquid Chromatography (HPLC) analysis was performed on the aliquots collected at different time intervals from batch experiments. HPLC results were analysed, and PPCPs removals by the various waste materials-based biochar (in terms of removal efficiency and adsorption capacity) from aqueous solution were reported.

3.2.1 SPE procedure

An optimized SPE method was used for the extraction of the samples. The SPE methodology was optimized based on the absolute recoveries of the target compounds from five trials. Details of the procedure followed during SPE optimization with their corresponding recoveries were reported by Biswas & Vellanki (2021). The samples were extracted using SPE methodology as reported by Biswas & Vellanki (2021), with few modifications. 6 cc-200 mg Oasis Hydrophilic-Lipophilic Balanced (HLB) cartridges with 12-position Agilent vacuum

SPE manifold were used for the SPE procedure. SPE cartridges were preconditioned with 5 mL methanol followed by 5 mL of LCMS grade water. 200 mL of samples were passed through the cartridges at a flow rate of 4-5 mLmin^{-1}. The cartridges were then rinsed with 5 mL LCMS grade water and dried for 5-10 minutes under vacuum. The analytes were eluted with two consecutive 4 mL elutions using methanol. The eluates were then dried under nitrogen at 40˚C. Crescent Scientific evaporator fitted to high purity nitrogen (>95%) was used for the evaporation process. Finally, the dried eluates were reconstituted with 90:10 v/v water: methanol solution to 1.5 mL final volume.

3.2.2 HPLC-MS analytical methodology

C18 column (Sunfire, 4.6 x 250 mm) was used for chromatographic separation. The column temperature was maintained at 40°C while the sample temperature was kept at 15°C. 10 µL injection volume and a 25-minute gradient method were used. 0.4 mLmin^{-1} constant flow rate was maintained throughout the gradient program. Water with 0.1% formic acid was used as mobile phase A while methanol with 0.1% formic acid was used as mobile phase B. The addition of formic acid promotes ionization resulting in better peak shape and greater sensitivity.

The gradient program started with 90% of mobile A and gradually lowered to 60% at 2 minutes. The flow for mobile phase A was stopped at 5 minutes and held up to 11 minutes. At 21 minutes, the flow was again increased to 100% then reduced to 60% at 22 minutes. At 24 minutes, the initial condition (90% of mobile phase A) was restored which was held up to 25 minutes. All the compounds were analysed at a capillary voltage of 3 kV while the individual cone voltages were fixed based on the direct infusion of standards. Nitrogen gas was used as a nebulizing gas. Quantification of the compound was done in single ion monitoring (SIM) mode.

3.2.3 Quality assurance (QA) and quality control (QC)

As a part of the quality assurance, three injections from each sample were analysed to avoid false positives. Retention time within ±15 seconds was considered for the identification of the target peaks. Field blanks used during all the sampling events were analysed to rule out interferences from the sampling equipments. Method blanks were run during both the calibration and sample analyses. 90:10 (v/v) water and methanol solution similar to the sample

reconstitute was used as method blank to avoid sample contamination from the solvents. Standards were analysed along with all the samples to track any deviation in retention time. Seven-point calibration curves were prepared for the target compounds. The method detection limit (MDL) and method quantification limit (MQL) for the ompounds were selected based on the effectiveness of the HPLC methodology in separating and identifying target peaks by ruling out matrix interferences. Both MDL and MQL were calculated based on Environmental Protection Agency (EPA).

3.2.4 Statistical data treatment

The target analytes (PPCPs and EDCs) data treatment is performed with XLSTAT, R Studio, and MINITAB, and has been tested for the normality distribution, with the help of Anderson-Darling, Jarque-Bera, Lilliefors, and Shapiro-Wilk tests. The data obtained across seasons and WWTPs have been subjected to numerous statistical tests involving hypothesis testing and identification of any significant trends/correlation between and within, the samples (as influents and effluents), their treatment with respect to seasons (Naveen et al., 2017), WWTPs based percentage removal and overall quality assessment. Besides univariate statistics (Mahapatra et al., 2014), Mann-Whitney test, Kolz-Smirnov test have been used for linking trends and measurement of the strengths in relationships. Moreover, for variance analysis and significance testing, One-way ANOVA, Kruskal-Wallis test, Tukey's pair-wise alignment, and Dunn's post hoc tests ($\alpha=0.05$) have been performed (Mahapatra et al, 2013), followed by verification of the standardized residues at 95%. To assess the effectiveness of abundance variations at various stages in RZT-based WWTP, a paired sample t-test was employed between influent and effluent (pre and post treatment) data (at a $p < 0.05$ significance level)
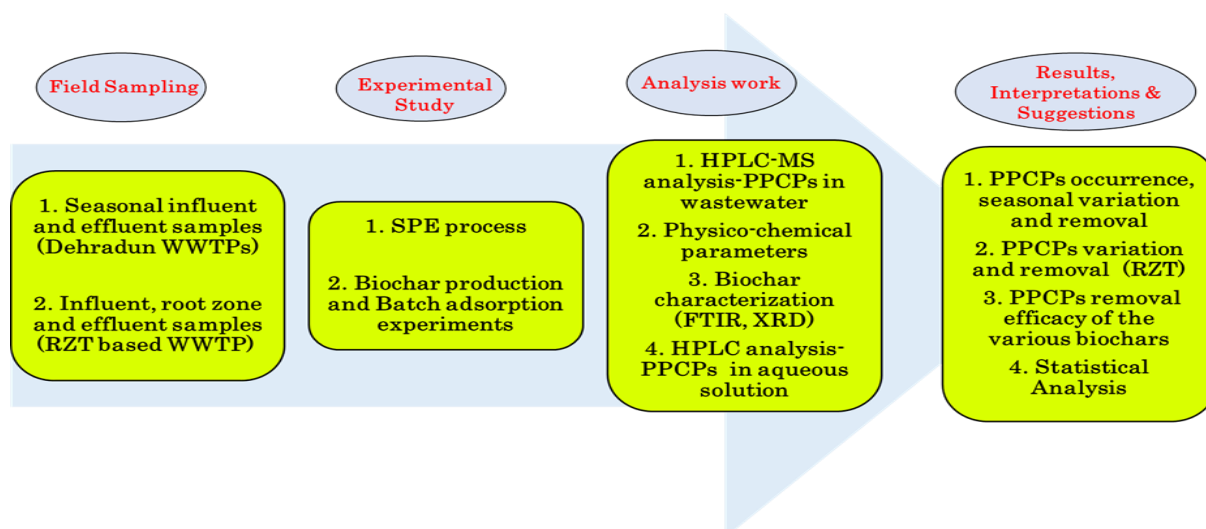
Figure 3.2. Schematic delineating methodology for the current research work.

Table 3.1. Analytical techniques used for the quantification of various parameters in the research work.

	Compounds/Parameters	Techniques/ Instruments used	Instruments specification
PPCPs	• Ciprofloxacin • Sulfamethoxazole • Diclofenac • Ketoprofen • Acetaminophen • Caffeine • Carbamazepine • Triclosan • Estrone	• HPLC-MS (for wastewater) • HPLC (for prepared aqueous solution)	• HPLC-MS instrument at Civil Engineering Department Lab, IIT Roorkee: Waters ACQUITY Liquid Chromatography system coupled to Waters SQ mass detector, C18 column (Sunfire, 4.6 x 250 mm) • HPLC: (LC-2030C 3D PLUS; Shimadzu), C18 column (4.6 x 250 mm, 5 μm)
***In-situ* parameters**	pH, EC, and TDS	Pro-DSS multiparameter probe	• (HI98194; Hanna Instruments, USA) • Range: pH: 0.00 to 14.00 EC: 0 to 200 mScm^{-1} TDS: 0 to 400000 mgL^{-1}
Physicochemical parameters	TSS, BOD, COD, and NO$_3^-$	• TSS- Filtration • BOD and COD- Titration • NO$_3^-$- UV-visible spectrophotometry	• Procedure prescribed by APHA 2012 • UV-VIS Spectrophotometer (UV-1900; Shimadzu), Wavelength range: 190 to 1100 nm
Adsorption-related properties (characterization)	• Surface functional group • Crystallographic structure$^-$	• Fourier-transform infrared spectroscopy (FTIR) • X-Ray Diffraction (XRD)	• FTIR: Fourier transform infrared spectrometer (Frontier FTIR; Perkin Elmer), equipped with deuterated triglycine sulfate (DTGS) detectors with an optional mercury cadmium telluride (MCT) detector (cooled with liquid nitrogen) • XRD: (D8 Advance Eco; Bruker)

In a nutshell, the various analytical techniques employed for the quantification of various parameters during the study are mentioned in Table **3.1**. In addition, the schematic representation for the methodology is depicted above in Figure **3.2**. The methodology has been described briefly in this section, as detailed methodologies (materials and methods) for each objective are explained comprehensively in objective-focused chapters (Chapter 4, Chapter 5, and Chapter 6).

CHAPTER 4: OCCURRENCE, SEASONAL VARIATION, AND REMOVAL OF PPCPs AND EDCs IN THE MUNICIPAL WASTEWATER TREATMENT PLANTS OF DEHRADUN CITY

4.1 Overview

Despite the substantial production and consumption of PPCPs and EDCs in India, there is a scarcity of literature addressing their occurrence, fate, and elimination within wastewater treatment facilities in Indian towns. The demand and supply imbalance for wastewater treatment exacerbates this issue (Anumol et al., 2016; Balakrishna et al., 2017). While a limited body of literature has documented the presence, fate, and removal of these compounds at WWTPs in certain Indian locations, this coverage primarily spans from southern Indian states (Anumol et al., 2016; Prabhasankar et al., 2016; Subedi et al., 2015, 2017) to only a handful of sites in northern Indian states (Mutiyar & Mittal, 2013, 2014; Singh & Suthar, 2021b). Consequently, the available published literature suggests an underexplored aspect, particularly regarding the occurrence and removal patterns of PPCPs/EDCs in WWTPs situated in northern Indian cities, as well as their subsequent fate in the surrounding environment, demanding further attention. Henceforth, a comprehensive investigation is warranted into the extent to which wastewater treatment systems contribute to the loading of PPCPs/EDCs in the environmental system, particularly within major northern urban cities in India. In the same context, this chapter focuses on the occurrence and removal of PPCPs/EDCs in four municipal WWTPs located in the Himalayan foothills. This is the first study of the most populous, major metropolitan, and capital city in the Indian state of Uttarakhand to evaluate the concentration of these compounds in the WWTPs.

The study will primarily focus on the seasonal variation of nine targeted PPCPs and EDCs concentrations along with their removal in the selected WWTPs in Dehradun city. The compounds targeted in the study have been chosen owing to their high consumption, reported low removal in conventional wastewater treatment, and high persistence in the aquatic environment. Results from this study could be helpful in assessing the extent of PPCPs/EDCs contribution to the local environment by these WWTPs and possible environmental threats.

4.2 Materials and Methods

4.2.1 Chemicals and materials

The nine targeted PPCPs and EDCs in this study belong to the seven therapeutic classes, which are mentioned in Table **4.1**. Additionally, Table **4.2** provides the list of the PPCPs and EDCs along with their chemical abstracts service (CAS) numbers and suppliers of the standards. High purity grade standards were used in this study. HPLC grade solvents were used for SPE and HPLC-MS analysis. 6 cc Oasis Hydrophillic-Lipophilic Balanced (HLB) cartridges were used for the SPE procedure. 100 ppm stock solutions of all the target compounds were prepared according to their solubilities. The working standards were prepared in 90:10 (v/v) water and methanol solution.

4.2.2 Study locations (WWTPs)

Wastewater samples collected from four WWTPs are investigated, out of which two of the WWTPs are major municipal WWTPs whereas the other two are the treatment facilities of an academic institution located in Dehradun, Uttarakhand, India. Locations of all the WWTPs selected for the wastewater sampling are represented in Figure **4.1**. WWTP-I (68 MLD capacity) and WWTP-II (20 MLD capacity) are situated in the southern part of the city and work on cyclic activated sludge technology (C-Tech process) and sequencing batch reactor (SBR) treatments, respectively. More importantly, both facilities account for the treatment of around 75% of urban wastewater generated from the city and discharge the treated effluent to the non-perennial streams. WWTP-III and WWTP-IV (0.25 MLD each) are located in the western part of the city, and both are based on aeration and fluidized media oxidation process. WWTP-III and WWTP-IV treat wastewater generated from two different campuses of an academic institution, and the effluent is used for horticulture purposes. The working flow diagram for all the sampled WWTPs is shown in Figure **4.2** along with wastewater sampling points.

Table 4.1. List of the studied PPCPs and EDCs with their respective classes and adverse environmental effects.

Category	Compound	Class	Potential adverse environmental impacts
PPCP	Ciprofloxacin	Antibiotic	Negative effects on surface water and groundwater quality (Ashiq et al., 2019; Li et al., 2018).
	Sulfamethoxazole		Bioaccumulation in aquatic organisms, Persuades antibiotic-resistant genes in

			various organisms (Ahmed et al., 2017; Huang et al., 2020).
	Diclofenac	Nonsteroidal anti-inflammatory drug (NSAID)	Toxic effects on many organisms (Bagheri et al., 2020)
	Ketoprofen		Accretion in agricultural soil (Anfar et al., 2020).
	Acetaminophen	Analgesic	Severe toxicity to the aquatic environment, Led to the development of antibiotic-resistant genes (Grisales-Cifuentes et al., 2021; Luo et al., 2020; Tran et al., 2020).
	Caffeine	Stimulant	Negative impacts on fish, microalgae, and other aquatic lives (Álvarez-Torrellas et al., 2015; Keerthanan et al., 2020).
	Carbamazepine	Anticonvulsant	Toxic effects and bioaccumulation (Naghdi et al., 2019; Vernouillet et al., 2010).
EDC	Estrone	Hormone	Disrupts the endocrine system, Effects include feminization, dysregulation of reproduction in organisms, Aid processes leading to carcinogenesis (Amenyogbe et al., 2020; Bohra & Bhateja, 2015; Henderson & Feigelson, 2000).
	Triclosan (TCS)	Antimicrobial	Disrupts the endocrine system, Induces tumor development (Delgado-Moreno et al., 2021; Dhillon et al., 2015).

Table 4.2. List of the studied analytes with their chemical abstracts service (CAS) numbers and supplier of the standards.

Compounds	CAS Number	M.W. (Da)	Supplier
Ciprofloxacin	85721-33-1	331.13	Sigma-Aldrich
Sulfamethoxazole	723-46-6	253.05	Sigma-Aldrich
Diclofenac	15307-86-5	295.01	Sigma-Aldrich
Ketoprofen	22071-15-4	254.09	TCI Chemicals
Acetaminophen	103-90-2	151.06	Sigma-Aldrich
Caffeine	58-08-2	194.08	Sigma-Aldrich
Carbamazepine	298-46-4	236.09	TCI Chemicals
Estrone	53-16-7	270.16	TRC, Canada
Triclosan	3380-34-5	287.95	Sigma-Aldrich
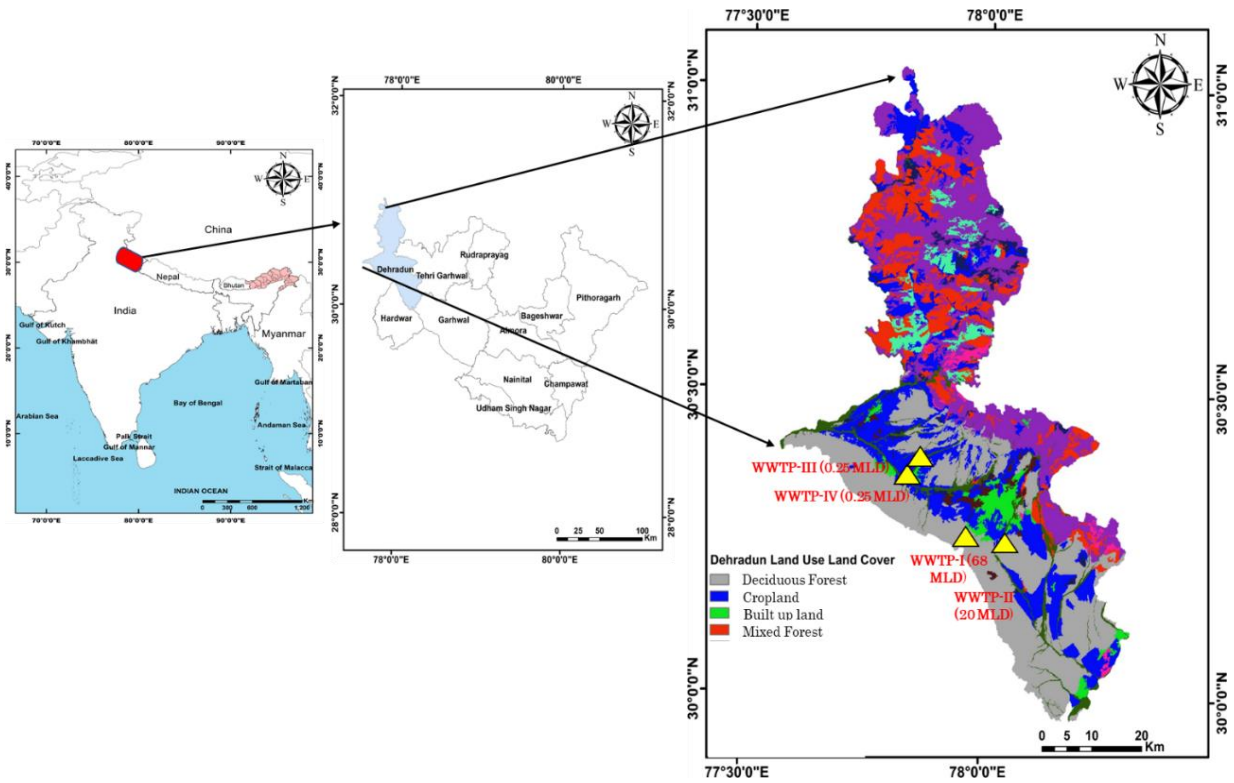
Figure 4.1. Location map of the various studied sites. Yellow triangular dots indicate the location of each of the sampling WWTP.
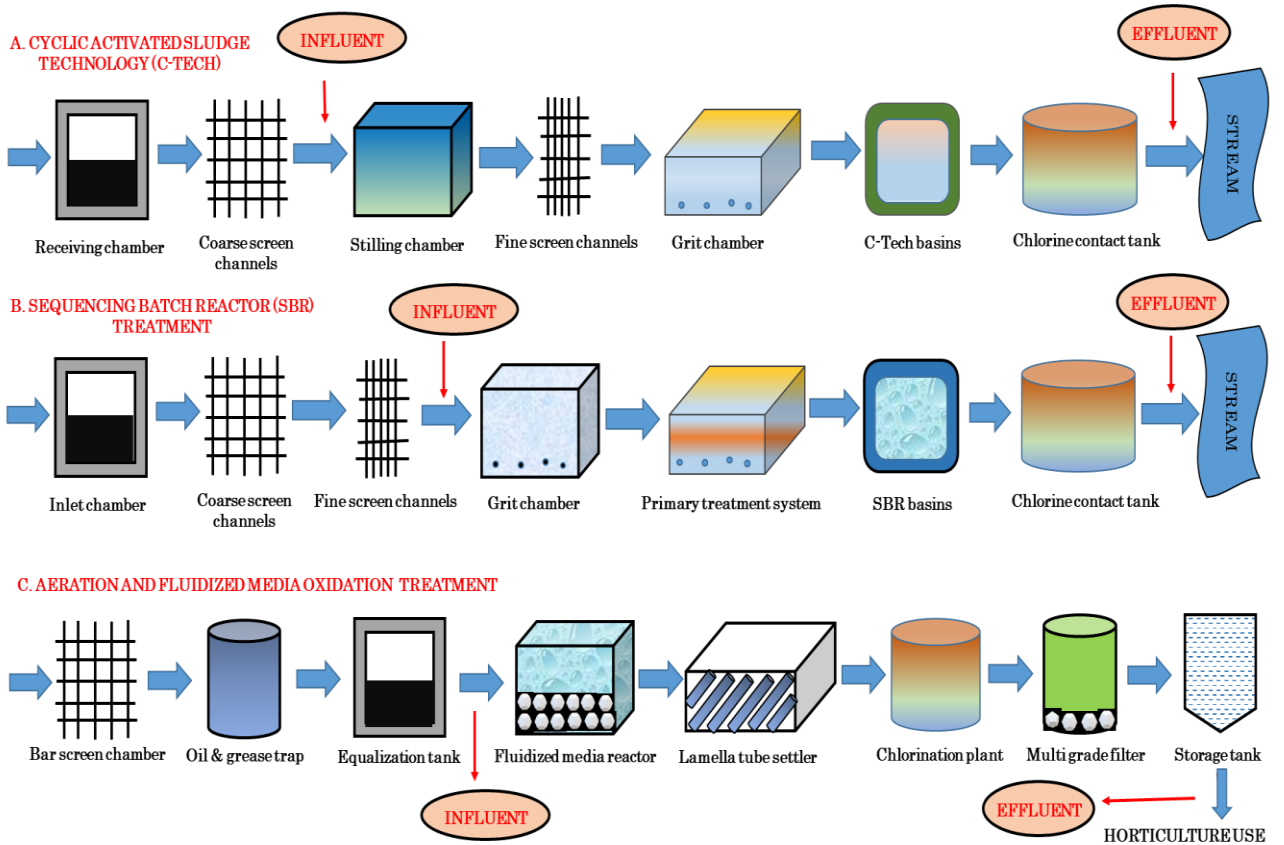
Figure 4.2. Working flow diagram of A. WWTP-I, B. WWTP-II, and C. WWTP-III & IV.

4.2.3 Sampling procedure

Sampling of wastewater was done from March 2022 to August 2022 (spring, summer, and monsoon) on the monthly frequency at the selected WWTPs. Seasonal sampling covers the wastewater samples from March and April (spring), May and June (scorching summer), and July and August (monsoon) to evaluate the seasonal variation. Grab samples were collected from the inlet and outlet locations of all the WWTPs. Sampling points as influent and effluent are also marked in Figure **4.2**. The sampling protocols and analysed physicochemical parameters information are detailed in Chapter 3 (Methodology).

4.2.4 SPE and HPLC-MS analysis

SPE process adopted for the work is mentioned comprehensively in Chapter 3 (Methodology). The methodology for HPLC-MS was optimized based on varying LC and MS parameters. The MS parameters were optimized by infusing target compounds at concentrations equal to $1 \ \mu gL^{1}$, while the LC parameters were optimized by changing the percentages of solvents in the gradient program. The method was then finetuned by varying the flow rate, column temperature, and injection volume. The detailed methodology for the analysis is provided in Chapter 3 (Methodology). The retention times and cone voltages of the target compounds are given in Table **4.3**.

4.2.5 Quality assurance (QA) and quality control (QC)

Field blanks were used during all the sampling events. Method blanks were run during both the calibration and sample analyses. 90:10 (v/v) water and methanol solution similar to the sample reconstitute was used as method blank to avoid sample contamination from the solvents. In the case of the detection of estrone in the method blank, a similar concentration was subtracted from each of the samples. Standards were run along with the samples to track any deviation in retention time. Seven-point calibration curves were prepared for all the target compounds. The MDL and MQL for the compounds were selected based on the effectiveness of the HPLC methodology in separating and identifying target peaks by ruling out matrix interferences. Both MDL and MQL were calculated based on EPA. Solutions of estrone were analysed seven times and using the standard deviation along with the Student's t-test score, MDL for the corresponding compound was calculated. MDL for the present methodology was calculated to be 0.5 μgL^{-1} while MQL was calculated by multiplying MDL with a factor of 3.18 which equals

to 1.59 μgL^{-1}. However, based on clear peak separation and peak shape on multiple injections, MDL was later on fixed as 1 μgL^{-1}. The MDL and MQL of the compounds are mentioned in Table **4.3**.

Table 4.3. List of the studied analytes with their respective LC and MS parameters.

Compounds	Cone voltage (V)	Retention time (min)	MDL (μgL^{-1})	MQL (μgL^{-1})
Ciprofloxacin	45	10.03	0.5	1
Sulfamethoxazole	35	11.9	0.5	1
Diclofenac	20	13.8	1	5
Ketoprofen	30	13.9	0.5	1
Acetaminophen	40	11.3	0.5	1
Caffeine	50	13.9	1	5
Carbamazepine	40	13.3	0.5	1
Estrone	30	14.8	0.5	1
Triclosan (TCS)	30	14.7	0.5	1

4.2.6 Distribution and statistical data treatment

The target analytes (PPCPs and EDCs) data treatment is performed with XLSTAT, RStudio, and MINITAB, and has been tested for normality distribution. The normality tests are performed with the help of Anderson-Darling, Jarque-Bera, Lilliefors, and Shapiro-Wilk tests which are the best-known test for identifying the data spread and distribution. The data obtained across seasons and WWTPs have been subjected to numerous statistical tests involving hypothesis testing (ANOVA) and identification of any significant trends/correlation between and within the samples (as influents and effluents), their treatment with respect to seasons, WWTPs-based percentage removal and overall quality assessment.

An outcome of the ANOVA test to determine if the means between two populations are significantly different is performed through the F statistics (F value). This is done through the F test that indicates if a group of variables is jointly significant. "Statistically significant" implies that the results achieved are not just due to chances. F statistics is used while deciding whether to support or reject the null hypothesis. In the F test results, both F value and F critical

value are indicated. The value that is calculated from the data is called the F Statistic or F value (without the critical part). However, F critical value is a specific value for comparative purposes. Here, if the calculated F value in a test is more than F critical value, then the null hypothesis is rejected. Importantly, the F statistic must be used together with the p-value when deciding if the overall results are significant. If the p-value is less than the alpha level (0.05), shows a statistical difference. After this, the individual p values are checked (Tukey's post hoc analysis, etc.) to identify those pinpointed variables that are statistically significant. The F value in one-way ANOVA addresses "whether the variance between the means of two populations is significantly different?". The F value in the ANOVA test also evaluates the p-value (probability); the p-value represents the probability of obtaining a result at least as extreme as the one that was observed, given that the null hypothesis is true.

Note: F value = Variance of the group means (mean square between the groups)/mean of the within group variances (mean squared error). Besides univariate statistics (Mahapatra et al., 2014), Mann-Whitney test, Kolz-Smirnov tests have been used for linking trends and measurement of the strengths in relationships. Moreover, for variance analysis and significance testing, One-way ANOVA, Kruskal-Wallis test, Tukey's pair-wise alignment, and Dunn's post hoc tests ($\alpha=0.05$) have been performed (Mahapatra et al, 2013) that provide the criteria based on individual p values for any possible statistical difference between specific parameters, followed by verification of the standardized residues at 95%.

4.3 Results and Discussion

4.3.1 PPCPs occurrence

The occurrence statistics of PPCPs in the WWTPs are presented in Table **4.4**. All seven target compounds have been detected in the WWTPs, with frequencies of detection greater than 40% and 10% in influent and effluent samples, respectively. Diclofenac and caffeine were detected in all the WWTPs influents. Similarly, diclofenac and caffeine were detected with higher frequencies at 91.7% in the WWTPs effluent. Among the PPCPs, the highest concentration in influent was recorded for caffeine (71653 ngL^{-1}) at WWTP-III in monsoon (July). This high concentration at the plant may be attributed to excessive consumption of major caffeine sources (tea and coffee) in the academic institution as various areas at the institution had tea/coffee stations for the people. This result matches with earlier reports in India as high levels of caffeine were also reported in wastewater influents such as 143700 ngL^{-1} (Mohapatra et al., 2016),

120000 and 45000 ngL^{-1} (Subedi et al., 2017) and 102840 ngL^{-1} (Archana et al., 2016). The total concentration of studied PPCPs in influent ranged from 1849 to 74187 ngL^{-1} in the WWTPs. The mean concentration in influent was observed highest for caffeine with a concentration of 32955 ngL^{-1}, followed by acetaminophen (4505 ngL^{-1}), ciprofloxacin (1797 ngL^{-1}), diclofenac (455 ngL^{-1}), ketoprofen (296 ngL^{-1}), sulfamethoxazole (53 ngL^{-1}) and carbamazepine (10 ngL^{-1}). These values of the compounds portray high consumption/release of PPCPs in the city, thus causing their high loading in the WWTPs. The observed concentration of targeted PPCPs was in agreement with earlier literature from India (Anumol et al., 2016; Mutiyar & Mittal, 2014; Prabhasankar et al., 2016; Singh & Suthar, 2021b; Subedi et al., 2015). Studies in China and U.S. also showed such concentrations of PPCPs in influent of their wastewater treatment facilities (Mohapatra et al., 2016; Sun et al., 2016). The comparison of the results of the current study with the earlier reported literature in India is summarized in Table **4.5**.

In the effluents, the highest concentration was again recorded for caffeine (62792 ngL^{-1}), at WWTP-III in summer (April). Archana et al. (2016) also reported higher levels of caffeine (46700 ngL^{-1}) during summer in wastewater effluents of a WWTP in Nagpur, India. The total concentration of studied PPCPs in effluent ranged from 22 to 64275 ngL^{-1} in the WWTPs. Similar to influent, the mean concentration in effluent was observed highest for caffeine with a concentration of 20981 ngL^{-1}, followed by ciprofloxacin (302 ngL^{-1}), acetaminophen (263 ngL^{-1}), diclofenac (158 ngL^{-1}), ketoprofen (93 ngL^{-1}), sulfamethoxazole (8 ngL^{-1}) and carbamazepine (5 ngL^{-1}). These significant values of the compounds in the effluent showcase the limitation of removal mechanisms in the WWTPs. The observed concentration of PPCPs in effluent was in correspondence with earlier literature from India (Anumol et al., 2016; Mutiyar & Mittal, 2014; Prabhasankar et al., 2016; Singh & Suthar, 2021b; Subedi et al., 2015, 2017) as well China (Sun et al., 2016), and United States (Mohapatra et al., 2016).

4.3.2 EDCs occurrence

The prevalence and abundance of the EDCs in the studied WWTPs have been elucidated in Table **4.6**. Out of the two target EDCs, estrone showed maximum detection frequencies i.e., 95.8% and 83.3% in the influent and effluents, respectively. TCS was detected at lower detection frequencies and concentrations in wastewater. The maximum concentration of TCS detected was 214 ngL^{-1} in the influents, which agrees with a few of the previously reported

maximum concentrations at the WWTPs, across the globe (Table **4.6**). On the other hand, higher concentrations of estrone were detected in wastewater, with a maximum of 123.9 μgL^{-1} in the influent of WWTPs investigated. Estrone is a natural steroid hormone secreted by the ovary, placenta, and adrenal cortex in both human beings and animals (Manickum & John, 2015). The hormone is excreted along with their urine and feces, which gets ultimately released into the environment (Manickum & John, 2014; Ying et al., 2002). Such high hormonal concentration might be primarily attributed to the presence of its inactive glucuronides and sulfate conjugates or free forms sourced from human excretion (urine and feces) in wastewater (Ting & Praveena, 2017). To the best of our knowledge, none of the earlier studies have reported estrone occurrence, prevalence, and build-up in Indian WWTPs systems influent. However, few studies have reported its concentration in influents of WWTPs in other regions of the world. The shockingly high prevalence of estrone in Indian waters (influents to WWTPs sourced from domestic sewers) is presently a matter of serious concern and needs immediate attention before it becomes ecologically unmanageable and poses adverse effects to local biota and affects the health and hygiene of the people in the neighbourhood. The numbers provided (estrone concentration) are the highest concentrations ever reported in wastewater systems, globally which is clear from Table **4.6**. The table enlists EDCs concentration (TCS and estrone) and puts forth a comparative account of the variations across the other regions in the world.

4.3.3 PPCPs seasonal variation

Several researchers have studied the seasonal variation of PPCPs in WWTPs globally (Mohapatra et al., 2016; Singh & Suthar, 2021b; Sun et al., 2016), to determine the seasonal effect on PPCPs consumption and their loading on the treatment facilities. For instance, Sun et al. (2016) reported a lower concentration of PPCPs in influent during monsoon as compared to summer and winter seasons. Singh & Suthar (2021b) also detected low levels of PPCPs in monsoon than in summer. Similarly, other studies observed lower levels of PPCPs in influent during monsoon as compared to other seasons (Sui et al., 2011; Sun et al., 2014; Yu et al., 2013). These low levels of PPCPs in the monsoon season as compared to other seasons, portray the dilution by the precipitation during the monsoon (Ternes, 1998). However, in the current study, total targeted PPCPs concentrations in the WWTPs showed somehow discordant seasonal variation. The average total PPCPs concentrations were observed higher in the influent water in spring (March and April), followed by monsoon (July and August) and scorching summer (May and June). The average total PPCPs concentrations in influent were

observed as 58189 ngL^{-1}, 49758 ngL^{-1}and 12275 ngL^{-1} in spring, monsoon, and summer seasons, respectively. Herein, the average total PPCPs concentrations were observed higher in monsoon, compared to summer. This increased levels of PPCPs in monsoon could be attributed to the leaching of PPCPs from various potential sources (comprising landfill waste, sludge from WWTPs, and livestock excretion) to the low-lying treatment facilities through high surface runoff during the precipitation in the hilly region. Similarly, the average total PPCPs concentrations in the effluent water were detected higher in spring (March and April), followed by monsoon (June and July) and summer (May and June) in the WWTPs. The average total PPCPs concentrations in effluent were observed as 36329 ngL^{-1}, 26155 ngL^{-1}, and 2935 ngL^{-1} in the spring, monsoon, and summer seasons, respectively. So, similar trends were observed for influents and effluents in the WWTPs, where average total PPCPs concentrations were reported higher in monsoon than in summer.

The targeted PPCPs concentrations detected in spring (March and April), summer (May and June), and monsoon (July and August) in influent and effluent of the studied WWTPs are given in Appendix section (A1 and A2). It was also quite interesting to observe the total PPCPs concentration seasonal variations among and within the WWTPs, which is effectively represented in Figure **4.3a**. In the influents, WWTP-I showed the highest total PPCPs concentrations in July (monsoon), WWTP-II in March (spring), WWTP-III in July (monsoon), and WWTP-IV in April (spring) as 62606 ngL^{-1}, 56505 ngL^{-1}, 74187 ngL^{-1} and 65478 ngL^{-1}, respectively. On the other hand, WWTP-I showed the highest total PPCPs concentrations in July (monsoon), WWTP-II in March (spring), WWTP-III in April (spring), and WWTP-IV in March (spring) as 40046 ngL^{-1}, 49847 ngL^{-1}, 64275 ngL^{-1} and 55423 ngL^{-1}, respectively in the effluents. In addition, Figure **4.3b** represents the seasonal variations in percentage composition of all the seven targeted compounds in influent and effluent of the studied WWTPs. Out of all the targeted compounds, caffeine is observed as the major loading PPCP in influent and effluent of the WWTPs. Furthermore, significant variations were observed in the occurrence of all the seven target compounds in spring (March and April), summer (May and June), and monsoon (July and August) in influent and effluent of the studied WWTPs. The occurrences, seasonal variations, and removal statistics of the individual targeted compounds are presented in Figures **4.4-4.10**.

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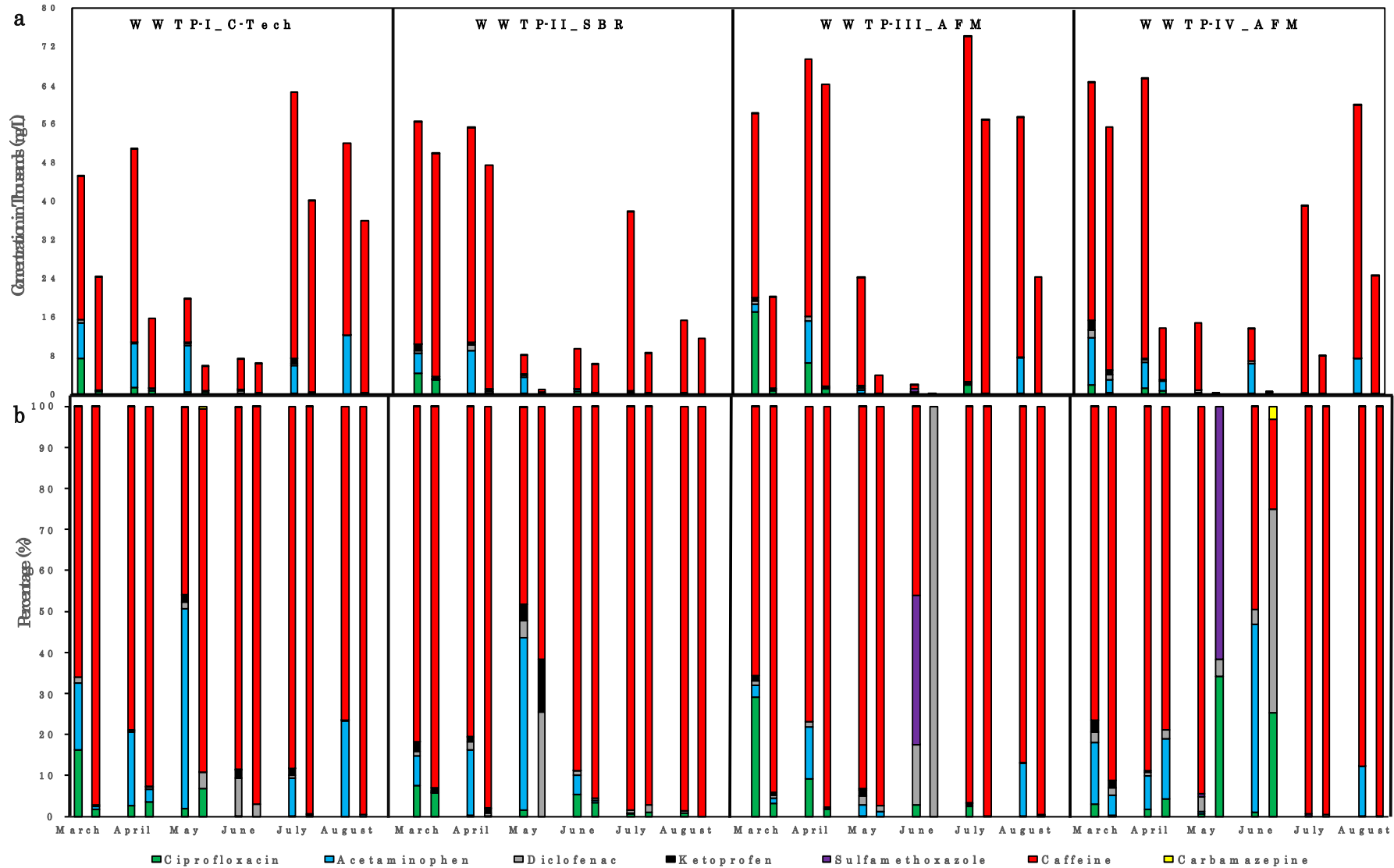
Figure 4.3. a) Temporal (monthly) variations in the a) cumulative concentration and b) percentage composition of the seven detected PPCPs in influents and effluents of the WWTPs. The first and second stacked column for each month represents influent and effluent, respectively.

Table 4.4. PPCPs detection and descriptive statistics in the studied WWTPs. Concentrations are expressed in ngL^{-1} and detection frequencies are in %.

WWTP location	Influent				Effluent			
PPCP	Frequency of detection	Maximum concentration	Minimum concentration	Mean concentration	Frequency of detection	Maximum concentration	Minimum concentration	Mean concentration
Ciprofloxacin	91.7	16931	BDL	1797	62.5	2871	BDL	302
Sulfamethoxazole	41.7	672	BDL	53	12.5	118	BDL	8
Diclofenac	100	1651	31	455	91.7	1032	BDL	158
Ketoprofen	66.7	1974	BDL	296	29.2	973	BDL	93
Acetaminophen	83.3	12102	BDL	4505	50	2688	BDL	263
Caffeine	100	71653	851	32955	91.7	62792	BDL	20981
Carbamazepine	75	51	BDL	10	50	43	BDL	5

BDL represents below detection limit.

Table 4.5. Collation of the targeted PPCPs results with the earlier reported literature in India.

PPCP	WWTP influent maximum concentration (µgL^{-1})	Area/Country	Reference
Ciprofloxacin	246.1 ± 0.3	Metropolitan city, Western India	Mohapatra et al. (2016)
	45.40	Okhla, Delhi, India	Mutiyar & Mittal (2014)
	24.51	Nagpur, Maharashtra, India	Archana et al. (2016)
	16.9	**Dehradun, Uttarakhand, India**	**Current study**
	0.036	Haridwar, Uttarakhand, India	Singh and Suthar (2021b)
Sulfamethoxazole	2.26	Manipal, Karnataka, India	Subedi et al. (2015)
	2.1± 0.2	Metropolitan city, Western India	Mohapatra et al. (2016)
	~1.00	Chennai, Tamil Nadu, India	Anumol et al. (2016)
	0.94	Karnataka, South India	Prabhasankar et al. (2016)

	0.69	Udupi, Karnataka, India	Subedi et al. (2017)
	0.7	**Dehradun, Uttarakhand, India**	**Current study**
	0.64	South India	Akiba et al. (2015)
Diclofenac	5.30	Chennai, Tamil Nadu, India	Anumol et al. (2016)
	1.6	**Dehradun, Uttarakhand, India**	**Current study**
Ketoprofen	**1.9**	**Dehradun, Uttarakhand, India**	**Current study**
	0.28	Haridwar, Uttarakhand, India	Singh and Suthar (2021b)
	0.05	Beur, Bihar, India	Subedi et al. (2015)
Acetaminophen	147.7 ± 25.9	Metropolitan city, Western India	Mohapatra et al. (2016)
	13.25	Nagpur, Maharashtra, India	Archana et al. (2016)
	12.1	**Dehradun, Uttarakhand, India**	**Current study**
	11.00	Udupi, Karnataka, India	Subedi et al. (2017)
	0.28	Haridwar, Uttarakhand, India	Singh and Suthar (2021b)
Caffeine	143.7 ± 51.4	Metropolitan city, Western India	Mohapatra et al. (2016)
	120.00	Udupi, Karnataka, India	Subedi et al. (2017)
	102.84	Nagpur, Maharashtra, India	Archana et al. (2016)
	71.6	**Dehradun, Uttarakhand, India**	**Current study**
	65.00*	Chennai, Tamil Nadu, India	Anumol et al. (2016)
	60.50	Manipal, Karnataka, India	Subedi et al. (2015)
	45.00	Mangalore, Karnataka, India	Subedi et al. (2017)
	42.50	Coimbatore, Tamil Nadu, India	Subedi et al. (2015)
	1.36	Haridwar, Uttarakhand, India	Singh and Suthar (2021b)
Carbamazepine	>3.00	Chennai, Tamil Nadu, India	Anumol et al. (2016)
	2.50	Coimbatore, Tamil Nadu, India	Subedi et al. (2015)
	0.26	Haridwar, Uttarakhand, India	Singh and Suthar (2021b)
	0.05	**Dehradun, Uttarakhand, India**	**Current study**

*Average Concentration

Table 4.6. EDCs detection in the studied WWTPs with a comparative account for literature previously undertaking similar studies. TCS concentrations are reported in ngL⁻¹ whereas estrone concentrations are in µgL⁻¹, and frequency is provided as %.

WWTP / Parameters	Influent				Effluent			
EDC	TCS	Previous reported Values	Estrone.	Previous reported values	TCS	Previous reported values	Estrone	Previous reported values
Frequency of detection	66.7	100[1,2,3] 98 and 81[4] 91.66[5]	95.8	100[1,6,7,8,9]	37.5	100[1,2,3,10] 91.66[5]	83.3	100[6,7,8,9]
Min. Conc.	BDL	13700[2] 2010[4] 570[10] <250[3] 250[1] 181[11] 150[12] BDL[5]	BDL	0.0857[7] 0.0422*[9] 0.032[1] 0.0131[6] 0.013[8]	BDL	990[4] 181[11] 180[2] 80.1[3] 79[1] 23[10] BDL[5] BDL[12]	BDL	0.011[6] 0.010[7] 0.0038*[9] 0.003[8] 0[1]
Max. Conc.	214	86200[2] 17600[4] >3000[13] 2500[12] 850[10] 790[1] 774[3] 260[5] 245[11]	123.9	0.351[8] 0.182[7] 0.111*[9] 0.104[6] 0.070[1]	159	13000[4] 5370[2] 2500[12] 434[10] 249.7[3] 171[11] 149[1] 139[5]	81.7	0.370[6] 0.078[8] 0.0304*[9] 0.0294[7] 0.024[1]
Mean Conc.	48	37838.3[2] 990–6100[4] 547[1] 98.9[5]	45	0.127[7] 0.084[8] 0.047[1]	18	1715[2] 142[10] 112[1] 62[5]	29.4	0.023[8] 0.0162[7] 0.006[1]
Av. + SD (Spring)	52.44±44.72	-	39.09±6.23	-	19.01±37.84	-	44.46+16.16	-
Av. + SD (Summer)	27.11±33.77	-	17.89±34.64	-	3.0±5.83	-	4.39+6.50	-
Av. + SD (Monsoon)	66.45±78.90	-	78.01±38.96	-	34.55±55.45	-	39.32+23.27	-

BDL represents below detection limit. *Average concentration.

([1]Behera et al., 2011; [2]Kumar et al., 2010; [3]Zhou et al., 2009; [4]Lehutso et al., 2017; [5]Singh & Suthar, 2021b; [6]Atkinson et al., 2012; [7]Huang et al., 2014; [8]Manickum & John, 2014; [9]Ye et al., 2012; [10]Ying & Kookana, 2007; [11]Yu & Chu, 2009; [12]Subedi et al., 2015; [13]Anumol et al., 2016).

Targeted antibiotics (ciprofloxacin and sulfamethoxazole) showed distinct patterns in their occurrence in various seasons. Maximum concentrations of ciprofloxacin were observed in spring (March) season in influents of all the WWTPs as compared to fewer concentrations detected in summer and monsoon seasons. This might be due to the higher antibiotics consumption in cold seasons (Davey et al., 2008; Ockene et al., 2004), as compared to hot or wet seasons. The highest concentration of ciprofloxacin was recorded as 16931 ngL^{-1} at WWTP-III in March. On the contrary, a maximum concentration of sulfamethoxazole was observed as 672 ngL^{-1} in summer (June) at WWTP-III, which was higher than recorded concentrations in spring and monsoon seasons at the WWTPs. In the effluents, maximum concentrations for ciprofloxacin (2872 ngL^{-1}) and sulfamethoxazole (118 ngL^{-1}) were detected in spring (March) at WWTP-II and summer (May) at WWTP- IV, respectively.

Statistical data treatment for the seasonal ciprofloxacin samples showed significant variations between the samples (F=5.613; p=0.00047), which shows very strong evidence for unequal means. Tukey's pairwise analysis showed a significant difference in the spring influent with spring effluent (p=0.009), summer influent (p=0.002), summer effluent (p=0.001), monsoon influent (p=0.002), and effluent (0.001). Mann-Whitney and Dunn's post hoc tests also indicated significant variation between influents and effluents of different seasons (p<0.05). The tests for normality distribution showed a non-normal distribution for most of the seasonal data set collected. The univariate statistical analysis showed the highest kurtosis (7.52) and skewness (2.72) for the monsoon influents. The seasonal variation of the ciprofloxacin in wastewater samples are being shown as box and violin plots indicating the data spread with whiskers and the distribution across the mean elucidated in Figure **4.4a**. Figure **4.4b** depicts the xy scatter plot and interaction between the influents and effluents across seasons within the 95% confidence ellipses. The seasonal removal efficiencies are represented with whisker plots in Figure **4.4c**.

The overall influents and effluents for ciprofloxacin samples showed no significant variation (F=3.61; p=0.06), which suggests no evidence for either equal or unequal means based on ANOVA. However, Mann-Whitney pairwise and Dunn's post hoc tests showed a difference between influents and effluents (p=0.04). The tests for normality distribution showed both the data sets are non-normally distributed. The univariate statistics showed relatively higher skewness (3.51) and kurtosis (14.09) for the effluent samples. The results from the overall influents and effluents values of ciprofloxacin are provided as box and violin plots, bi-

histograms showing the ideal distribution and the present data distribution, samples variation with normal order statistical medians and time series of the influents and effluents variations are shown as Figure **4.4(d-g)**.

Figure 4.4. Ciprofloxacin samples a) Seasonal variation b) Influent effluent linkages across seasons c) Seasonal treatment efficiencies d) Overall variation of influents and effluents e) Histogram Biplots for influents and effluents f) Samples and Normal order statistics medians linkage g) Time series for samples variations (influents and effluents) h) Comparative account of influents and effluents across treatment systems i) Van krevelen plots for treatment systems and j) Removal efficiencies of various treatment systems.

A comparative account of the four treatment systems for ciprofloxacin showed substantial evidence for equal means (F=1.515; p=0.19). Except for WWTP-I effluents, all others showed non-normally distributed data, and the highest skewness (2.42) and kurtosis (5.89) were observed in WWTP II effluent. No significant difference was observed between the removal

efficiencies, with strong evidence for equal means (F=0.16; p = 0.91). Subsequently, the WWTPs influents and effluents variations with their removal efficiencies are shown in Figure **4.4(h-j)**.

Figure 4.5. Sulfamethoxazole samples a) Seasonal variation b) Influent effluent linkages across seasons c) Seasonal treatment efficiencies d) Overall variation of influents and effluents e) Histogram Biplots for influents and effluents f) Samples and Normal order statistics medians linkage g) Time series for samples variations (influents and effluents) h) Comparative account of influents and effluents across treatment systems i) Van krevelen plots for treatment systems and j) Removal efficiencies of various treatment systems.

Statistical data treatment for the sulfamethoxazole seasonal samples showed no significant variations between the samples (F=1.39; p=0.24), which shows substantial evidence for equal means. Mann-Whitney pairwise comparison indicated a significant difference between the

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monsoon effluents compared to other seasonal samples (p=0.029). Dunn's post hoc test also indicated significant variations between monsoon effluents (p=0.02) and summer influents (p=0.03) compared to other seasonal samples. The tests for normality distribution showed a non-normal data distribution (p<0.05) for most of the seasonal dataset collected. The univariate statistical analysis showed the highest kurtosis (8) and skewness (2.82) for both spring and monsoon effluents. The seasonal variation of the sulfamethoxazole in wastewater samples are being shown as box and violin plots indicating the data spread with whiskers and the distribution across the mean elucidated in Figure **4.5a**. Figure **4.5b** shows the xy scatter plot and interaction between the influents and the effluents across seasons within the 95% confidence ellipses. The seasonal removal efficiencies are represented with whisker plots in Figure **4.5c**.

The overall influents and effluents for sulfamethoxazole samples showed no significant variation (F=2.39; p=0.128), which suggests no evidence for either equal or unequal means based on ANOVA. However, Mann-Whitney pairwise test and Dunn's post hoc tests reported a difference between influents and effluents (p=0.025). The tests for normality distribution showed both the data sets are non-normally distributed. The univariate statistics showed relatively higher skewness (4.12) and kurtosis (18.38) for the influent samples. The results from the overall influents and effluents values of sulfamethoxazole are provided as box and violin plots, bi-histograms showing the ideal distribution and the present data distribution, samples variation with normal order statistical medians and time series of the influents and effluents variations are shown as Figure **4.5(d-g)**.

A comparative account of the four treatment systems for sulfamethoxazole showed substantial evidence for equal means (F=1.376; p=0.24). Except for WWTP-I influents, all others showed non-normally distributed data, and the highest skewness (2.44) and kurtosis (6) were observed in all WWTP effluents. No significant difference was observed between the removal efficiencies, with no evidence for either equal or equal means (F=0.195; p = 0.388). The tests for normal distribution indicated normally distributed data for WWTP II and IV. The WWTPs influents and effluent variations with their removal efficiencies are shown in Figure **4.5(h-j).**

The occurrence of NSAIDs (diclofenac and ketoprofen) showed similar seasonal variations. Maximum concentrations of diclofenac were observed in spring (March) and summer (April) in influents of the WWTPs as compared to fewer concentrations detected in monsoon season.

The highest concentration of diclofenac was recorded as 1651 ngL^{-1} at WWTP-IV in March. Similarly, maximum concentrations of ketoprofen were observed in spring (March) in influents of the studied WWTPs, except for WWTP-I where the compound was not detected. The highest concentration of ketoprofen was observed as 1974 ngL^{-1} in March at WWTP-IV, which was higher than recorded concentrations in spring and monsoon seasons at the WWTPs. The higher presence of NSAIDs in spring as compared to summer and monsoon seasons might be attributed to their higher consumption in cold seasons (Davey et al., 2008; Ockene et al., 2004). Also, WWTP-IV influent possessed maximum concentrations of the targeted NSAIDs in spring, portraying their high consumption at the academic institution during the season. In the effluents, maximum concentrations for diclofenac (1032 ngL^{-1}) and ketoprofen (973 ngL^{-1}) were detected in spring (March) at WWTP- IV.

Statistical data treatment for the diclofenac seasonal samples showed a greater statistically significant variation between the influent and effluent samples (F=9.77; p=0.000003), which shows decisive evidence for unequal means. Tukey's pairwise analysis showed a significant difference in the spring influent with spring effluent (p=0.002), summer influent (p=0.021), summer effluent (p=0.000025), monsoon influent (p=0.0001), and effluent (p=0.000004). Mann-Whitney and Dunn's post hoc tests also indicated higher significant variation between influents and effluents of different seasons (p=0.05 and lower). The tests for normality distribution showed a normal data distribution (p>0.05) for the influents of spring and summer seasons. The univariate statistical analysis showed the highest kurtosis (5.7) and skewness (2.29) for spring effluent samples. The seasonal variation of the diclofenac in wastewater samples are being shown as box and violin plots indicating the data spread with whiskers and the distribution across the mean elucidated in Figure **4.6a**. Figure **4.6b** shows the xy scatter plot and interaction between the influents and the effluents across seasons within the 95% confidence ellipses. The seasonal removal efficiencies are represented with whisker plots in Figure **4.6c**.

The overall influent and effluent for diclofenac samples showed highly significant variation (F=11.17; p=0.0016), which suggests strong evidence for unequal means based on ANOVA. However, Mann-Whitney pairwise and Dunn's post hoc tests reported a significant difference between influents and effluents (p=0.0002). The tests for normality distribution showed both the data sets are non-normally distributed. The univariate statistics showed relatively higher skewness (12.77) and kurtosis (3.21) for the influent samples. The results from the overall

influents and effluents values of diclofenac are provided as box and violin plots, bi-histograms showing the ideal distribution and the present data distribution, samples variation with normal order statistical medians and time series of the influents and effluents variations are shown as Figure **4.6(d-g)**.
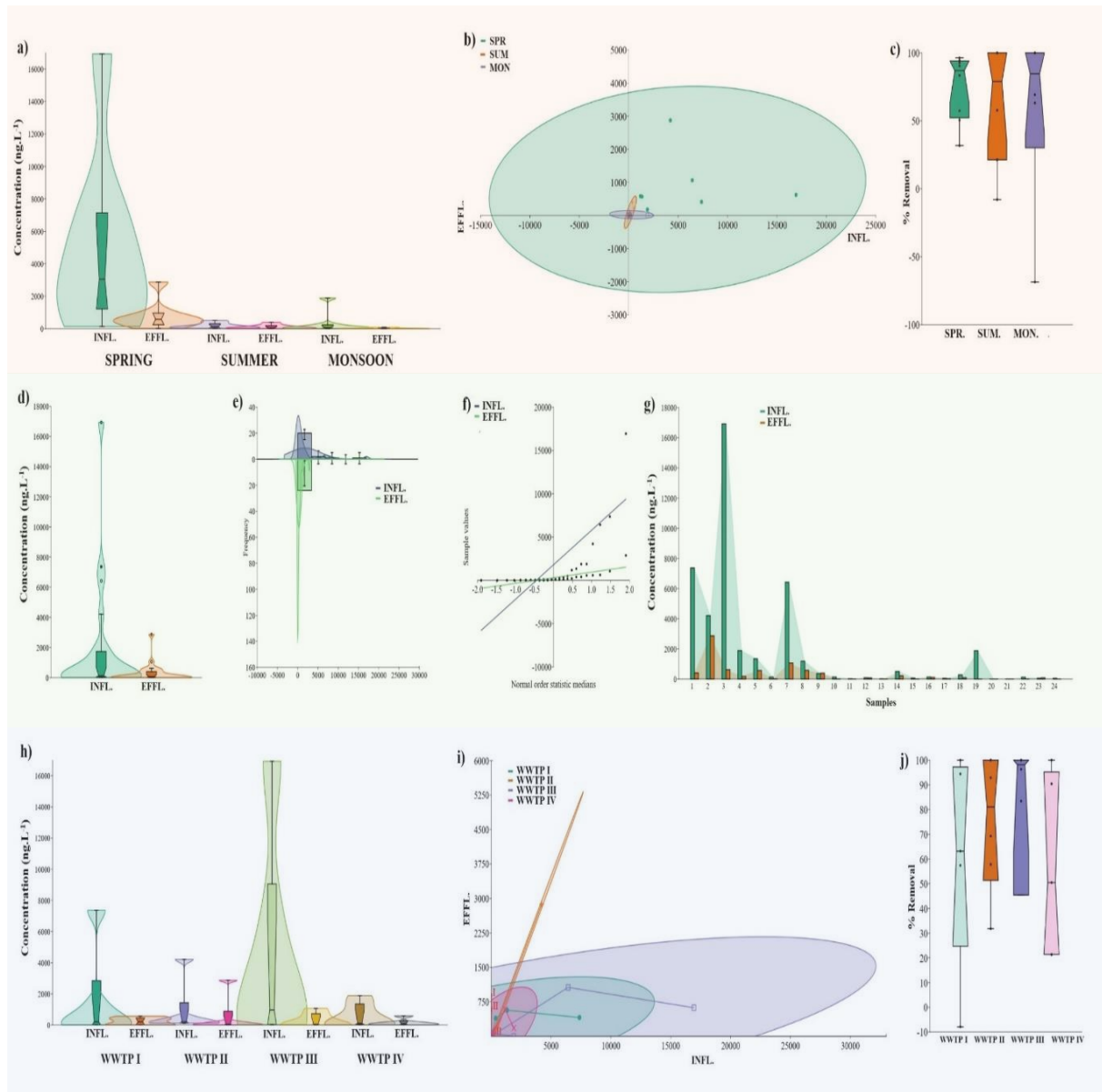

Figure 3.6. Diclofenac samples a) Seasonal variation b) Influent effluent linkages across seasons c) Seasonal treatment efficiencies d) Overall variation of influents and effluents e) Histogram Biplots for influents and effluents f) Samples and Normal order statistics medians variation g) Time series for samples variations (influents and effluents) h) Comparative account of influents and effluents across treatment systems i) Van krevelen plots for treatment systems and j) Removal efficiencies of various treatment systems.

A comparative account of the four treatment systems for diclofenac showed substantial evidence for equal means (F=1.738; p=0.12). However, Mann-Whitney pairwise and Dunn's

post hoc tests reported a significant difference between WWTP-I effluents (p=0.03) and WWTP III effluents (p=0.013) from WWTP-I influent samples. Except for WWTP-IV effluents, all others showed normally distributed data. The highest skewness (2.046) and kurtosis (4.38) were also observed in WWTP-IV effluents. No significant difference was observed between the removal efficiencies, with evidence for equal means (F=1.395; p=0.27). The tests for normal distribution indicated standard Gaussian data for all WWTPs. The WWTPs influents and effluent variations with their removal efficiencies are shown in Figure **4.6(h-j)**.
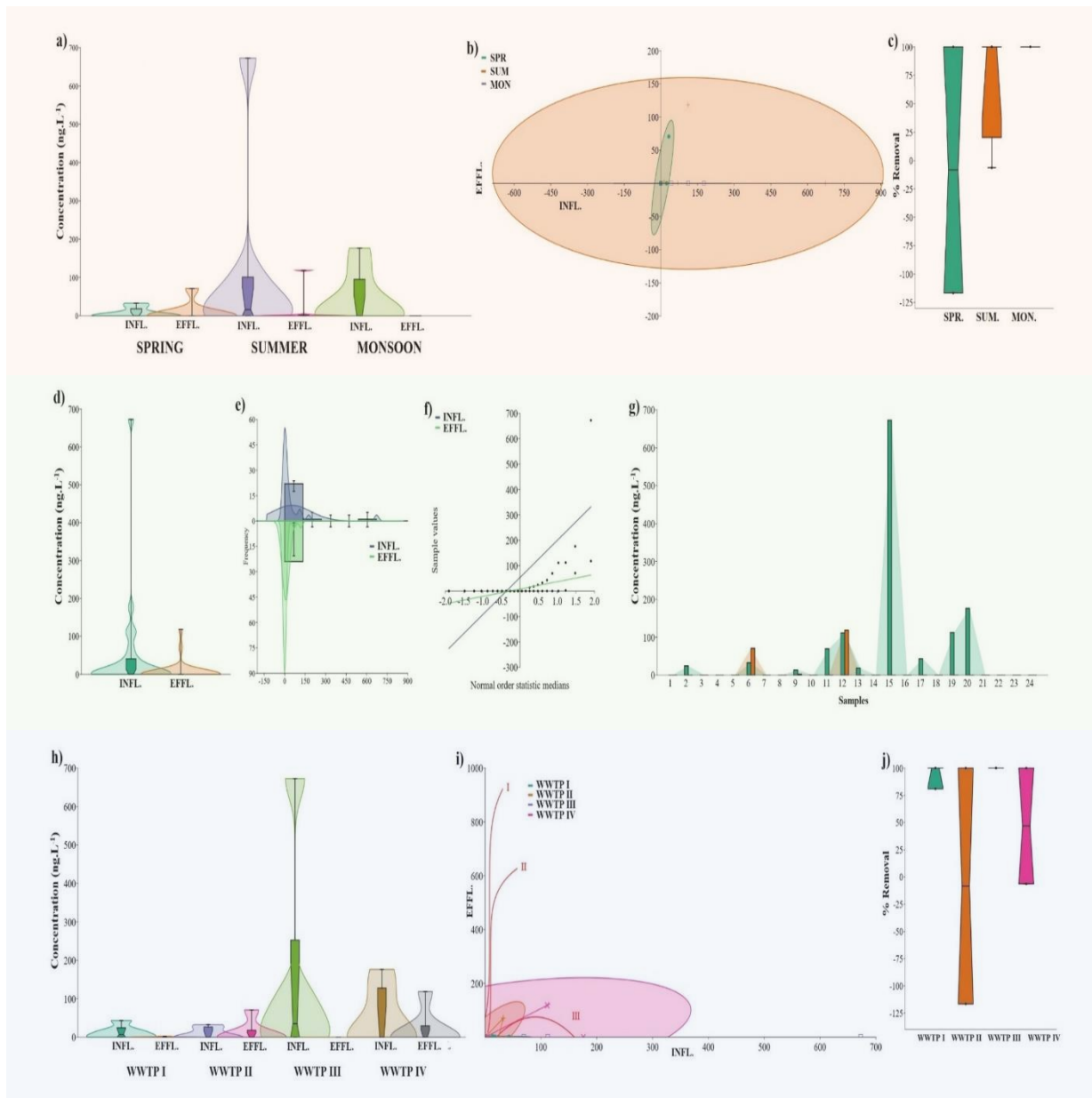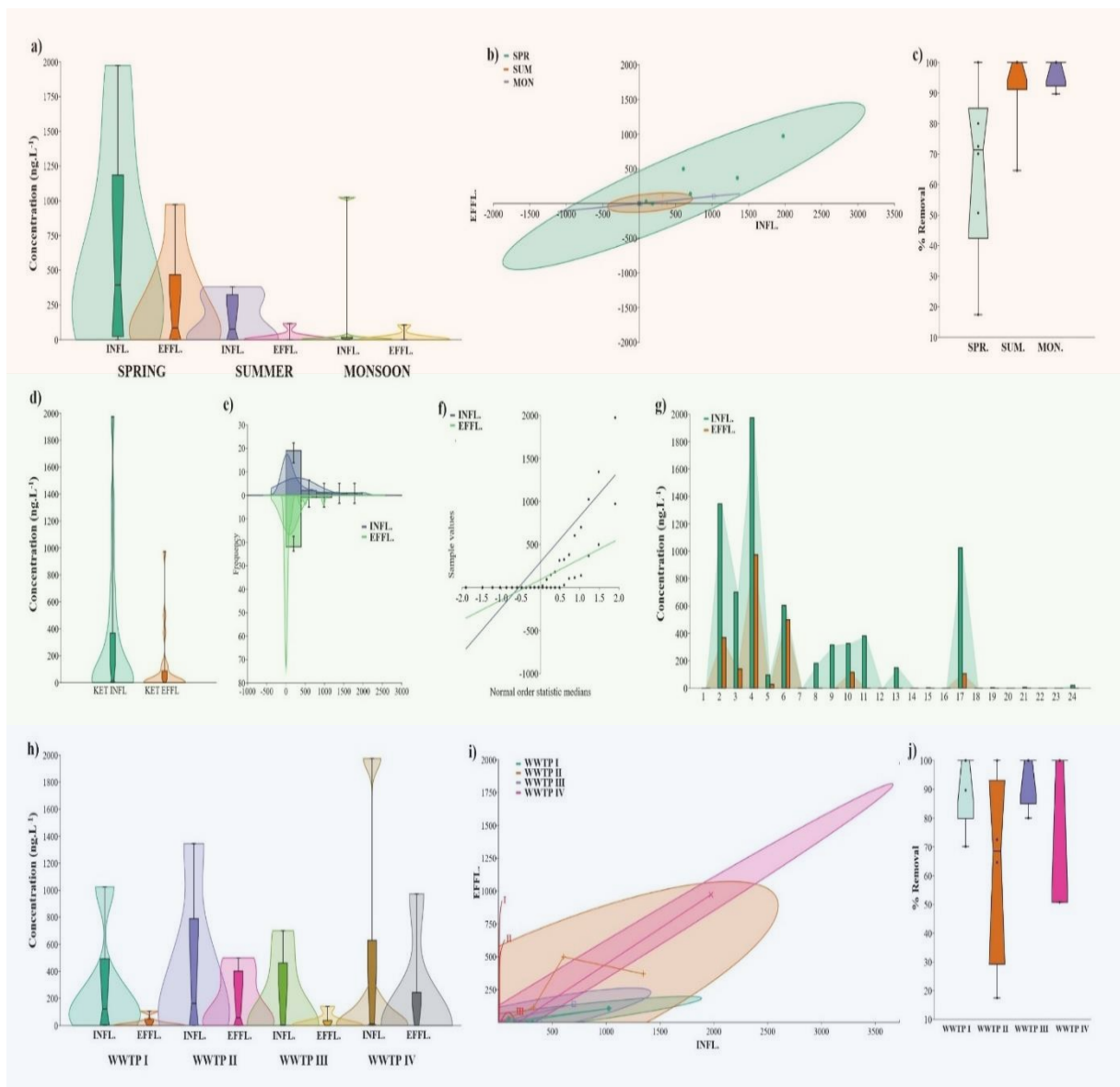

Figure 4.7. Ketoprofen samples a) Seasonal variation b) Influent effluent linkages across seasons c) Seasonal treatment efficiencies d) Overall variation of influents and effluents e) Histogram Biplots for influents and effluents f) Samples and Normal order statistics medians variation g) Time series for samples variations (influents and effluents) h) Comparative account of influents and effluents across treatment systems i) Van krevelen plots for treatment systems and j) Removal efficiencies of various treatment systems.

Statistical data treatment for the ketoprofen seasonal samples showed significant variation between the influent and effluent samples at p<0.05 level (F=3.003; p=0.0209), which shows meager evidence for either equal or unequal means. Tukey's pairwise analysis showed a significant difference between the spring influents with summer effluents (p=0.0238) and monsoon effluents (0.0234). Mann-Whitney test indicated a higher significant variation of summer and monsoon effluents with spring influents (p=0.0128) and effluents (p=0.04); and summer influents (p=0.017). Similar findings were also observed with Dunn's post hoc test. The tests for normality distribution showed a normal data distribution (p>0.05) for influents and effluents of spring season samples. The univariate statistical analysis showed the highest kurtosis (8) and skewness (2.82) for effluent of summer and monsoon samples. The seasonal variation of the ketoprofen in wastewater are being shown as box and violin plots indicating the data spread with whiskers and the distribution across the mean elucidated in Figure **4.7a**. Figure **4.7b** shows the xy scatter plot and interaction between the influents and effluents across seasons within the 95% confidence ellipses. The seasonal removal efficiencies are represented with whisker plots in Figure **4.7c**.

The overall influent and effluent for ketoprofen samples showed no significant variation (F=3.245; p=0.078), which suggests no evidence for either equal or unequal means based on ANOVA. However, Mann-Whitney pairwise and Dunn's post hoc tests reported a significant difference between influents and effluents (p=0.017). The tests for normality distribution showed both the data sets are non-normally distributed. The univariate statistics showed relatively higher skewness (3.12) and kurtosis (10.4) for the influent samples. The results from the overall influents and effluents values of ketoprofen are provided as box and violin plots, bi-histograms showing the ideal distribution and the present data distribution, samples variation with normal order statistical medians and time series of the influents and effluents variations are shown as Figure **4.7(d-g)**.

A comparative account of the four treatment systems for ketoprofen showed very strong evidence for equal means (F=0.64; p=0.71). However, the Mann-Whitney pairwise and Dunn's post hoc tests reported a significant difference between WWTP-III effluents and WWTP-I influents (p=0.013; p=0.036) from WWTP-I influent samples. Except for WWTP-II influents and effluents, all others showed non-normally distributed data. The highest skewness (2.44) and kurtosis (6) were observed in WWTP-III and WWTP-IV effluents. No significant difference was observed between the removal efficiencies, with evidence for equal means

(F=1.375; p=0.3). The tests for normal distribution indicated a higher normally distributed data set for WWTP-I and WWTP-II. The WWTPs influents and effluents variations with their removal efficiencies are shown in Figure **4.7(h-j)**.

Acetaminophen (analgesic) showed seasonal variation in contrast to antibiotics and NSAIDs. Maximum average concentrations for the compound were observed in summer (April, 8000 ngL^{-1}), followed by monsoon (August, 6698 ngL^{-1}) and spring (March, 5730 ngL^{-1}) in the influents of the WWTPs. The maximum concentration of acetaminophen was observed as 12102 ngL^{-1} at WWTP-I in August. In the effluents, the compound was either not detected or detected in low concentrations in summer (May and June) and monsoon (July and August) seasons at the WWTPs. The maximum concentration for the compound was recorded as 2688 ngL^{-1} in spring (March) at WWTP- IV.

Statistical data treatment for the acetaminophen seasonal samples showed a greater statistically significant variation between the influent and effluent samples (F=8.051; p=0.000025), which shows decisive evidence for unequal means. Tukey's pairwise analysis showed a significant difference in the spring influent with spring effluent (p=0.0006), summer influent (p=0.03), summer effluent (p=0.00012), and monsoon effluent (p=0.00012). Moreover, the monsoon influents were also very different from summer influents (p=0.045) and effluents (0.046). The Mann-Whitney and Dunn's post hoc tests also indicated higher significant variation between influents and effluents of different seasons (p<0.05 and lower). The tests for normality distribution showed a normal data distribution (p>0.05) for influents of spring season. The univariate statistics analysis showed the highest kurtosis (8) and skewness (2.82) for monsoon effluent samples. The seasonal variation of the acetaminophen in wastewater samples are being shown as box and violin plots indicating the data spread with whiskers and the distribution across the mean elucidated in Figure **4.8a**. Figure **4.8b** shows the xy scatter plot and interaction between the influents and the effluents across seasons within the 95% confidence ellipses. The seasonal removal efficiencies are represented with whisker plots in Figure **4.8c**.

The overall influent and effluent for acetaminophen samples showed highly significant variation (F=25.67; p=0.000007), which suggests decisive evidence for unequal means based on ANOVA. Tukey's pairwise analysis showed a higher magnitude of difference between the means (p=0.000007). Mann-Whitney pairwise and Dunn's post hoc tests also reported a significantly high difference between influents and effluents (p=0.00005). The tests for

normality distribution showed both the data sets are non-normally distributed. The univariate statistics showed relatively higher skewness (3.18) and kurtosis (9.61) for the effluent samples. The results from the overall influents and effluents values of acetaminophen are provided as box and violin plots, bi-histograms showing the ideal distribution and the present data distribution, samples variation with normal order statistical medians and time series of the influents and effluents variations are shown as Figure **4.8(d-g)**.
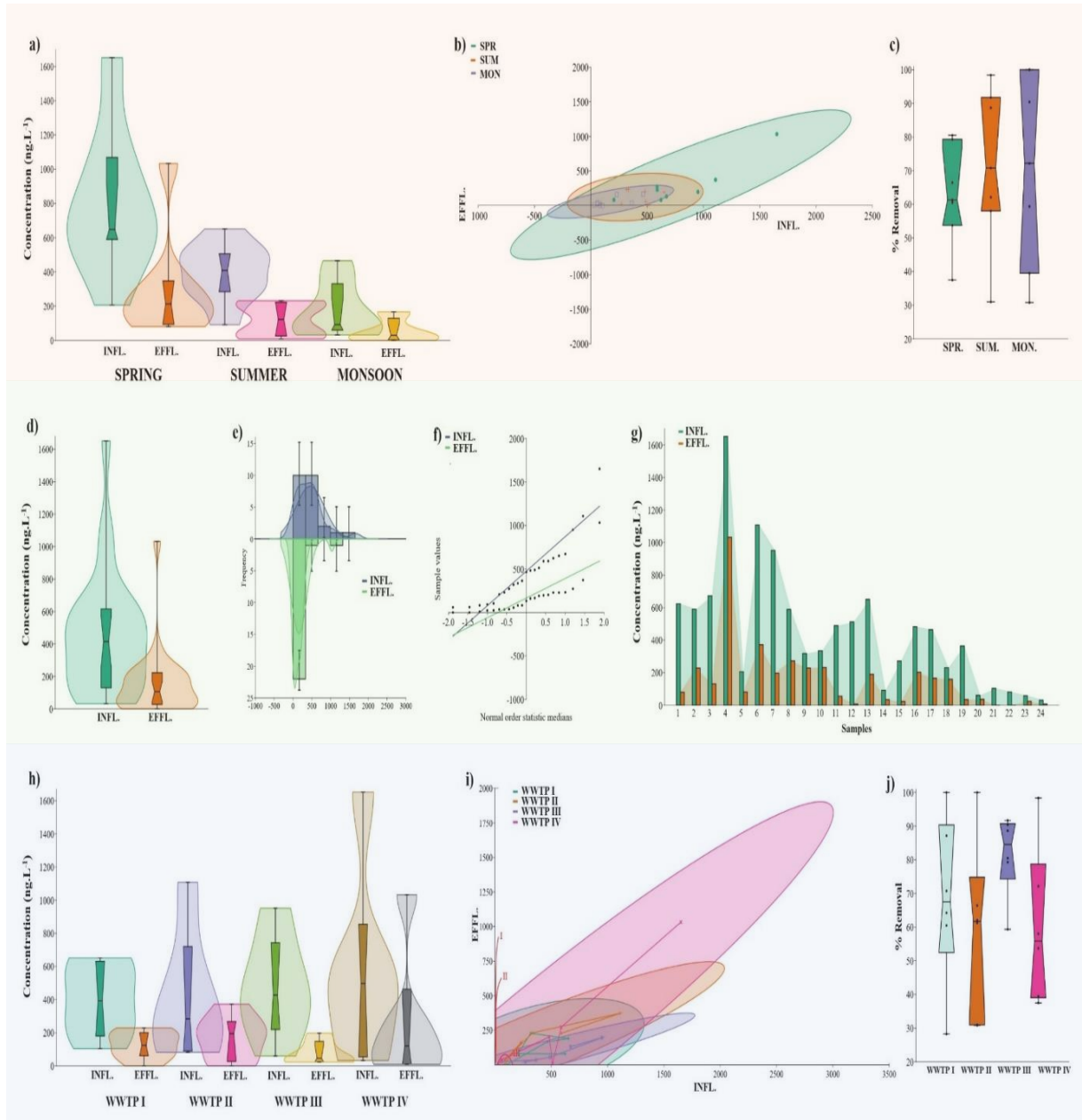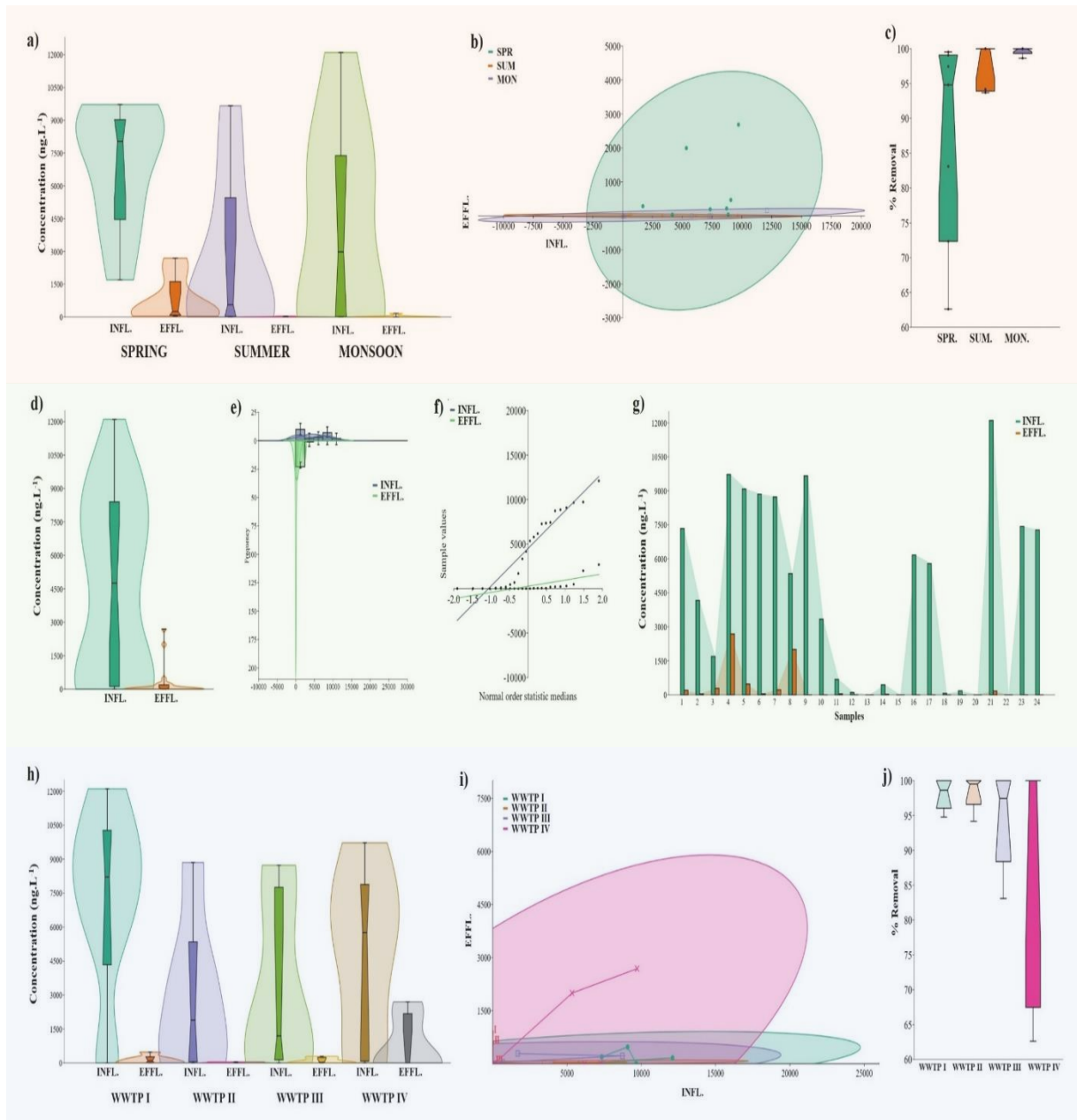

Figure 4.8. Acetaminophen samples a) Seasonal variation b) Influent effluent linkages across seasons c) Seasonal treatment efficiencies d) Overall variation of influents and effluents e) Histogram Biplots for influents and effluents f) Samples and Normal order statistics medians variation g) Time series for samples variations (influents and effluents) h) Comparative account of influents and effluents across treatment systems i) Van krevelen plots for treatment systems and j) Removal efficiencies of various treatment systems.

A comparative account of the four treatment systems for acetaminophen showed substantial evidence for unequal means (F=5.474; p=0.12). Tukey's pairwise analysis showed a significant difference in the WWTP-I influents with WWTP-I, II, III, and IV effluents (p=0.0014; 0.0011; 0.0013 and 0.0046, respectively). Mann-Whitney and Dunn's post hoc tests also indicated a higher significant variation between influents and effluents WWTPs (p=0.05 and below). WWTP-I, II, and IV influents and WWTP-I effluents showed normally distributed data. The highest skewness (1.35) and kurtosis (1.61) were also observed in WWTP-I effluents. No significant difference was observed between the removal efficiencies, with substantial evidence for equal means (F=1.474; p = 0.259). The tests for normal distribution indicated normally distributed data from WWTP-I and III. The WWTPs influents and effluents variations with their removal efficiencies are shown in Figure **4.8(h-j)**.

Caffeine (stimulant) was reported in the highest concentrations among studied PPCPs in the WWTPs. Caffeine is used in many beverages, processed foods, and medicines, and India is one of the countries, where per head per day consumption of these caffeinated substances in India is significantly higher than the global average consumption thus found commonly in Indian WWTPs (Singh & Suthar, 2021b). Maximum average concentrations for the compound were observed in July (50697 ngL^{-1}), followed by April (49026 ngL^{-1}), March (40894 ngL^{-1}), and August (39304 ngL^{-1}) in the influents of the WWTPs. Average concentrations in hot summer (May and June) were found significantly lower than in spring and monsoon seasons. This might be due to the lower consumption of major caffeine sources (tea and coffee) by the people during the hot season in the studied area. The highest concentration of caffeine was recorded as 71653 ngL^{-1} at WWTP-III in July. In the effluents, similar variations were observed for caffeine as influents, where the compound was either detected in low concentrations or not detected in the hot summer (May and June) season at the WWTPs. The maximum concentration for the compound was recorded as 62792 ngL^{-1} in April at WWTP-III.

Statistical data treatment for the caffeine seasonal samples showed a highly significant variation between the influent and effluent samples (F=14.29; p=3.5 X 10^{-8}), which shows decisive evidence for unequal means. Tukey's pairwise analysis showed a significant difference in the spring influents and effluent samples with summer influent (p=4.6 X 10^{-5}, 0.0064) and summer effluent (p=2.26 X 10^{-6}, 0.00039). In addition, the summer influents and effluents values were significantly different from monsoon influents (p=0.0004; 2.21 X 10^{-6}) and monsoon effluents (p=0.014). Mann-Whitney and Dunn's post hoc tests also indicated

higher significant variation between influents and effluents of different seasons (p<0.001 and lower). The tests for normality distribution showed a normal data distribution (p>0.05) for all seasonal samples except for summer effluents. The univariate statistics analysis showed relatively higher kurtosis (1.89) and skewness (1.23) for summer influent samples. The seasonal variations of the caffeine samples in wastewaters are shown as box and violin plots indicating the data spread with whiskers and the distribution across the mean elucidated in Figure **4.9a**. Figure **4.9b** shows the xy scatter plot and interaction between the influents and the effluents across seasons within the 95% confidence ellipses. The seasonal removal efficiencies are represented with whisker plots in Figure **4.9c**.
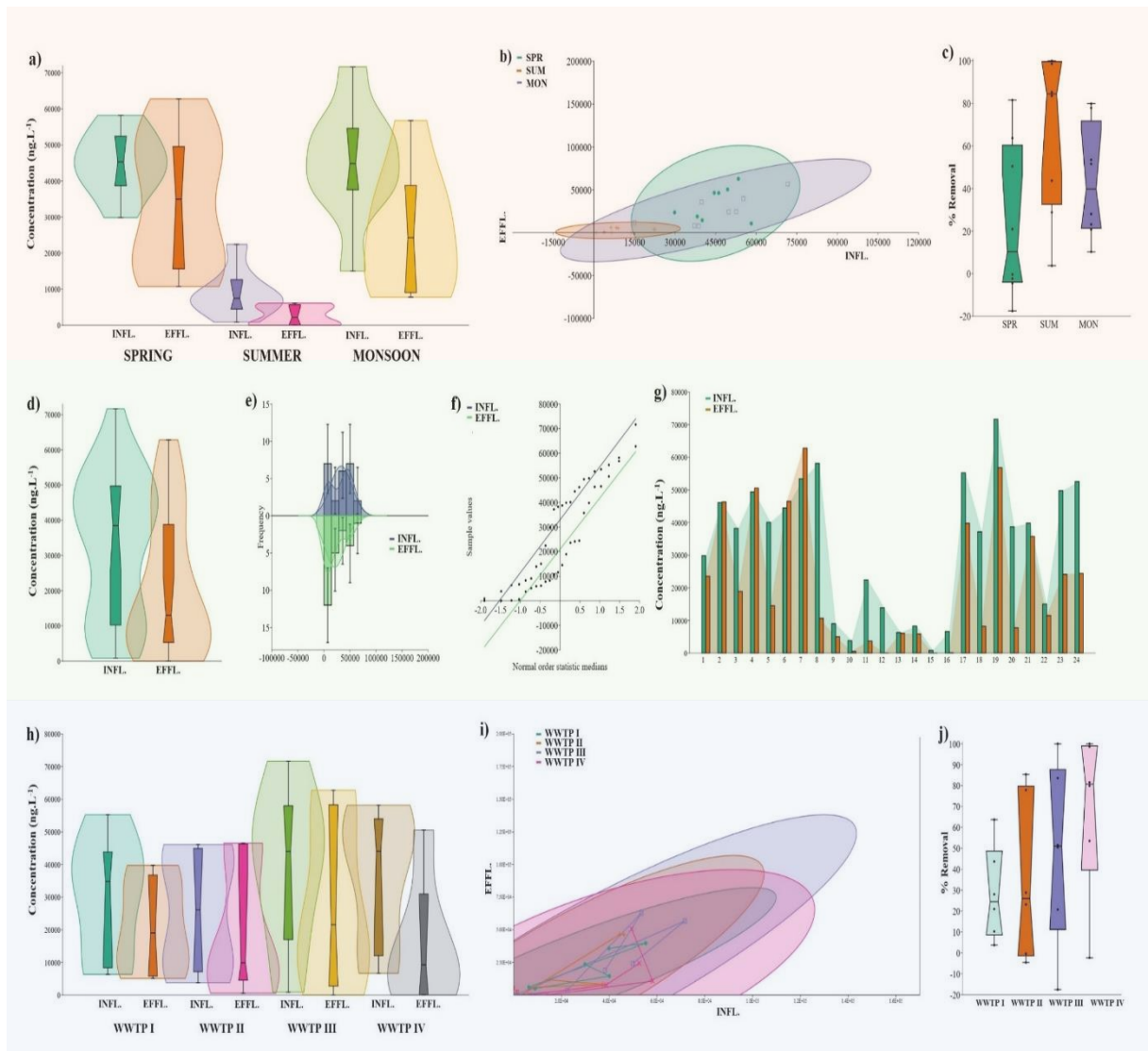
Figure 4.9. Caffeine samples a) Seasonal variation b) Influent effluent linkages across seasons c) Seasonal treatment efficiencies d) Overall variation of influents and effluents e) Histogram Biplots for influents and effluents f) Samples and Normal order statistics medians variation g) Time series for samples variations (influents and effluents) h) Comparative account of influents and effluents across treatment systems i) Van krevelen plots for treatment systems and j) Removal efficiencies of various treatment systems.

The overall influent and effluent for caffeine samples showed some significant variation (F=4.198; p=0.046), which suggests decisive lower evidence for either equal or unequal means based on ANOVA. Tukey's pairwise analysis showed a difference between the means (p=0.046). Mann-Whitney pairwise and Dunn's Post hoc tests also showed a significantly high difference between influents and effluents (p=0.04). The tests for normality distribution showed the influents samples to be normally distributed. The univariate statistics showed the lowest kurtosis and skewness among all samples for which the data set is mostly a normal distribution. The results from the overall influents and effluents values of caffeine are provided as box and violin plots, bi-histograms showing the ideal distribution and the present data distribution, samples variation with normal order statistical medians, and time series of the influents and effluents variations are shown in Figure **4.9(d-g)**.

A comparative account of the four treatment systems for caffeine showed substantial evidence for equal means and insignificant differences (F=0.92; p=0.49). Mann-Whitney and Dunn's post hoc tests also indicated no significant variation between WWTPs influents and effluents (p>0.05). Except for WWTP-II effluent samples, all of the data sets for the treatments are normally distributed. The univariate statistics showed the lowest kurtosis and skewness among all samples for which the data set is mostly a normal distribution. No significant difference was observed between the removal efficiencies, with substantial evidence for equal means (F=1.427; p = 0.264). The tests for normal distribution indicated normally distributed data for all the WWTPs. The WWTPs influents and effluents variations with their removal efficiencies are shown in Figure **4.9(h-j)**.

Carbamazepine (anticonvulsant) was detected in lower concentrations among studied compounds in the WWTPs. Maximum average concentrations for carbamazepine were observed in spring (12 ngL^{-1}), followed by summer (11 ngL^{-1}) and monsoon (6 ngL^{-1}) in the influents of the WWTPs. Average concentrations in spring and summer were found slightly higher than monsoon season. The maximum concentration for the compound was recorded as 51 ngL^{-1} at WWTP-I in May. In the effluents, the compound was either detected in low concentrations or not detected at the WWTPs. Similar to the influents, the average concentration for the compound in monsoon was found lower than in spring and summer in effluents at the WWTPs. The maximum concentration for the compound was detected as 43 ngL^{-1} in March at WWTP-II.

Statistical data treatment for the carbamazepine seasonal samples showed no significant variation between the influent and effluent samples (F=0.62; p=0.67), which shows strong evidence for equal means. Mann-Whitney and Dunn's post hoc tests also indicated no significant variation between influents and effluents for different seasons (p<0.05). The tests for normality distribution showed a standard Gaussian distribution (p>0.05) for spring and monsoon influent samples. The univariate statistics analysis showed relatively higher kurtosis (6.6) and skewness (2.53) for summer influent samples. The seasonal variation of the carbamazepine in wastewater samples are being shown as box and violin plots indicating the data spread with whiskers and the distribution across the mean elucidated in Figure **4.10a**. Figure **410b** shows the xy scatter plot and interaction between the influents and the effluents across seasons within the 95% confidence ellipses. The seasonal removal efficiencies are represented with whisker plots in Figure **4.10c**.

The overall influent and effluent for carbamazepine samples showed no significant variation (F=1.668; p=0.2), which suggests no evidence for either equal or unequal means based on ANOVA. Mann-Whitney pairwise and Dunn's post hoc tests also showed no significant difference between influents and effluents (p=0.05 or lower). The tests for normality distribution showed both influents and effluents to be non-normally distributed. The univariate statistics showed the highest kurtosis (6.85) and skewness (2.66) for effluent samples for which the data set is mostly a non-normal distribution. The results from the overall influents and effluents values of carbamazepine are provided as box and violin plots, bi-histograms showing the ideal distribution and the present data distribution, samples variation with normal order statistical medians and time series of the influents and effluents variations are shown as Figure **4.10(d-g)**.

A comparative account of the four treatment systems for carbamazepine showed strong evidence for equal means and insignificant differences (F=1.07; p=0.39). However, Dunn's post hoc test indicated a significant variation between WWTP-IV influents and WWTP-III effluents (p=0.02). WWTP-II, II, and IV influents and WWTP-IV effluent showed a normal distribution. The univariate statistics showed the highest kurtosis (5.75) and skewness (2.38) for WWTP-III effluent samples for which the data set is mostly a non-normal distribution. No significant difference was observed between the removal efficiencies, with substantial evidence for equal means (F=0.251; p = 0.859). The tests for normal distribution indicated

standard Gaussian distribution data for WWTP-I, II, and IV. The WWTPs influents and effluents variations with their removal efficiencies are shown in Figure **4.10(h-j)**.
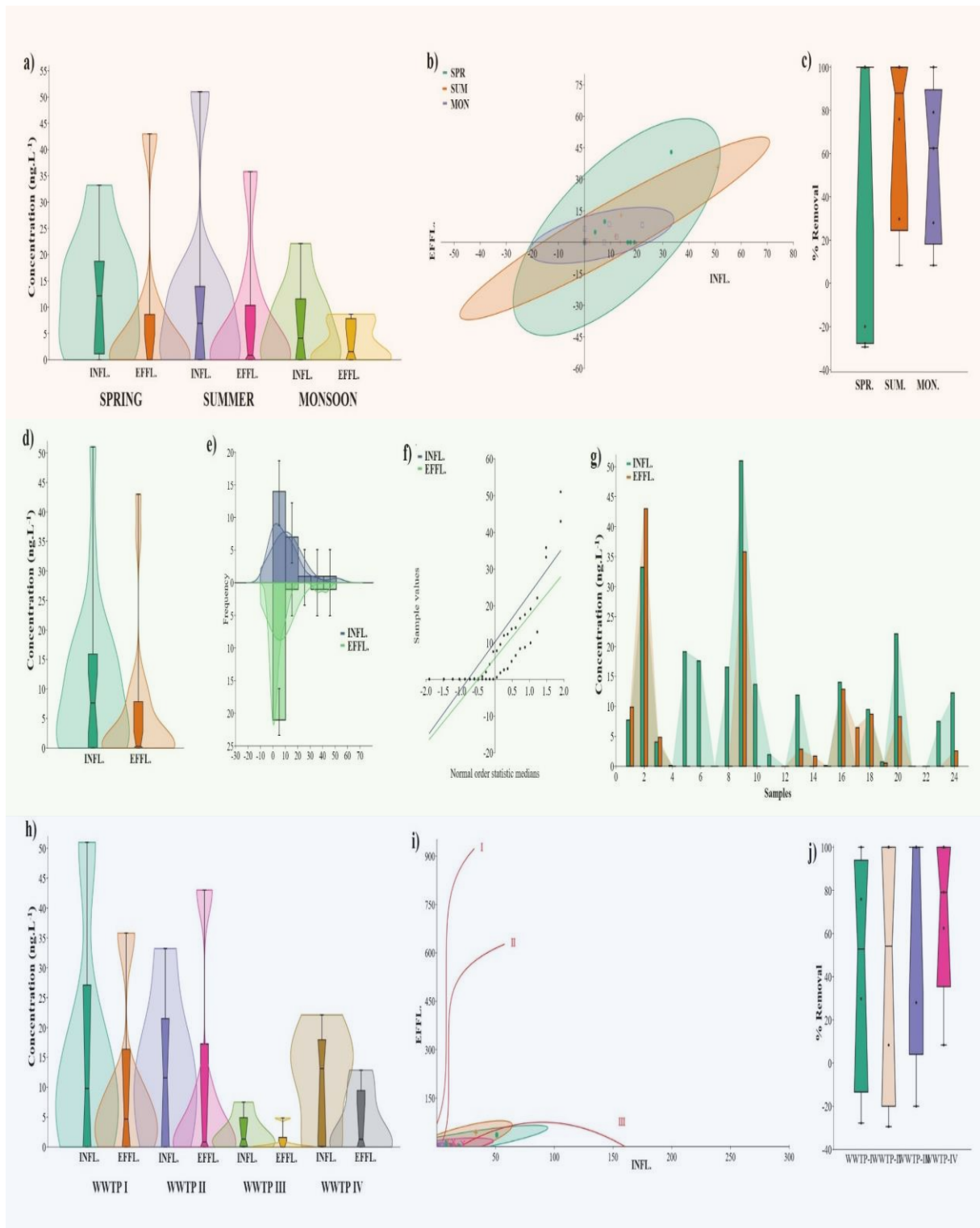
Figure 4.10. Carbamazepine samples a) Seasonal variation b) Influent effluent linkages across seasons c) Seasonal treatment efficiencies d) Overall variation of influents and effluents e) Histogram Biplots for influents and effluents f) Samples and Normal order statistics medians variation g) Time series for samples variations (influents and effluents) h) Comparative account of influents and effluents across treatment systems i) Van krevelen plots for treatment systems and j) Removal efficiencies of various treatment systems.

4.3.4 EDCs seasonal variation

Numerous researchers have studied seasonal variations and trends of PPCPs and EDCs in WWTPs across different locations of the world (Mohapatra et al., 2016; Singh & Suthar, 2021; Sun et al., 2016). These studies have been conducted to figure out the seasonal effect on their loading and removal at treatment facilities. Earlier studies have reported lower concentrations of EDCs in the influent during monsoon as compared to other seasons (Singh & Suthar, 2021; Sun et al., 2016; Yu et al., 2013). These low levels of these compounds in the wet season as compared to other seasons are attributed to the dilution by the precipitation during the wet season (Ternes, 1998). However, in this study, EDCs concentrations in the WWTPs showed a contrasting trend with respect to seasons. The maximum concentrations of EDCs were detected in the WWTP influent during monsoon as compared to spring and summer. High EDCs in the wastewater during monsoon could be attributed to their runoff from various non-point potential sources (landfill waste, sludge from WWTPs, and livestock excrement) in the area. As the city resides in the hilly terrain, so based on drainage the movement and accumulation of EDCs from these sources to the low-lying treatment facilities are prevalent through high surface runoff during the precipitation. The average TCS concentrations at the WWTPs inlets were 66, 52, and 27 ngL^{-1} during monsoon, spring, and summer, respectively. Similarly, the average estrone concentrations at the inlets of the WWTPs were 78, 39, and 18 μgL^{-1} during monsoon, spring, and summer, respectively. The maximum concentration of TCS (214 ngL^{-1}) and estrone (123.9 μgL^{-1}) has been witnessed at WWTP-IV and WWTP-III, respectively in August (monsoon). A higher treatment of TCS (88%) and estrone (50%) was witnessed with WWTP-I which is based on C-Tech process, that encompasses excess aerated condition and efficient biodegradation of these compounds in a single stage. Interestingly, a lower treatment efficiency for the WWTPs-III and IV can be due to a relatively high influent concentration of the EDCs. Incidence of larger concentrations of EDCs in the influent of WWTP–III, and IV, i.e. wastewater generated from an academic institution can be possibly due to higher usage of personal care products in the student hostels and a possibility of lower degradation of these compounds due to a shorter residence time (time of transport) for the institution as compared to the city samples, that can be in the city sewers from hours until days before being pumped into the city WWTPs.

In the effluent water, the average TCS concentrations were 34 (max.), 19, and 3 ngL^{-1} during monsoon, spring, and summer, respectively for the WWTPs. Nonetheless, the average effluent estrone concentrations were 44.5, 39.3, and 4.4 μgL^{-1}, for spring, monsoon, and summer,

respectively. Interestingly, the soaring of estrone concentration in the effluents as compared to influents, especially during the spring season is a unique phenomenon. This soar in effluent concentrations is due to the frequent negative removal rates observed for estrone in the spring season at the WWTPs. This negative removal efficiency of estrone at the plants might be to the decoupling of estrogen conjugates, and oxidation of 17β-estradiol to estrone by the microorganisms (Ting & Praveena, 2017). Moreover, similar trends were observed for influents and effluents at the WWTPs, where the average EDCs concentrations were higher during the monsoon season than in spring and summer. The studied EDCs concentrations detected in various seasons in WWTPs influent and effluent have been provided in niceties in the Appendix section (A3).

The seasonal data analysis for TCS abundance in the influent samples collected from various WWTPs, did not show any significant difference in the concentration (One-way ANOVA: $F=1.019$; $p=0.37$). The other tests i.e. Tukey's pairwise test, Kruskal-Wallis test ($p=0.4839$: No statistical difference between the sample medians), Mann-Whitney pairwise analysis and Dunn's post hoc analysis also resulted in similar inference for the influent TCS samples (details provided in the Appendix section-A4). For the effluents, similar trends were observed (ANOVA: $F=1.316$; $p=0.2896$), where no significant difference was observed for the samples across seasons. Tukey's pairwise test, Kruskal-Wallis test ($p=0.3848$: No statistical difference between the sample medians), Mann-Whitney pairwise analysis and Dunn's post hoc analysis also resulted in similar inference for the effluent TCS samples (details provided in the Appendix section-A4). Figure **4.11a** depicts the changes in the TCS concentration for WWTPs (I-IV) influents and effluents, showing bar charts with silhouette. The distribution of the WWTPs water samples data representing TCS concentrations seasonally have been provided as violin and box plot integrated diagrams (Figure **4.11b**), which depict the variation in the data set and possible skewness and kurtosis. Figure **4.11c** indicates the treatment efficiencies in terms of % removal across seasons. The 95% ellipse indicating the correlation between the input and effluent TCS concentrations is shown in Figure **4.11d**. Figure **4.11e** indicates the treatment efficiencies of the various treatment technologies studied in terms of % removal across different locations. Data spread and dispersion, with the measure of central tendencies, are depicted in Figure **4.11f**. In addition, the bar charts (Figure **4.11g**) depicting the mean standard error and deviation for the influents and effluents across various WWTPs have been also elucidated.
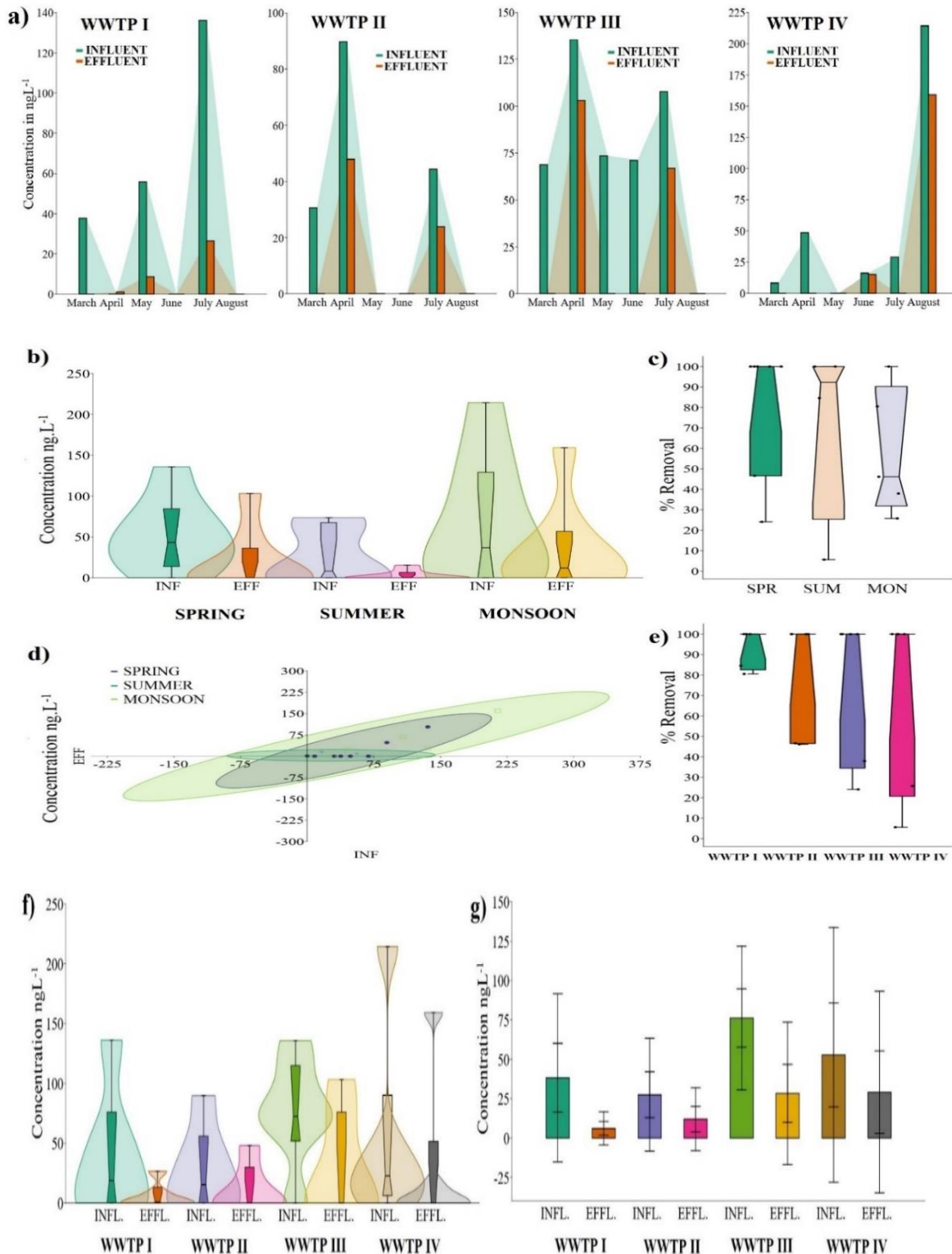
Figure 4.11. TCS samples a). Barcharts with silhoutte depicting influent and effluent concentration (ngL^{-1}) variations inferring treatability over months for WWTP I-IV, b). Seasonal variations of influents and effluents concentration of TCS, c). % removal of TCS in various seasons, d). Influent and effluent relationships across various seasons, e). % removal of TCS across different WWTP, f). Integrated violin and box plots for influent and effluent samples for WWTP I-IV showing the nature of distribution and extent of spread and g). Bar chart for influent and effluent samples for the various WWTP types indicating errors and standard deviation.

The seasonal comparison between the influent and the effluent concentrations for TCS during spring, summer, and monsoon (Mann-Whitney pairwise analysis) showed effluent samples from the summer season significantly varying from other samples (p=0.0072). The same was also observed with Dunn's post hoc results (p=0.0085). Stirringly, there was no significant difference in the treatment efficiencies based on % removal of TCS (ANOVA: F=5.045; p=0.4133). Tukey's pairwise test, Kruskal-Wallis test (p=0.3261: no statistical difference between the sample medians), Mann-Whitney pairwise analysis, and Dunn's post hoc analysis also resulted in similar inference for the effluent TCS samples (details provided in the Appendix section-A4).

Influent estrone concentrations during the various seasons showed a significant difference between and within the samples corrected seasonally (F=8.094; p=0.0025). Especially the summer (p=0.0019) and the monsoon (p=0.45) samples were statistically different from the other samples as per Tukey's pairwise analysis. The analysis of variance (ANOVA) conducted through the Mann-Whitney pairwise test and Dunn's post hoc analysis showed that the monsoon samples were very different from the summer samples (p=0.00078 i.e. p<0.001), and the summer samples were significantly different from the spring samples (p=0.04 i.e. p<0.05) indicating a phenomenal difference in both occurrence and treatability. This can be due to multiple reasons, i.e. interconversion of steroidal hormones owing to changes in the redox environment, as under transitions from aerobic to anaerobic conditions, there is a greater chance for the transformation of 17α-estradiol, 17β-estradiol to estrone especially in sulphur and nitrate limiting conditions. Similarly, the seasonal variability of the effluent samples shows a great statistical difference in the concentrations (ANOVA: F=13.49; p=0.00017 i.e. p<0.001). In the effluent estrone concentrations, a significantly higher difference was marked between the spring and the summer (Tukey's pairwise analysis: p=0.00029 i.e. p<0.001), moreover a phenomenal difference was also witnessed between monsoon and summer (Tukeys pairwise analysis: p=0.00123 i.e. p<0.01) owing to abiotic and abiotic factors aided by high temperature. However, Mann-Whitney and Dunn's post hoc tests showed a very clear statistical difference between the seasonal estrone concentrations a). spring and summer (p=0.00034) and b). summer and monsoon (p=0.0018), indicating temporal variability due to seasonality and differential treatment activities owing to physicochemical environments and microbial activity.

Figure **4.12a** depicts the changes in the estrone concentration for WWTPs (I-IV) influents and effluents, showing bar charts with silhouette and varying concentrations with every sampling.

The distribution of the WWTPs water samples representing estrone concentrations seasonally have been provided as violin and box plot integrated diagrams (Figure **4.12b**), that indicate the variation in the data set detailing the extent of skewness and kurtosis. Figure **4.12c** indicates the treatment efficiencies in terms of %removal across the season (spring, summer, and monsoon). The 95% ellipse indicating a possible correlation between the input and effluent estrone concentration is elucidated in Figure **4.12d**. Figure **4.12e** indicates the treatment efficiencies of the various treatment technologies studied in terms of % estrone removal across different locations. The data spread and dispersion, with the measure of central tendencies, are depicted in Figure **4.12f**. In addition, the bar charts (Figure **4.12g**) depicting the mean, standard error, and deviation for the influents and effluents estrone concentration across various WWTPs have been also shown.

The samples involving estrone concentrations in wastewaters across influents and effluents also showed a wide variation (ANOVA: F=8.463; p=0.000023 i.e. p<0.0001; Appendix section-A5). This was also established when other tests have been applied, indicating marked seasonal impacts in the wastewater estrone concentrations along with the treatment abilities of the four treatment systems chosen. It becomes imperative to learn whether the spatiotemporal variation in the estrone concentration is mostly to do with seasonality or treatment, and therefore needs more data sets for future factorial and interaction analysis. This extends the scope of the present study for more frequent sampling and consequent statistical data treatment. This exercise might eventually aid in the development of a model that will be able to predict the effluent estrone concentration with transitions in space, season, and treatment as a function of time. It is interesting, to note that among the four treatment systems, there has been a strikingly high statistical difference in the treatment efficiency (ANOVA: F=8.463; p=0.0000132), which can be owing to a multitude of factors based on physicochemical and redox environments, anthropogenic factors and conducive environment for estrone to estradiol and estriol interconversions. WWTP-IV showed uniqueness and a phenomenal difference in the treatment ability (p=0.045, Mann-Whitney pairwise analysis) with hyperaccumulation of estrone that brought down the treatment levels to -293% than other WWTPs plausibly due to the aforementioned reasons for its hyperaccumulation upon prior interconversions. Based on the nature and type of treatment, hormones can interact with the different bed materials (abiotic) and microbes (biotic) under aerobic/anaerobic conditions (different redox conditions). Under such anaerobic conditions, other forms of female estradiol hormones such as 17α and β get converted to estrone, possibly leading to hyperaccumulation of estrone (Mashtare et al.

2013). Such types of treatments can cause to be a source of estrone via isomeric and abiotic interconversion resulting in negative treatment. These reasons ought to be tested and validated, with an enhanced collection of spatiotemporal data, as it is critical for the ecological integrity of the aquatic systems post-discharge of the effluents into surface and groundwater.
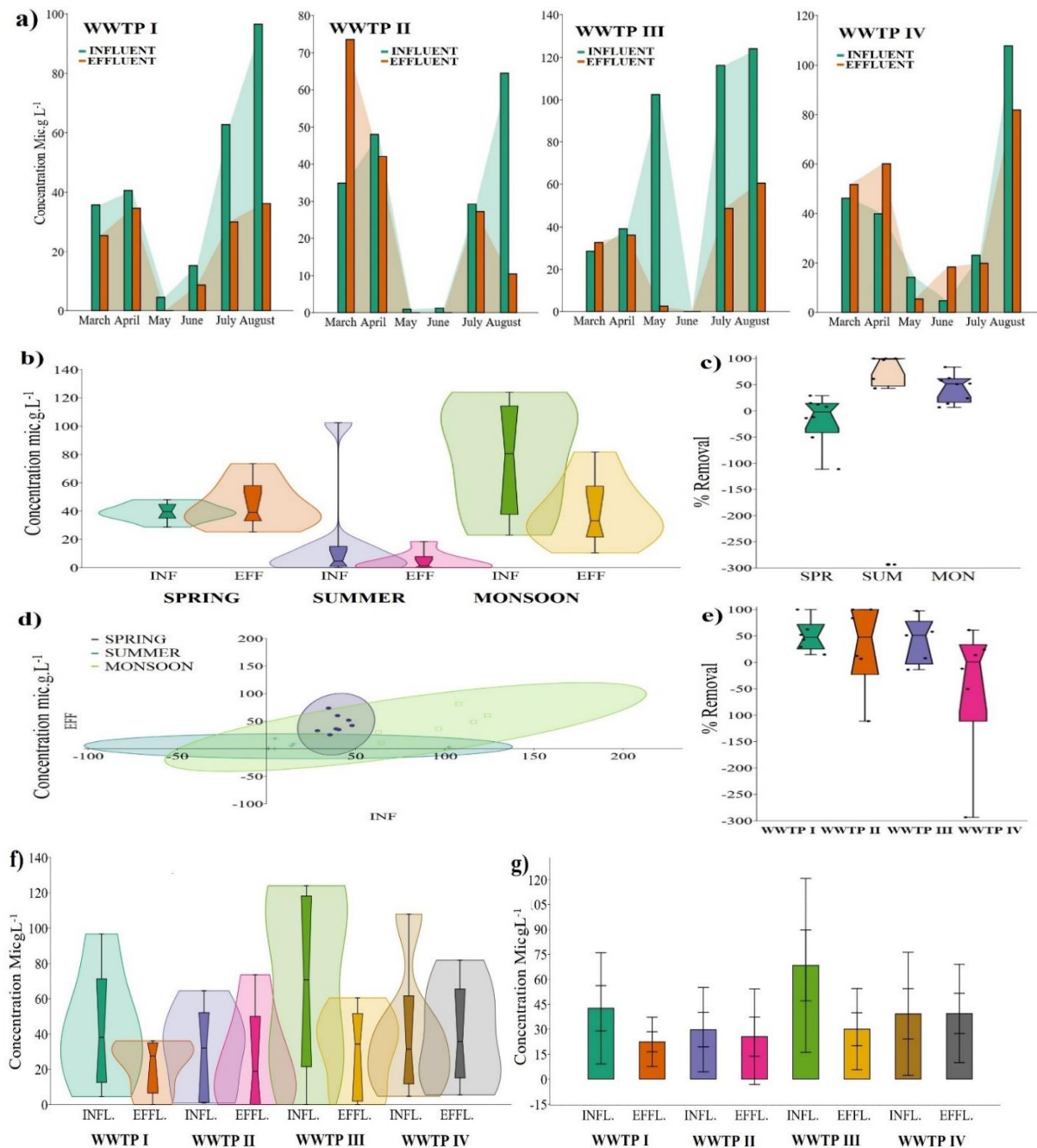
Figure 4.12. Estrone samples a). Bar charts depicting influent and effluent concentration (µgL^{-1}) variations over months for WWTP I-IV, b). Seasonal variations of influents and effluents concentration of estrone, c). % removal of estrone in various seasons, d). In influent and effluent relationships across various seasons for estrone samples e). % removal of estrone with different WWTPs, f). Integrated violin and box plots for influent and effluent samples for WWTP I-IV and g). Bar chart for influent and effluent samples for the various WWTP I-IV.

4.3.5 PPCPs removal

Various treatment processes have different removal efficiency for PPCPs, and it varies from compound to compound. As mentioned earlier, 4 WWTPs working on 3 different secondary treatment processes, i.e., C-Tech, SBR, and aeration and fluidized media oxidation were studied in this study. The average removal of total PPCPs occurred highest at WWTP-IV (71%), followed by WWTP-III (56%), WWTP-I (44%), and WWTP-II (41%). The results showed different removal efficiencies at various WWTPs, which might be due to variable PPCPs load in influent, daily wastewater load, hydraulic retention time (HRT) rate, adsorption and biological degradation rate of PPCPs, chemical nature of individual PPCPs, difference in population served, meteorological parameters, etc. (Singh & Suthar, 2021b). However, the average removal of total PPCPs was observed highest in the aeration and fluidized media oxidation process, followed by C-Tech and SBR treatments. Additionally, high total PPCPs removals at the WWTPs were observed in summer than in spring and monsoon seasons, indicating a higher biodegradation rate at the plants in the hot season owing to optimum temperature conditions. Mohapatra et al. (2016) also observed similar results with higher removal of pharmaceuticals during summer as compared to other seasons in Indian WWTPs.

The variation in PPCPs removal efficiency at individual WWTPs varied significantly and is represented in the form of box-plot in Figure **4.13(a-d)**. WWTP-I (based on C-Tech process) showed significant removal of various compounds. The highest average removal efficiency at the plant was observed for acetaminophen (98%), sulfamethoxazole (93%), ketoprofen (91%), diclofenac (68%), ciprofloxacin (61%), carbamazepine (44%) and caffeine (28%). Negative removal rates of 27% and 7% were observed for carbamazepine and ciprofloxacin in March (spring) and May (summer), respectively indicating a higher concentration of these compounds in effluent than influent. The increase in concentration could be attributed to the deconjugation of its conjugated metabolite forms (present in influent) to the parent compound during biological treatment at the plant (Kumar et al., 2023).

WWTP- II (based on SBR) also showed considerable removal of the compounds. The highest average removal efficiency at the plant was observed for acetaminophen (98%), followed by ciprofloxacin (75%), ketoprofen (63%), diclofenac (58%), carbamazepine (44%) and caffeine (35%). Similar to the C-Tech treatment system (WWTP-I), negative removal of 29% was recorded for carbamazepine in March (spring) at the SBR plant. In addition, negative removal

rates of 0.3% and 4% were observed for caffeine in March (spring) and April (summer) respectively, again could be attributed to the deconjugation of its conjugated metabolite forms (present in influent) to the parent compound during biological treatment at the plant (Kumar et al., 2023).

WWTP- III and WWTP-IV (both based on aeration and fluidized media oxidation process) showed better PPCPs removal, compared to the WWTP-I and WWTP-II. At WWTP-III, the highest average removal efficiency at the plant was observed for sulfamethoxazole (100%), followed by ketoprofen (95%), acetaminophen (94%), diclofenac (81%), ciprofloxacin (68%), carbamazepine (61%) and caffeine (48%). Similar to WWTP-I, a negative removal rate of 68% was observed for ciprofloxacin at the plant in August. Additionally, negative removal rates of 19% and 17% were observed for carbamazepine (March) and caffeine (April) respectively, similar to what was observed in WWTP-II. Kumar et al. (2022) reported that the highest negative removals were observed for carbamazepine in the conventional WWTPs, globally and might be attributed to the transformation of the conjugated form into the original compound or desorption of PPCPs from the settled or reused sludge. At WWTP-IV, the highest average removal efficiency at the plant was observed for acetaminophen (86%), followed by ketoprofen (83%), carbamazepine (70%), caffeine (68%), diclofenac (59%), ciprofloxacin (56%). Similar to WWTP-II and WWTP-III, a negative removal rate of 2% was also observed for caffeine at the plant in March.

The correlation analysis between the various PPCPs in the wastewater across all influent samples showed strong relationships for acetaminophen with diclofenac (r=0.77) and ketoprofen (r=0.62). In addition, diclofenac was profoundly linked with ketoprofen (r=0.89). Ciprofloxacin was also positively correlated with carbamazepine (r=0.65). The higher-order relationships are elucidated in the boxed correlation matrix plots (Figure **4.14a**). Similarly, for the effluents, a positive correlation was noted between diclofenac and ketoprofen (r=0.69). A low-strength negative correlation was observed for acetaminophen and sulfamethoxazole (r=-0.39; Figure **4.14b**).

Statistical data treatment for the PPCPs samples for the inlets showed a greater statistically significant variation between the influent and effluent samples (F=54.2; p=3.48 X 10^{-36}), which shows highly decisive evidence for unequal means. Tukey's pairwise analysis showed a highly significant difference of the caffeine influents with all other PPCPs (p<<<0.001), Mann-

Whitney and Dunn's post hoc tests also indicated higher significant variation between PPCPs samples (p<<<0.001). The tests for normality distribution showed a non-normal data distribution (p>0.05) for all PPCPs except for caffeine influents. The univariate statistical analysis showed the highest kurtosis (18.38) and skewness (4.12) for sulfamethoxazole samples.

Similarly, the data treatment for the PPCPs samples for the outlets (effluents) showed a greater statistically significant variation between the PPCPs samples (F=26.27; p=1.14 X 10^{-21}), which shows highly decisive evidence for unequal means. Tukey's pairwise analysis showed a highly significant difference in the caffeine effluents with all other PPCPs (p<<<0.001), Mann-Whitney and Dunn's post hoc test also indicated higher significant variation between PPCPs samples (p<<<0.001). The tests for normality distribution showed a non-normal data distribution for all PPCPs (p>0.05). The univariate statistical analysis showed the highest skewness (3.57) for sulfamethoxazole samples and the highest kurtosis (14.09) for ciprofloxacin samples.
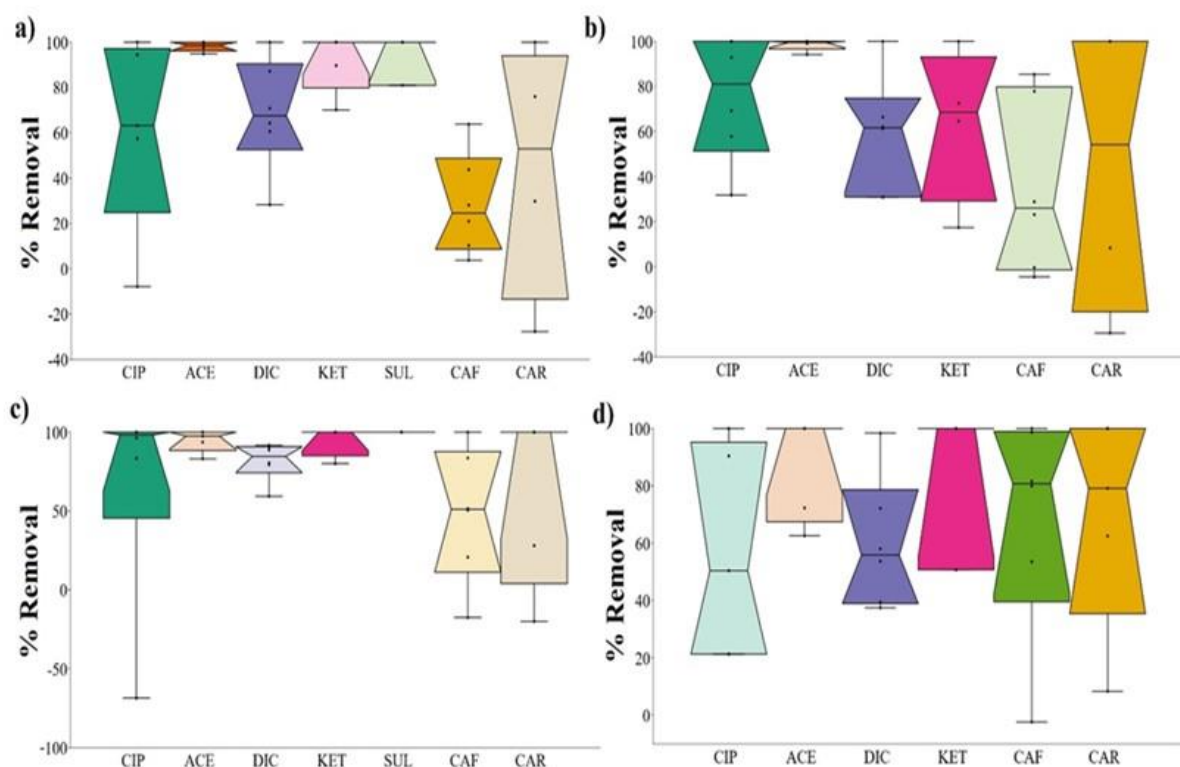
Figure 4.13. Box plot showing variation in removal efficiencies of detected PPCPs in a) WWTP-I (C-Tech process), b) WWTP-II (SBR process), c) and d) WWTP-III and WWTP-IV (aeration and fluidized media oxidation process), respectively.
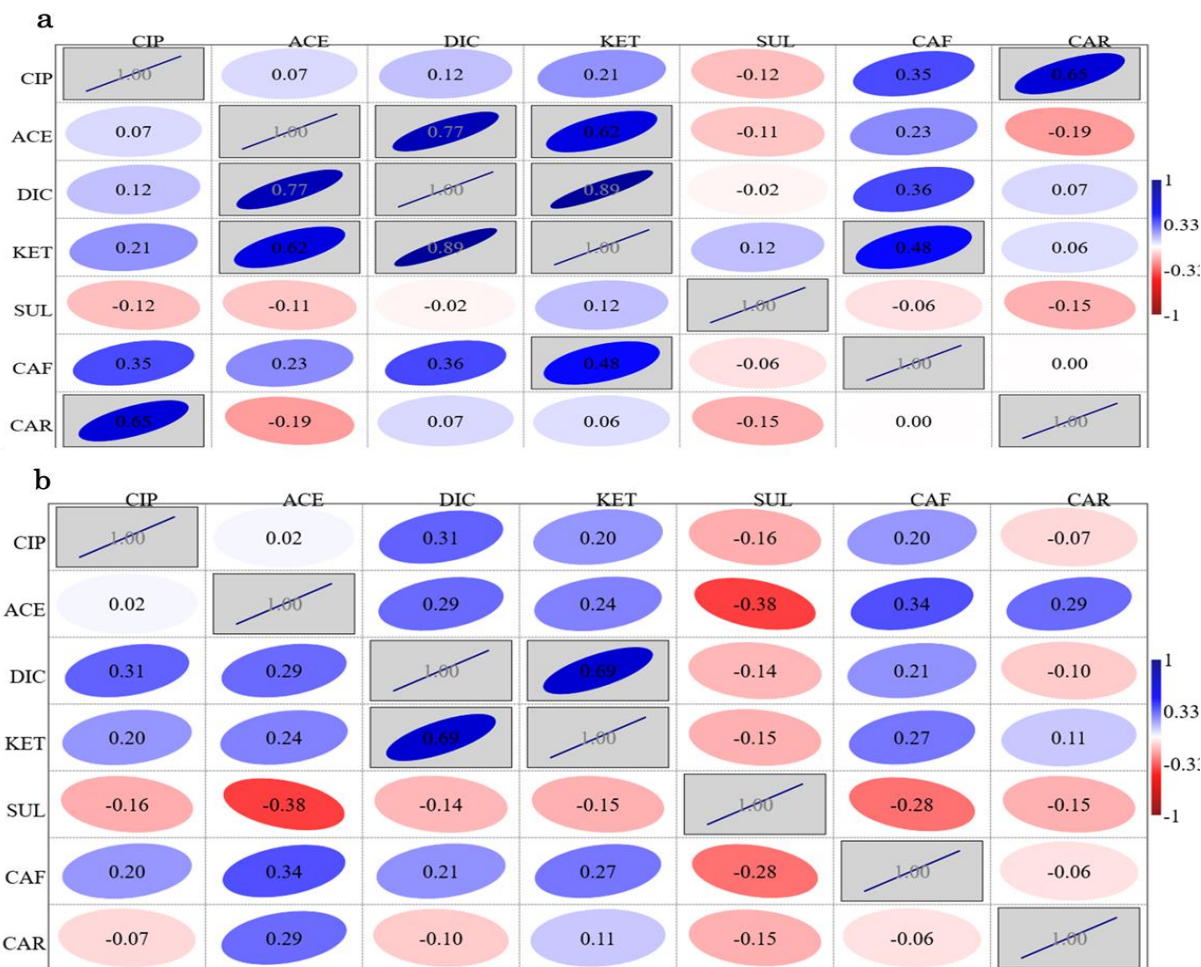
Figure 4.14. Correlation Matrix for PPCPs in a) Influents and b) Effluents. [CIP: Ciprofloxacin, ACE: Acetaminophen, DIC: Diclofenac, KET: Ketoprofen, SUL: Sulfamethoxazole, CAF: Caffeine, CAR: Carbamazepine].

4.3.6 EDCs overall trends, distribution loadings, and removal

The univariate statistics for both EDCs are provided in the Appendix section (A4 and A5). The data dispersion with necessary tests showed most of the data sets were not normally distributed (absence of Standard Gaussian curve). Firstly in the case of TCS, both the influents and the effluents values showed non-normal distribution Shapiro-Wilk (INFL.: p=0.0012; EFFL.: p=2.5×10^{-7}; p<0.05 indicates non-normal distribution); Anderson-Darling test (INFL.: p=0.0029; EFFL.: p=3.6×10^{-11}); Lilliefors test (INFL.: p=0.0021; EFFL.: p=0.0001) and Jarque-Bera test (INFL.: p=0.013; EFFL.: p=3.3×10^{-12}). For estrone samples, the influents concentration showed non-normal distribution except for Jarque-Bera test i.e., but all effluent samples showed normal distribution i.e. Shapiro-Wilk (INFL.: p=0.0138; EFFL.: p=0.123; p<0.05 indicates non-normal distribution); Anderson-Darling test (INFL.: p=0.016; EFFL.:

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p=0.284); Lilliefors test (INFL.: p=0.0047; EFFL.: p=0.5366) and Jarque-Bera test (INFL.: p=0.2701; EFFL.: p=0.4933; Appendix section -A5).

The details of the overall distribution and data dispersion for TCS and estrone as violin and whisker plots are shown in Figures **4.15a$_1$** and **4.15b$_1$**, respectively. A bihistogram indicating the nature of the data distribution and a comparative account of its deviation from the standard Gaussian curve is depicted in Figure **4.15a$_2$**, indicating a higher kurtosis for the effluent samples for TCS but moderate kurtosis and skewness for estrone samples (Figure **4.15b$_2$**). Figures **4.15a$_3$** and **4.15b$_3$** showed the variation of the individual sample values of influents and effluents with the normal order statistical means for TCS and estrone, respectively. The changes in the TCS and estrone concentration as a time series with every sampling event is shown as bar charts with variations represented as silhouette in Figures **4.15a$_4$** and **4.15b$_4$**. The details of the test for normal distribution and normal probability test are provided in the Appendix section (A4, TCS and A5, estrone). The frequency histogram that depicts an ideal normal distribution viz a viz the present distribution also highlights the disparity of the distribution represented as bihistograms for the influent (top) and the effluent (bottom) samples.

The bi-histogram shows a bi-modal distribution in the case of TCS and influents of estrone. However, effluents with estrone samples show a normal distribution (matched remarkably close to the ideal bell-shaped standard Gaussian distribution). The whiskers show 95% confidence for the data. The normal distribution curve compared to the kernel density shows the magnitude and type of deviation for the sample distribution that are skewed with varying kurtosis (Appendix sections- A4 and A5). The bars pointing towards the bottom of the figure correspond to the EDCs influent concentration frequency classes (5 numbers) and the one that projects to the top are the frequency intervals for the EDCs concentration effluent classes. The bi-histogram plots showing distribution charts very clearly indicate the non-normal nature of most of the sample population apparent from the distribution curves fitted in Figure **4.15**. For the effluent samples in WWTPs, the univariate analysis showed a higher kurtosis (6.97) and skewness (2.69) compared to the values from influents. The scatter plots and fittings of the studied sample concentrations with the statistic median values show the extent to which the data is aligned for normality. The bar plots show the unit-wise difference in concentrations of influents and effluents (treatability) across the entire samples showing the range and variations in concentration of samples from influents and effluents with the extent of treatment.

A comparative account of the removal efficiency for the various treatment systems showed no significant difference among the treatment facilities (WWTP-I, II, III, and IV) for estrone ($F=1.586$; $p=0.2258$). Moreover, higher negative removals of 293.46% and 111.22% were recorded for estrone at the WWTPs. Tan et al. (2007) reported higher negative removal efficiency of 219.8% in conventional activated sludge (CAS) based WWTP. Similarly, another study also observed negative removal efficiency of estrone in CAS treatment system (Atkinson et al., 2012). This increase in concentrations of estrone in effluent at the plant may be attributed to the decoupling of estrogen conjugates, particularly sulfate conjugates, or oxidation of 17β-estradiol to estrone by the microorganisms under aerobic conditions (Atkinson et al., 2012; Braga et al., 2005; Nelson et al., 2007). However, the overall samples collected over the period of six months showed no significant difference ($F=2.819$; $p=0.099$) between the means of TCS sample collected i.e., influents and effluents for all the treatment cases (WWTP-I, II, III, and IV).
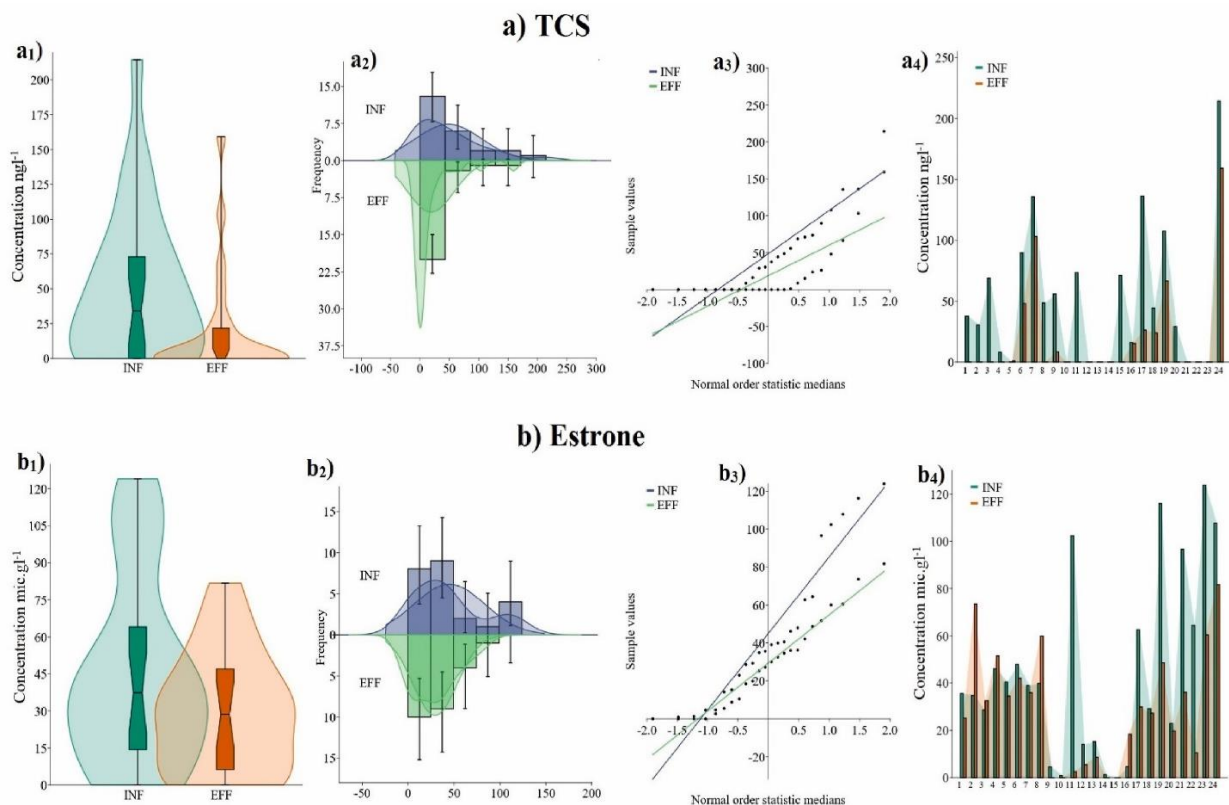
Figure 4.15. Overall influent and effluent characteristics for a) TCS samples – a₁) TCS–distribution (Integrated violin-box plots), a₂) Frequency distribution - high kurtosis and skewness in the effluent samples, a₃) Scatter of data sets aligned with statistic medians and a₄) Bar charts depicting extent of treatment and magnitude of influent and effluent concentrations for the total number of samples and b) Estrone samples – b₁) data set distribution (Integrated violin-box plots), b₂) Bi-histogram showing frequency distribution and bell curve fitting with existing distribution, b₃) Scatter plot of the estrone concentration data set aligned with statistic medians and b₄) Influent-effluent concentration for estrone in wastewater samples for the total number of samples collected and analysed.

Table 4.7. General physicochemical parameters in various studied WWTPs (mgL⁻¹; except pH and EC in units and μScm⁻¹, respectively).

WWTP	Parameter	March Influent	March Effluent	April Influent	April Effluent	May Influent	May Effluent	June Influent	June Effluent	July Influent	July Effluent	August Influent	August Effluent
WWTP-I	pH	7.15	7.27	7.1	7.22	7.25	7.42	6.95	7.15	7.6	7.78	7.4	7.6
	EC	588	556	509	475	587	552	591	560	529	392	524	375
	TDS	422	393	337	321	382	359	390	377	344	271	404	314
	TSS	288	35	305	36	320	41	278	35	240	56	244	43
	BOD	-	-	-	-	-	-	-	-	150	27	153	32
	COD	-	-	-	-	-	-	-	-	245	76	213	72
	Nitrate	-	-	-	-	-	-	-	-	9.25	4.69	12.38	7.95
WWTP-II	pH	7.23	7.44	7.4	7.6	7.55	7.68	7.24	7.4	7.5	8.1	7.4	7.7
	EC	566	539	488	472	535	518	552	530	345	286	465	348
	TDS	410	378	342	331	375	363	380	372	276	220	269	191
	TSS	260	31	295	40	303	34	245	32	255	45	230	36
	BOD	-	-	-	-	-	-	-	-	165	34	145	29
	COD	-	-	-	-	-	-	-	-	270	92	218	80
	Nitrate	-	-	-	-	-	-	-	-	7.85	5.17	11.34	6.04
WWTP-III	pH	7.35	7.55	7.5	7.65	7.62	7.75	7.22	7.4	7.4	7.8	7.3	7.6
	EC	556	520	549	525	515	508	621	593	275	228	330	305
	TDS	385	367	370	338	383	365	410	387	176	158	198	167
	TSS	311	43	298	38	307	39	288	35	235	37	265	49
	BOD	-	-	-	-	-	-	-	-	121	54	85	53
	COD	-	-	-	-	-	-	-	-	160	75	135	77
	Nitrate	-	-	-	-	-	-	-	-	9.53	4.77	10.17	6.23
WWTP-IV	pH	7.52	7.68	7.6	7.8	7.72	7.88	7.35	7.5	7.7	7.9	7.52	7.79
	EC	633	594	540	528	569	541	605	568	213	180	324	306
	TDS	412	401	373	362	388	370	396	381	147	123	239	213
	TSS	303	40	290	45	288	31	265	40	262	61	251	52
	BOD	-	-	-	-	-	-	-	-	78	45	75	40
	COD	-	-	-	-	-	-	-	-	120	62	106	61
	Nitrate	-	-	-	-	-	-	-	-	6.16	4.97	9.84	5.76

- denotes not determined

4.3.7 General physicochemical parameters

Key wastewater quality parameters (pH, EC, TDS, TSS, BOD, COD, and NO_3^-) were analysed in influent and effluent samples to observe the variation of these critical parameters among the studied WWTPs, and their removal efficiency in various treatment-based plants. The results of the analysis for the parameters are shown in Table **4.7.** The pH in influent and effluent ranged between 6.95-7.72 and 7.15-8.10 respectively among the WWTPs. On the other hand, TDS and EC in influent varies from 147-422 mgL^{-1} and 213-633 μScm^{-1}, respectively; whereas in effluent from 123-401 mgL^{-1} and 180-594 μScm^{-1} respectively. The TSS in all influent samples was found to be greater than 200 mgL^{-1}, whereas in effluent samples found to be well below the limit prescribed by Central Pollution Control Board (CPCB), India, i.e., 100 mgL^{-1} for discharge into inland surface water bodies. The average TSS removal was observed as 84%, 86%, 85%, and 83% in WWTP-I, WWTP-II, WWTP-III, and WWTP-IV, respectively.

The high value of BOD_5 and COD in influents in the monsoon (July and August) season indicates a significant load of organic pollutants in the studied WWTPs. The BOD_5 in influents ranged between 75 and 165 mgL^{-1} at the WWTPs. The average BOD removal was observed as 80%, 79%, 46%, and 44% in WWTP-I, WWTP-II, WWTP-III, and WWTP-IV, respectively in monsoon season. The observed removal values indicated that C-Tech and SBR treatment processes (WWTP-I and WWTP-II) showed higher BOD removal capacity than aeration and fluidized media oxidation treatment process (WWTP-III and WWTP-IV). In the effluents, BOD_5 ranged between 27 and 54 mg/L at the WWTPs in monsoon. The BOD_5 in WWTP-I and WWTP-II effluents generally lie below or slightly above the limit prescribed by CPCB, India, i.e., 30 mgL^{-1} for discharge into inland surface water bodies. On the other hand, BOD_5 in WWTP-III and WWTP-IV effluents were found to be well below the limit prescribed by CPCB, India, i.e., 100 mgL^{-1} for discharge on land for irrigation purposes. The COD in influents ranged between 106 and 270 mgL^{-1} at the WWTPs in monsoon. The average COD removal was observed as 67%, 64%, 48%, and 45% in WWTP-I, II, III, and IV, respectively. In the effluents, COD ranged between 61 and 92 mgL^{-1} at the WWTPs in monsoon, which is far below the limit prescribed by standards in India, i.e., 250 mgL^{-1} for discharge into inland surface water bodies. The NO_3^- in influents ranged between 6.16 and 12.38 mgL^{-1} at the WWTPs in monsoon. The average NO_3^- removal was observed as 42%, 40%, 44%, and 30% in WWTP-I, II, III, and IV, respectively which might be due to low nitrification phenomenon occurring in the WWTPs (Singh & Suthar, 2021b). In the effluents, NO_3^- ranged between 4.69

and 7.95 mgL^{-1} at the WWTPs in monsoon, which is well below the limit prescribed by standards in India, i.e., 10 mgL^{-1} for discharge into inland surface water bodies. The results showed that BOD$_5$, COD, and NO$_3^-$ (nutrient) loading in discharged effluents from the WWTPs is majorly in compliance with the standards, thus posing less threat to the environment in regard to these parameters contamination.

4.4 Summary

The present chapter investigated the occurrence, prevalence, and distribution of the nine PPCPs and EDCs in four WWTPs located in the capital city of state Uttarakhand, India, where two WWTPs serve as a treatment point for around 75% of wastewater generated from the city. Among all the studied compounds, diclofenac and caffeine were observed in influents of all the WWTPs. The substantial concentration in influent of all WWTPs demonstrates the excess use of PPCPs in the area. Among the studied PPCPs, caffeine (stimulant) was detected in higher concentrations in influent water. Phenomenally high amount of EDCs has been recently recorded through this study in the influents of the studied WWTPs. Highest-ever concentrations of estrone (123.9 μgL^{-1}) in the influents of the WWTPs have been seen, while relatively lower levels of TCS have been recorded. The total concentration of studied PPCPs in influent and effluent ranged from 1849 to 74187 ngL^{-1} and 22 to 64275 ngL^{-1}, respectively in the WWTPs.

The correlation analysis indicated acetaminophen strong correlation with diclofenac (r=+0.77) and ketoprofen (r=+0.62), diclofenac profoundly linked with ketoprofen (r=+0.89) and ciprofloxacin was positively correlating with carbamazepine (r=+0.65). The tests for distribution showed a non-normal data distribution (p>0.05) for all wastewater PPCPs samples except for caffeine influents. PPCPs samples showed a significant variation between and within the influent and effluent samples (p<<<0.001), which shows highly decisive evidence for unequal means. Significant seasonal variations in PPCPs concentrations were also observed (p<0.001). The results of the EDCs analysed data have shown a non-normal data distribution with bimodal variations as per the statistical studies performed.

Seasonal variations in PPCPs and EDCs concentrations were also observed. Results showed the mean total PPCPs concentrations were detected higher in spring, followed by monsoon and summer in influents of the WWTPs. On the other hand, the mean EDCs concentrations were higher during monsoon season in wastewater samples indicating a significant run-off

component. The average removal efficiency of total PPCPs was observed highest at aeration and fluidized media oxidation-based treatment facilities, followed by C-Tech and SBR plants. The maximum removals were observed for acetaminophen, ketoprofen, and triclosan among different WWTPs. Negative removal rates were observed for four compounds, i.e., ciprofloxacin, carbamazepine, caffeine, and estrone in the WWTPs. Hyperaccumulation post-treatment leading to negative removal of estrone samples was observed in WWTPs, owing to the multitude of factors mostly involving interconversion among steroidal forms. The current study suggests that the WWTPs located in the city, discharging in the non-perennial streams are contributing to a load of emerging contaminants (especially alarmingly elevated levels of EDCs as estrone) in the dry streams bed during the non-monsoon period. This could lead to the concentrated (non-diluted) effluent causing severe threats to the soil, groundwater, and local environment in the area.

CHAPTER 5: SCREENING AND REMOVAL OF PPCPs ALONG *in-situ* RZT-BASED WASTEWATER TREATMENT SYSTEM

5.1 Overview

This chapter primarily focuses on the tracing of organic contaminants (majorly PPCPs) in the wastewater at various stages/processes of the RZT-based WWTP, where quantification of organic contaminants/PPCPs in terms of abundances is reported. Additionally, the characterization of removal efficiency for PPCPs at various stages of the plant is done to conclude the effectiveness of the RZT system as a potential PPCPs remediation approach.

As mentioned in the literature, *in-situ* RZT system studies for the removal of various organic pollutants especially PPCPs are scarce and need more attention. The WWTP in the current study is different from the conventional WWTPs as it is based on the CW system i.e., RZT system, henceforth evaluating the effectiveness of the plant for removal of PPCPs needs to be explored. The plant used in the RZT system is *Canna Indica*, owing to its high biomass production with a fast development rate which led to increased biofilm surface area on its roots as compared to other plant species (Pinninti et al., 2022; Zhu et al., 2018). Moreover, *Canna indica* is presently being studied as a potential option for CWs/RZT, and to date few literatures have discussed the removal of PPCPs using *Canna indica* in the RZT system (Karungamye, 2022).

In addition, lately, the disposal of out-of-date and unused PPCPs in landfills has been identified as the major source of PPCPs in the environment (Mompelat et al., 2009; Yang et al., 2017). Subsequently, these PPCPs enter the leachates in Municipal Solid Waste (MSW) landfills and end up contaminating the surrounding water environment with serious adverse effects. However, the PPCPs occurrence, fate, and removal from landfill leachates have rarely been examined yet, which makes landfill an underestimated source of PPCPs intrusion in the environment (Yu et al., 2020). This knowledge gap could generate an idea to use RZT as a potential treatment system for the removal of PPCPs from landfill leachates. The results from the current study can also be effective in the implementation of the RZT system buffer zone between the landfill site and surrounding water bodies to see the extent of PPCPs removal by the zone, which might be one of the future prospects of PPCPs remediation from landfill sites.

5.2 Materials and Methods

5.2.1 Wastewater treatment plant

We investigated wastewater samples collected from the RZT plant situated at an academic institution (AI) located in Gandhinagar, Gujarat, India. A schematic diagram of the WWTP is shown in Figure **5.1**. The AI treatment plant is basically a decentralized WWTP with no mechanical parts and consumes a negligible amount of energy. The AI treats and recycles its wastewater with minimum use of chemicals employed for treatment. The WWTP has a capacity of 2,360 m^3/day and RZT was equipped as a part of an innovative decentralized wastewater treatment system in the plant that treats all wastewater generated by AI dwellers. The first unit in the plant is a settler tank in which heavy particles and suspended solids present in untreated wastewater were removed. Afterward, wastewater was treated biologically through the anaerobic baffled chamber, where anaerobic degradation of organic matter occurred. In the third stage, the wastewater flowed through a planted gravel filter, namely RZT system, where organic pollutants from the wastewater get absorbed by the roots of the *Canna indica* plant. In the fourth stage, wastewater flowed through a pressure sand filter to reduce turbidity and BOD of the wastewater. In the last step, tertiary treatment was performed through the chlorination process and ultimately the final effluent was pumped to separate storage tanks in water service centers. Presently, the water is pumped directly to irrigation tanks and used for AI irrigation purposes.
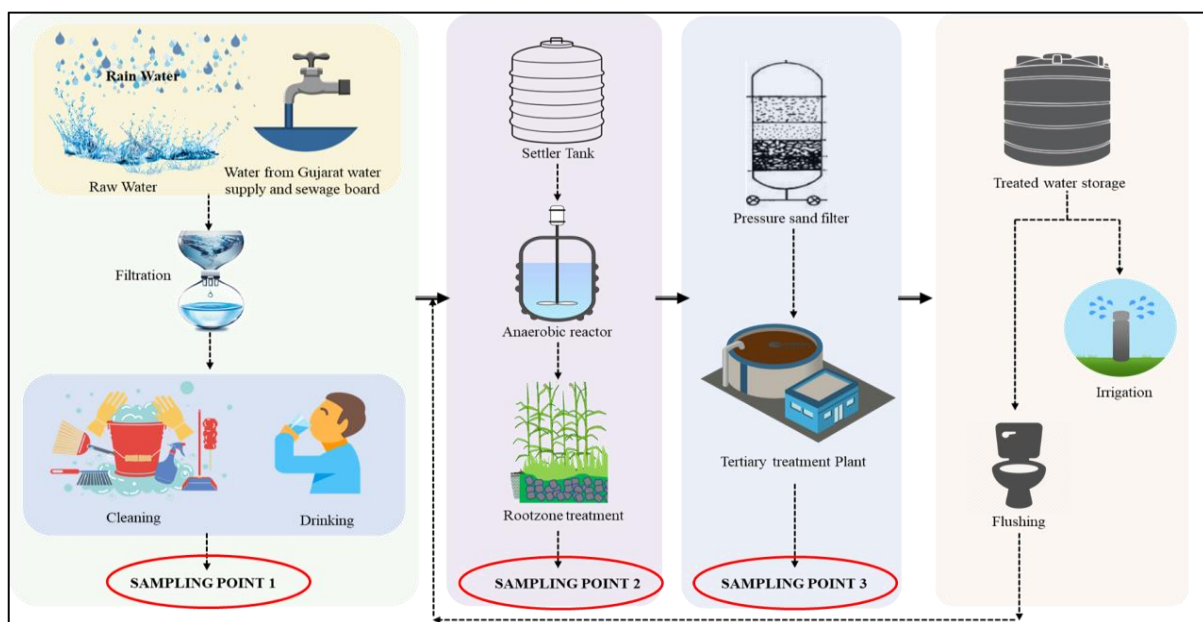
Figure 5.1. Working flow schematic of the studied WWTP present in an academic institution.

5.2.2 Sampling procedure

Wastewater sampling in the form of grab samples was done in the month of October 2019 at the plant. The samples were collected from 3 locations of WWTP i.e., influent (point 1), root zone treatment effluent (point II), and the main effluent (point III) of the plant. Sampling points are also marked in Figure **5.1**. The sampling protocol information is detailed in Chapter 3 (Methodology).

5.2.3 Target compounds

The targeted organic contaminants are from wide categories including the PPCPs, flavoring agents, insecticides, metabolites, nucleotides, and ceramides. The organic contaminants were detected with the help of High-Resolution Liquid Chromatography-Tandem Mass Spectrometry (HRLC-MS) analysis.

5.2.4 SPE procedure and analytical method

SPE was performed in order to load our target analyte into the cartridges. SPE process adopted for the work is mentioned comprehensively in Chapter 3 (Methodology). After SPE, sample extracts were filtered through 0.2-micron filter papers prior to HRLC-MS analysis. Samples were analysed through HRLC coupled with quadrupole time-of-flight (Q-TOF) mass spectrometry (1290 Infinity Ultra High-Performance Liquid Chromatography (UHPLC) System, 1260 infinity Nano HPLC with Chipcube, 6550 iFunnel- Agilent Technologies, USA) equipped with a Pinnacle MAX (4.6 x 250 mm, 4 μm) column. Based on the compound's chemical properties, the target compounds were analysed using electrospray ionization (ESI) in positive or negative mode. The final LC-MS analysis was done using a mobile phase consisting of water (augmented with 0.1% formic acid (FA) and acetonitrile (ACN) gradient elution at a flow rate of 0.3 mLmin^{-1} for 60 min. The mobile phase procedure comprised of five stages with a varying ramp rate. Firstly, there was a gradual increase in ACN from 10% to 30% over 10 min, followed by a constant hold at 30% up to 30 min, rapid increase up to 90% at 50 min, reduced back to 10 % at 52 min, and finally remained constant at this level up to 60 min.

5.2.5 Quality control (QC) and statistical approaches

For QC, field blank samples were used during all the sampling events, and field, procedural and instrumental blanks were used during the analysis. No abundance of organic contaminants

was found in the experimental blanks, portraying no significant contamination during the sampling and analysis procedure. Data were analysed for quantification in terms of normalized abundance for all organic contaminants in the WWTP. The paired sample *t*-test, a statistical procedure was used between influent and effluent (pre and post treatment) at various stages to portray the effectiveness of abundance variations (at a $p < 0.05$ level of significance).

5.3 Results and Discussion

A total of 26 contaminants were found in influent, 37 at root zone treatment, and 29 at effluent of the AI WWTP. The root zone treatment plant consists of the *Canna indica* plant which helps to further treat the effluent before being discharged. The contaminants detected comprise of PPCPs and other organic compounds. The various categories of organic compounds detected in wastewater samples after the analysis are listed in Table **5.1**. The organic contaminants detected in the wastewater matrices in the form of abundance values and subsequently were expressed in the form of normalized abundance i.e., ratio of abundance value to total abundance value. The normalized abundance of the various groups of detected compounds is shown in Figure **5.2**. The full data set for abundances/normalized abundances for detected contaminants at various phases of the WWTP can be found in Tables **5.2, 5.3,** and **5.4**. Out of all detected compounds, key emphasis has been kept on detailed discussion for the occurrence and removal of PPCPs at the various stages of the AI WWTP. The interplay between the physicochemical and biological features of the soil, PPCPs, and *C. indica* plants was thought to be the cause of the variances in the absorption and translocation characteristics displayed by the plants. Additionally, compared to their parent compounds, the metabolites are found to have lower distribution coefficient (log D) values, higher structural stability, and thus, lower removal efficiencies (Lee et al., 2013).

5.3.1 Pharmaceutical compounds in wastewater

Pharmaceutical compounds from various therapeutic classes have been identified in the wastewater phases of the treatment plant. A total number of 17 pharmaceutical compounds/ metabolites were detected at various stages of the WWTP. Homatropine (Anticholinergic), cytisine (stimulant), carbenoxolone (antiulceric), and 4,2',4',6'-tetrahydroxychalcone (antiallergic) were the pharmaceutical compounds detected in the wastewater influent. Out of the above detected pharmaceuticals, cytisine was observed with a maximum normalized

abundance of 0.037, followed by homatropine (0.018), carbenoxolone (0.016), and 4,2',4',6'-tetrahydroxychalcone (0.012).

In the root zone treated effluent, cytisine (stimulant), carbenoxolone (Antiulcer), oxyphencyclimine (Anticholinergic), norpromazine (Antidepressant), norethynodrel (progestin/estrogen), fexofenadine (antihistamine), indinavir (protease inhibitor), estradiol valerate (estrogen) and pregn-4-en-20-one,3b,17-dihydroxy-6a-methyl- (steroid) were the detected pharmaceutical compounds. Cytisine and carbenoxolone were also detected in the root zone effluent, hence portraying the ineffectiveness of RZT for the removal of these pharmaceutical compounds. On the other hand, homatropine and 4,2',4',6'-tetrahydroxychalcone are found to be absent in the root zone effluent matrix showing the potential of this treatment for the removal of these pharmaceutical compounds. Out of the above detected pharmaceuticals, cytisine was observed with a maximum normalized abundance of 0.052, followed by norpromazine (0.028), norethynodrel (0.025), indinavir (0.024), carbenoxolone (0.015), estradiol valerate and pregn-4-en-20-one,3b,17-dihydroxy-6a-methyl- (0.012), oxyphencyclimine and fexofenadine (0.009). It was quite interesting to observe cytisine in higher abundance in the root zone treated effluent as compared with its influent abundance. The negative removal rate of 27% was observed for the compound which may be due to the deconjugation of its metabolites to its parent compound form during the RZT phase in the plant.

In the main effluent of the WWTP, it was quite interesting to observe the presence of drug metabolites apart from the parent pharmaceutical compounds. norpromazine (antidepressant), norethynodrel (progestin/estrogen), metoprolol (beta-blocker), gabapentin (anticonvulsant), estradiol valerate (estrogen), dextroamphetamine (CNS stimulant), 3-hydroxymorphinan (psychoactive) were the detected parent pharmaceutical compounds in the effluent. In the case of metabolites, N,O-didesmethylvenlafaxine (a metabolite of venlafaxine), and 4-oxo-isotretinoin (a metabolite of isotretinoin) were detected in the effluent matrix. The absence of parent compounds of these metabolites in the influent and root zone effluent raises the ambiguity in clearly justifying the reason for their presence in the main effluent matrix as they might be the probable transformation products formed during any of these treatment stages. Cystisine, carbenoxolone oxyphencyclimine, fexofenadine, indinavir, and pregn-4-en-20-one,3b,17-dihydroxy-6a-methyl- were found to be absent in the main effluent, hence portraying potential of pressure sand filter and tertiary treatment (chlorination) for removal of these

pharmaceutical compounds. Fexofenadine was found to be removed at ~100% rate through the stage at the WWTP, which is contrary to the average removal rate (-70%) for the compound reported by Styszko et al. (2021) through the activated sludge process (ASP). Another study reported a positive average removal rate of 49% for fexofenadine through biological nutrient removal (BNR) modules based on ASP (Archer et al., 2017). On the other hand, norpromazine, norethynodrel, and estradiol valerate were present in the effluent matrix showing the ineffectiveness of pressure sand filter and tertiary treatment (chlorination) for removal of these pharmaceutical compounds. Out of the above detected pharmaceuticals, dextroamphetamine was observed with a maximum normalized abundance of 0.208, followed by N,O-didesmethylvenlafaxine (0.055), gabapentin (0.030), estradiol valerate (0.021), norethynodrel (0.021), norpromazine (0.020), 3-hydroxymorphinan (0.018), metoprolol (0.015) and 4-oxo-isotretinoin (0.005) in the main effluent.

5.3.2 Personal care products (PCPs) in wastewater

After analysis, a few PCPs have been identified in the different wastewater phases of the treatment plant. A total number of 5 PCPs were detected at various stages of the WWTP. Phytosphingosine and octadecanedioic acid were the PCPs detected in the wastewater influent. Phytosphingosine is a lipid generally used in skin care products (cosmetics/hair shampoo/conditioners), enhances skin's barrier function that protects the body from allergens and helps in locking the moisture. On the other hand, octadecanedioic acid is often used a colorant for PCPs (cosmetics, tattoo inks, hair dye). Out of the above detected PCPs, phytosphingosine and octadecanedioic acid were observed with a normalized abundance of 0.033 and 0.017, respectively.

In the root zone treated effluent, phytosphingosine, meradimate, and 1-hexadecylamine were the three detected PCP compounds. Meradimate is an ingredient used as a UV light absorber in cosmetics and sunscreens products whereas 1-hexadecylamine is used for producing resin, senior detergent, etc. Phytosphingosine was also detected in the root zone effluent, hence portraying the ineffectiveness of root zone treatment for the removal of this PCP. On the other hand, octadecanedioic acid was found to be absent in the root zone effluent matrix showing the potential of this treatment for the removal of this PCP. Out of the above detected PCPs, phytosphingosine, meradimate, and 1-hexadecylamine were observed with a normalized abundance of 0.108, 0.011, and 0.012, respectively in the root zone effluent. Similar to the

cytisine drug, phytosphingosine was observed in higher abundance in the root zone treated effluent as compared with its influent abundance. A negative removal rate as high as 200% was observed for the compound which may be again due to a high level of deconjugation of its metabolites to its parent compound form during the RZT phase in the plant.

In the main effluent of the WWTP, phytosphingosine, 1-hexadecylamine, and 1-hexadecanoyl-sn-glycerol were the detected compounds. 1-hexadecanoyl-sn-glycerol is a lipid used as an emollient in cosmetic products. Meradimate was found to be absent in the main effluent, hence portraying the potential of a pressure sand filter and tertiary treatment (chlorination) for its removal. On the other hand, phytosphingosine and 1-hexadecylamine were also present in the effluent matrix showing the ineffectiveness of a pressure sand filter and tertiary treatment (chlorination) for the removal of these pharmaceutical compounds. Out of the above detected PCPs, phytosphingosine, 1-hexadecylamine, and 1-hexadecanoyl-sn-glycerol were detected with a normalized abundance of 0.021, 0.015, and 0.037, respectively in the main effluent.

Statistically, a paired sample t-test was conducted for RZT and tertiary treatment stages to determine the effectiveness of these treatment stages on organic contaminants abundance variations in influent and effluent. For the RZT stage, results of the test indicate a significant difference between abundance in influent (M= 507940.1; SD=469906) and abundance in effluent (M= 196030.3; SD= 349537.2); [t(25)= 3.33, p= 0.0013]. The p-value for the test was observed significantly less than a 0.05 significance level and indicated a difference between the means of the samples. We, therefore, reject the null hypothesis as there was a significant difference between the means and conclude that there was a substantial effect of RZT on abundance variations of the organic contaminants i.e., led to a decrease in abundances in effluent portraying their better removal through the RZT system. For the tertiary treatment stage, results of the test also indicate a significant difference between abundance in influent (M= 327542.4; SD= 300135.2) and abundance in effluent (M= 71390; SD= 125511.6); [t(36)= 5.61, p< 0.001]. Similar to the RZT, p-value for the test was observed significantly less than 0.05 significance level and indicated a difference between the means of the samples. We, therefore, reject the null hypothesis here too as there was a significant difference between the means and conclude that there was a substantial effect of tertiary treatment on abundance variations of the organic contaminants i.e., led to a decrease in abundances in effluent portraying their significant removal through the tertiary treatment system.

Table 5.1. Classification of organic compounds detected in the wastewater phases of the AI WWTP.

Category	Compound	Compound type	Environmental Hazards/Concerns	Influent	RZT Effluent	Main Effluent
Pharmaceutical Compounds/Metabolites	Homatropine	Anticholinergic drug	Non-hazardous	+	-	-
	Cytisine	Stimulant	• Acute toxicity, oral • Skin corrosion/irritation • Serious eye damage/eye irritation • Specific target organ toxicity, single exposure; Respiratory tract irritation	+	+ ↑	-
	Carbenoxolone	Antiulceric drug	Non-hazardous	+	+	-
	Indinavir	Antiretroviral protease inhibitor	Non-hazardous	-	+	-
	Fexofenadine	Antihistamine drug	Non-hazardous	-	+	-
	Norpromazine	Antidepressant	• Skin corrosion/irritation • Serious eye damage/eye irritation • Specific target organ toxicity, single exposure; Respiratory tract irritation	-	+	+
	Norethynodrel	Progestin	• Carcinogenicity • Reproductive toxicity	-	+	+
	4,2',4',6'-Tetrahydroxychalcone (THC)	Antiallergic drug	Non-hazardous	+	-	-
	Oxyphencyclimine	Anticholinergic drug	Non-hazardous	-	+	-
	Estradiol valerate	Estrogen	• Acute toxicity (oral, dermal, inhalation) • Carcinogenicity • Reproductive toxicity (effects on or via lactation) • Hazardous to the aquatic environment, long-term hazard	-	+	+ ↑

	Pregn-4-en-20-one, 3b,17-dihydroxy-6a-methyl- (PRG)	Steroidal drug	Non-hazardous	-	+	-
	Metoprolol	Beta-blocker	• Skin corrosion/irritation • Serious eye damage/eye irritation • Specific target organ toxicity, single exposure; Respiratory tract irritation	-	-	+
	Gabapentin	Anticonvulsant	• Skin corrosion/irritation • Serious eye damage/eye irritation, • Specific target organ toxicity, single exposure; Respiratory tract irritation, Reproductive toxicity	-	-	+
	Dextroamphetamine	Central Nervous System (CNS) stimulant	• Flammable liquid • Acute toxicity, oral • Skin corrosion/irritation	-	-	+
	3-hydroxymorphinan	Psychoactive	Non-hazardous	-	-	+
	N,O-didesmethylvenlafaxine (NODMV)	Venlafaxine metabolite	Non-hazardous	-	-	+
	4-oxo-isotretinoin	Isotretinoin metabolite	Non-hazardous	-	-	+
Personal Care Compounds	Phytosphingosine	Lipid used in skin care products (cosmetics/hair shampoo/conditioners)	• Serious eye damage/eye irritation • Hazardous to the aquatic environment (acute hazard, long-term hazard)	+	+ ↑	+
	Octadecanedioic acid	Colorant for personal care products	• Skin corrosion/irritation • Serious eye damage/eye irritation	+	-	-
	Meradimate	UV light absorber in cosmetics and sunscreens products	• Skin corrosion/irritation • Serious eye damage/eye irritation • Specific target organ toxicity, single exposure; Respiratory tract irritation	-	+	-

	1-hexadecanoyl-sn-glycerol (1HSG)	Lipid used as an emollient in cosmetic products	Non-hazardous	-	-	+
	1-Hexadecylamine	Producing resin, senior detergent, anti-caking agent	• Acute toxicity, oral • Aspiration hazard • Skin corrosion/irritation • Serious eye damage/eye irritation • Specific target organ toxicity, repeated exposure • Hazardous to the aquatic environment, (acute hazard, long-term hazard)	-	+	+
Other organic compounds (food additives/flavoring agents, insecticides, metabolites, nucleotides, and ceramides)	Val lys tyr	Metabolite/Amino acid	Non-hazardous	+	-	-
	Tomatidine	Steroid alkaloid	• Acute toxicity, oral • Inhalation	+	-	-
	N-(2-hydroxyethyl)heptadecanamide (NHDA)	Fatty amide	Non-hazardous	+	-	-
	Lys leu glu	Aminoacid/Glutamic Acid/Leucine/Lysine	Non-hazardous	+	-	-
	Gpetnnme(O-14:0/O-14:0) (GPE)	Metabolite	Non-hazardous	+	-	-
	Estriol benzyl ether	Mikromol, Impurity standards, Hormones	Non-hazardous	+	-	+
	Cys cys glu	Peptides	Non-hazardous	+	-	-
	Acetyl tyrosine ethyl ester (ATEE)	Human metabolite	Non-hazardous	+	-	-
	25-hydroxyvitamin D2 25-(beta-glucuronide)/25 hydroxyergocalciferol 25-(beta-glucuronide) (25 HV)	Human Metabolite (Generated in liver)	Non-hazardous	+	-	-

13S-hydroxy-9E,11Z-octadecadienoic acid (13ODA)	Fatty acid	Non-hazardous	+	-	-
3-hydroxy-N-glycyl-2,6-xylidine (3-Hydroxyglycinexylidide) (3HGX)	Anesthetic/Lidocaine Metabolites	Non-hazardous	-	+	-
Norcotinine	Tobacco/Human Metabolite	• Acute toxicity (oral, dermal, inhalation) • Skin corrosion/irritation • Serious eye damage/eye irritation • Specific target organ toxicity, single exposure; Respiratory tract irritation	-	+	-
4-Biphenylamine	Dye intermediate/Rubber antioxidant	• Acute toxicity, oral • Carcinogenicity	-	+	-
Lys ser lys	Antimicrobial Peptide/Metabolite/Amino compound	Non-hazardous	-	-	+
His phe	Aminoacids/Peptides	Non-hazardous	-	+	-
Leu met	Dipeptide metabolite	Non-hazardous	-	+	-
Pterin-6-carboxylic acid (PCA)	Pterin carboxylates/Carboxylic Acids	Non-hazardous	-	+	+
L-Urobilin	Urochrome/Tetrapyrrole compound	Non-hazardous	+	+	+
D-Urobilinogen	Colorless byproduct of bilirubin reduction	Non-hazardous	+	-	-
(+/-)-12-HEPE	Metabolite	Non-hazardous	-	+	+
Fluorescein	Dye/Fluoroscent tracer	• Acute toxicity, oral • Serious eye damage/eye irritation	-	+	+
Madecassic acid	Pentacyclic triterpenoid	Non-hazardous	-	+	-
N-(2R-methyl-3-hydroxy-ethyl)-16,16-dimethyl-	Fatty amide	Non-hazardous	+	+	-

5Z,8Z,11Z,14Z-docosatetraenoyl amine (NMDA)					
13-amino-tridecanoic acid (13ATA)	Fatty acids	Non-hazardous	-	+	+ ↑
3alpha-hydroxy-5beta-chola-8(14),11-dien-24-oic Acid (3AHOA)	Bile acid alcohol derivatives	Non-hazardous	+	+	-
6alpha-hydroxy-3-oxo-5beta-cholan-24-oic Acid (6AHOA)	Bile Acid lipid molecule	Non-hazardous	-	+	-
2R-aminohexadecanoic acid (2AHDA)	Alpha amino fatty acid	Non-hazardous	+	+	-
Tetradecylamine	Accelerators, activators, oxidation agents, reducing agents	• Acute toxicity, oral • Aspiration hazard • Skin corrosion/irritation • Serious eye damage/eye irritation • Specific target organ toxicity, single exposure; Respiratory tract irritation • Specific target organ toxicity, repeated exposure • Hazardous to the aquatic environment, acute hazard, long-term hazard	+	+	-
3beta-hydroxychol-4-en-24-oic Acid (3BHOA)	Bile acid alcohol derivatives	Non-hazardous	+	+	-
Dihydrosphingosine	Ceramide skin lipid membrane	Non-hazardous	-	+	-
(Z)-N-(2-hydroxyethyl)icos-11-enamide (ZHIE)	Anticonvulsant	Non-hazardous	-	-	+
Asn asn asn	Carboxylic/Amino acid	Non-hazardous	-	-	+
GPA(19:3(10Z,13Z,16Z)/0:0) (GPA)	Carboxylic acid	Non-hazardous	-	-	+
Arg val val	Peptides	Non-hazardous	-	-	+

5-octadecylenic acid	Unsaturated fatty acid	• Skin corrosion/irritation • Serious eye damage/eye irritation • Specific target organ toxicity, single exposure; Respiratory tract irritation	-	-	+
12S-hete	Angiogenesis inducing agent/human metabolite	Non-hazardous	+	+	-
N-(2-hydroxyethyl)icosanamide (NHIA)	Fatty amide	Non-hazardous	+	+↑	+
8-hydroxy-17-octadecene-10,12-diynoic acid (8ODA)	Fatty acids	Non-hazardous	-	+	-
Anandamide (22:6, n-3)	Omega 3 fatty Acid	Non-hazardous	-	+	+
Ergosta-5,7,22,24(28)-tetraene-3beta-ol (ETB)	Ergosterols and C24-methyl derivatives	Non-hazardous	+	+	
5-Cholestene-3beta,7alpha,12alpha,24-tetrol (5CT)	Bile acid, alcohol derivative	Non-hazardous	-	+	-
3beta,6beta,7alpha-trihydroxy-5beta-cholan-24-oic Acid (3TCOA)	Bile acid, alcohol derivative	Non-hazardous	-	+	-
15-deoxy-delta-12,14-PGJ2 (15DPG)	Anti-inflammatory lipid mediator	Non-hazardous	-	-	+
11-amino-undecanoic acid (11AUDA)	Fatty acid	Non-hazardous	-	-	+
7,10,13,16,19-docosapentaynoic acid (7DPA)	Lipid	Non-hazardous	-	-	+

+Present in the matrix; -Absent in the matrix; ↑Abundance increment.
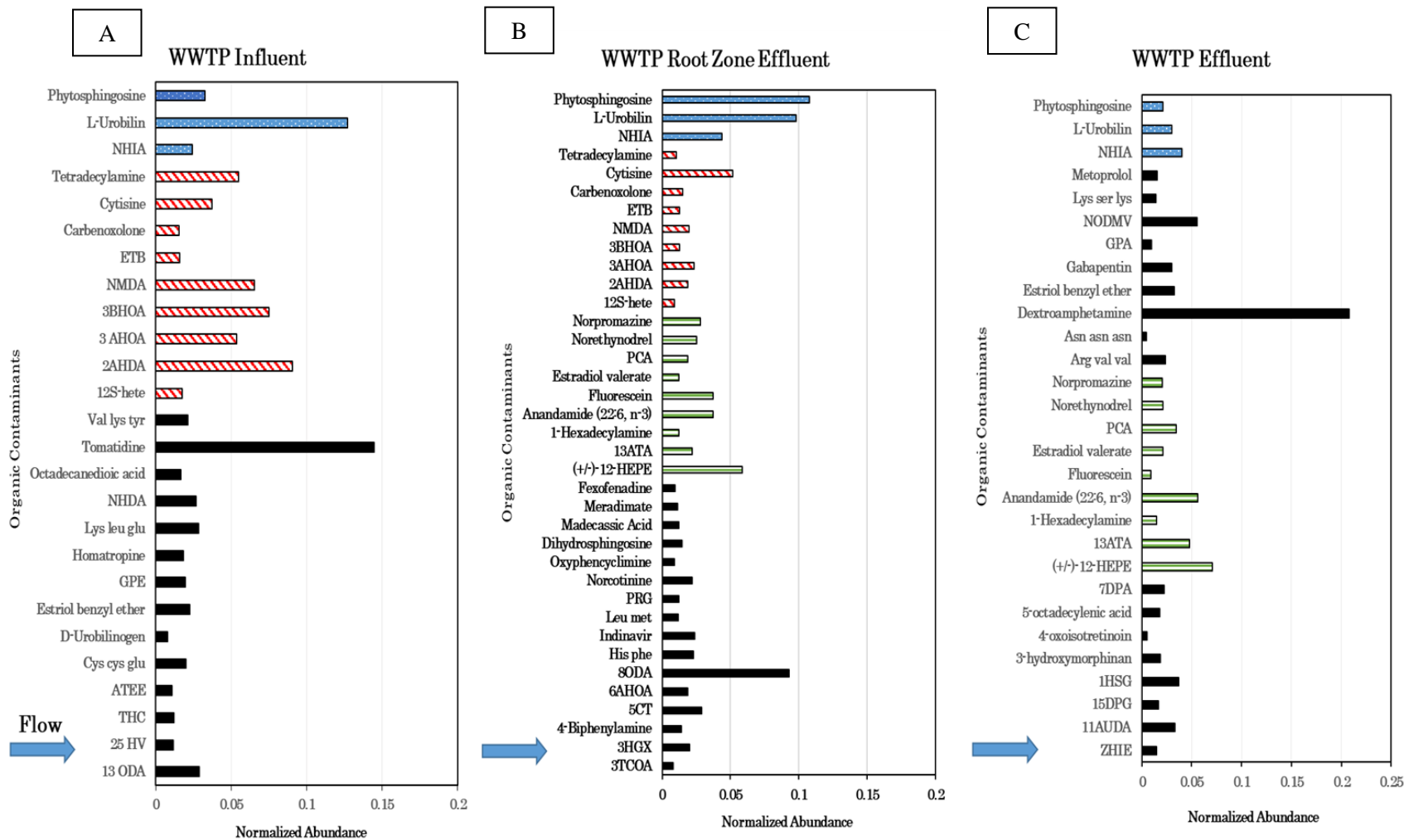
Figure 5.2. Chart showing normalized abundance of the various organic compounds detected in A. AI WWTP Influent B. AI WWTP Root Zone Effluent and C. AI WWTP Main Effluent. Blue bars represent compounds present in all the stages of WWTP, Red bars represent compounds present in influent and root zone effluent of WWTP, and Green bars represent compounds present in root zone effluent and main effluent of WWTP.

Table 5.2. Quantification of various organic contaminants detected in influent of the AI WWTP.

S.No	Organic Compound	Abundance	Normalized Abundance
1	12S-HETE	234108	0.018
2	13S-hydroxy-9E,11Z-octadecadienoic acid	379309	0.029
3	25-hydroxyvitamin D2 25-(beta-glucuronide) / 25 hydroxyergocalciferol 25-(beta-glucuronide)	152568	0.012
4	2R-aminohexadecanoic acid	1196676	0.091
5	3alpha-Hydroxy-5beta-chola-8(14),11-dien-24-oic Acid	706902	0.054
6	3beta-Hydroxychol-4-en-24-oic Acid	990326	0.075
7	4,2',4',6'-tetrahydroxychalcone	161406	0.012
8	Acetyl tyrosine ethyl ester	140759	0.011
9	Carbenoxolone	206760	0.016
10	Cys cys glu	266233	0.020
11	Cytisine	489762	0.037
12	D-urobilinogen	105110	0.008
13	Ergosta-5,7,22,24(28)-tetraene-3beta-ol	212011	0.016
14	Estriol benzyl ether	295498	0.022
15	Gpetnnme(O-14:0/O-14:0)	261252	0.020
16	Homatropine	241548	0.018
17	L-urobilin	1676189	0.127
18	Lys leu glu	377682	0.029
19	N-(2-hydroxyethyl)heptadecanamide	355200	0.027
20	N-(2-hydroxyethyl)icosanamide	319281	0.024
21	N-(2R-methyl-3-hydroxy-ethyl)-16,16-dimethyl-5Z,8Z,11Z,14Z-docosatetraenoyl amine	864456	0.065
22	Octadecanedioic acid	223195	0.017
23	Phytosphingosine	432568	0.033
24	Tetradecylamine	724694	0.055
25	Tomatidine	1912066	0.145
26	Val lys tyr	280884	0.021

Table 5.3. Quantification of various organic contaminants detected in root zone effluent of the AI WWTP.

S.No	Organic Compound	Abundance	Normalized Abundance
1	3-Hydroxy-N-glycyl-2,6-xylidine (3-Hydroxyglycinexylidide)	242256	0.020
2	L-urobilin	1184800	0.098
3	Norcotinine	262132	0.022
4	4-biphenylamine	167093	0.014

5	Cytisine	623518	0.052
6	His phe	274584	0.023
7	Meradimate	137007	0.011
8	Leu met	143669	0.012
9	Estradiol valerate	145475	0.012
10	Pterin-6-carboxylic acid	224816	0.019
11	Carbenoxolone	179820	0.015
12	Indinavir	284861	0.024
13	(+/-)-12-hepe	705588	0.058
14	Norethynodrel	304354	0.025
15	Madecassic acid	149804	0.012
16	Fluorescein	448220	0.037
17	Fexofenadine	112078	0.009
18	Norpromazine	339143	0.028
19	N-(2R-methyl-3-hydroxy-ethyl)-16,16-dimethyl-5Z,8Z,11Z,14Z-docosatetraenoyl amine	234324	0.019
20	13-amino-tridecanoic acid	264631	0.022
21	Pregn-4-en-20-one, 3b,17-dihydroxy-6a-methyl-	145161	0.012
22	Oxyphencyclimine	109943	0.009
23	3alpha-Hydroxy-5beta-chola-8(14),11-dien-24-oic Acid	283675	0.024
24	6alpha-Hydroxy-3-oxo-5beta-cholan-24-oic Acid	224441	0.019
25	Tetradecylamine	123723	0.010
26	3beta-Hydroxychol-4-en-24-oic Acid	153338	0.013
27	Dihydrosphingosine	175736	0.015
28	1-hexadecylamine	147283	0.012
29	12s-hete	108985	0.009
30	Phytosphingosine	1300958	0.108
31	N-(2-hydroxyethyl)icosanamide	525435	0.044
32	8-hydroxy-17-octadecene-10,12-diynoic acid	1119932	0.093
33	Anandamide (22:6, n-3)	451918	0.037
34	Ergosta-5,7,22,24(28)-tetraene-3beta-ol	153772	0.013
35	5-Cholestene-3beta,7alpha,12alpha,24-tetrol	347855	0.029
36	3beta,6beta,7alpha-Trihydroxy-5beta-cholan-24-oic Acid	94299	0.008
37	2R-aminohexadecanoic acid	224441	0.019

Table 5.4. Quantification of various organic contaminants detected in main effluent of the AI WWTP.

S.No	Organic Compound	Abundance	Normalized Abundance
1	(+/-)-12-HEPE	483091	0.071
2	(Z)-N-(2-hydroxyethyl)icos-11-enamide	99731	0.015
3	11-amino-undecanoic acid	224721	0.033
4	13-amino-tridecanoic acid	327441	0.048
5	15-deoxy-delta-12,14-PGJ2	112493	0.016

6	1-hexadecanoyl-sn-glycerol	251999	0.037
7	1-hexadecylamine	99682	0.015
8	3-hydroxymorphinan	125342	0.018
9	4-oxoisotretinoin	33982	0.005
10	5-octadecylenic acid	121642	0.018
11	7,10,13,16,19-Docosapentaynoic acid	152424	0.022
12	Anandamide (22:6, n-3)	384240	0.056
13	Arg val val	163256	0.024
14	Asn asn asn	32583	0.005
15	Dextroamphetamine	1418827	0.208
16	Estradiol valerate	145480	0.021
17	Estriol benzyl ether	221626	0.032
18	Fluorescein	62332	0.009
19	Gabapentin	206217	0.030
20	Gpa(19:3(10z,13z,16z)/0:0)	65422	0.010
21	L-urobilin	205058	0.030
22	Lys ser lys	98563	0.014
23	Metoprolol	104391	0.015
24	N-(2-hydroxyethyl)icosanamide	273541	0.040
25	N,o-didesmethylvenlafaxine	378630	0.056
26	Norethynodrel	142208	0.021
27	Norpromazine	138290	0.020
28	Phytosphingosine	145211	0.021
29	Pterin-6-carboxylic acid	234857	0.034

The removal rates of various organic contaminants through RZT and tertiary treatment phases are depicted in Figure **5.3**. It was quite interesting to observe phytosphingosine in the three-wastewater phases, henceforth implying the incompetency for its removal by all treatment processes of the AI WWTP. The various organic contaminants resistant to all the treatments in the RZT-based WWTP with normalized abundances are shown in Figure **5.4**. Henceforth, all PPCPs except phytosphingosine present in the influent were removed with ~100% removal efficiency by the RZT-based AI WWTP. PPCPs detected in the current study are also reviewed in the literature to get an idea about their removal from other various treatment processes. Treatment processes with their removal efficacy for the PPCPs (detected in the current study) reported by the previous literature are listed in Table **5.5**.
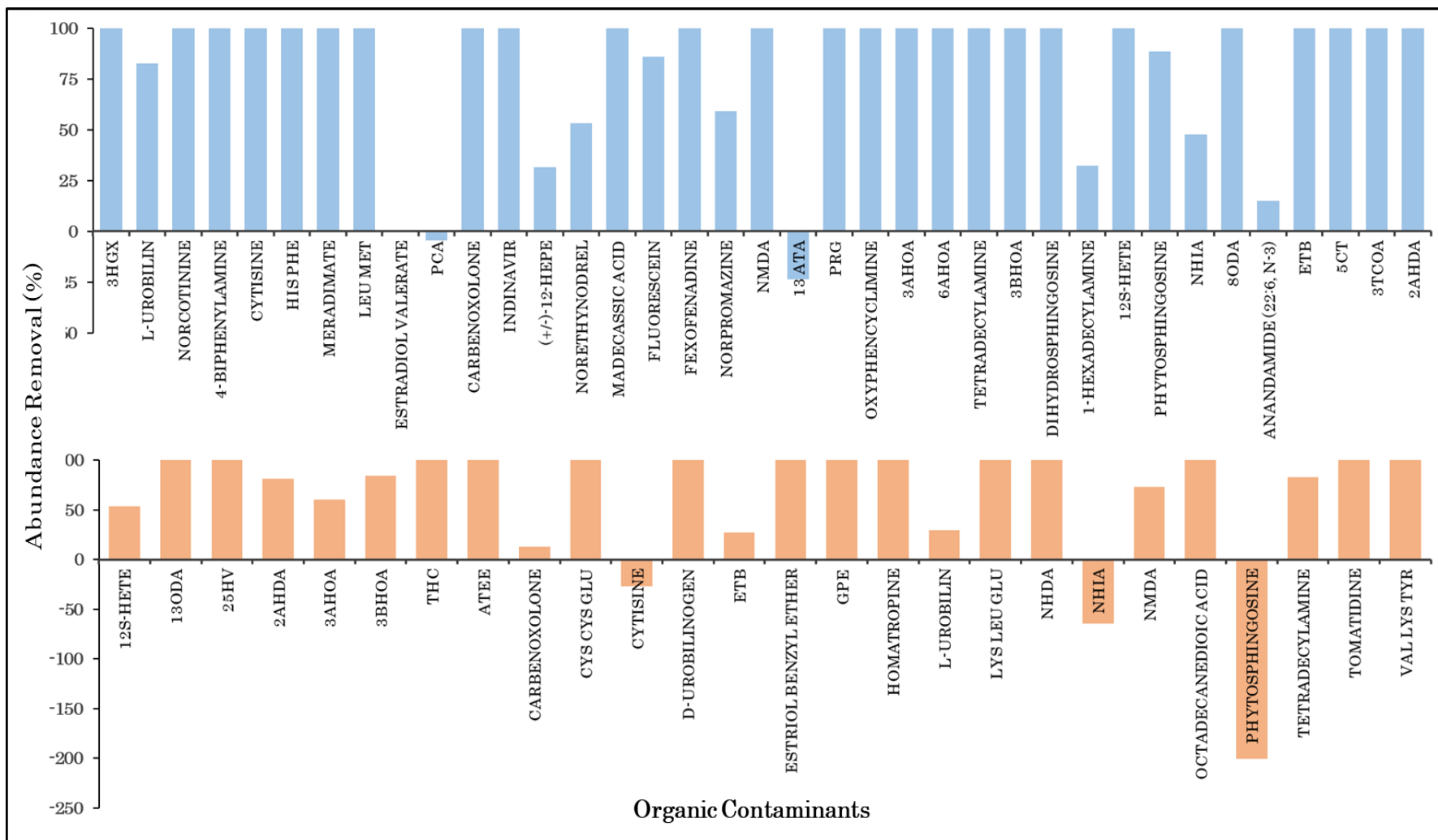
Figure 5.3. Removal rates of various organic contaminants through Tertiary treatment (top) and RZT phase (bottom) in the AI WWTP.

Table 5.5. Relevant PPCPs removal efficiency of the various treatment processes reported by literature.

PPCP	Treatment Process	Influent Concentration/ Load	Effluent Concentration/ Load	Average Removal Efficacy (%)	Reference
Fexofenadine	Combination of biological and chemical processes including a denitrification–nitrification process	542 ngL^{-1}	445 ngL^{-1}	18%	Kosonen & Kronberg (2009)
	Treatment consists of screening, preliminary clarification, conventional activated sludge plant (nitrification, denitrification), phosphate removal, and final clarification	-	-	-70% (negative removal)	Styszko et al. (2021)
	Treatment consists of four biological nutrient removal (BNR) modules based on the activated sludge process.	107.5 ± 88.5 gday^{-1}	54.9 ± 6.2 gday^{-1}	49%	Archer et al. (2017)
Estradiol Valerate	Pilot membrane bioreactor (MBR) system (biological treatment coupled with ultrafiltration)	20.4 µgL^{-1}	2.8 µgL^{-1}	86.1%	Helmig et al. (2005)
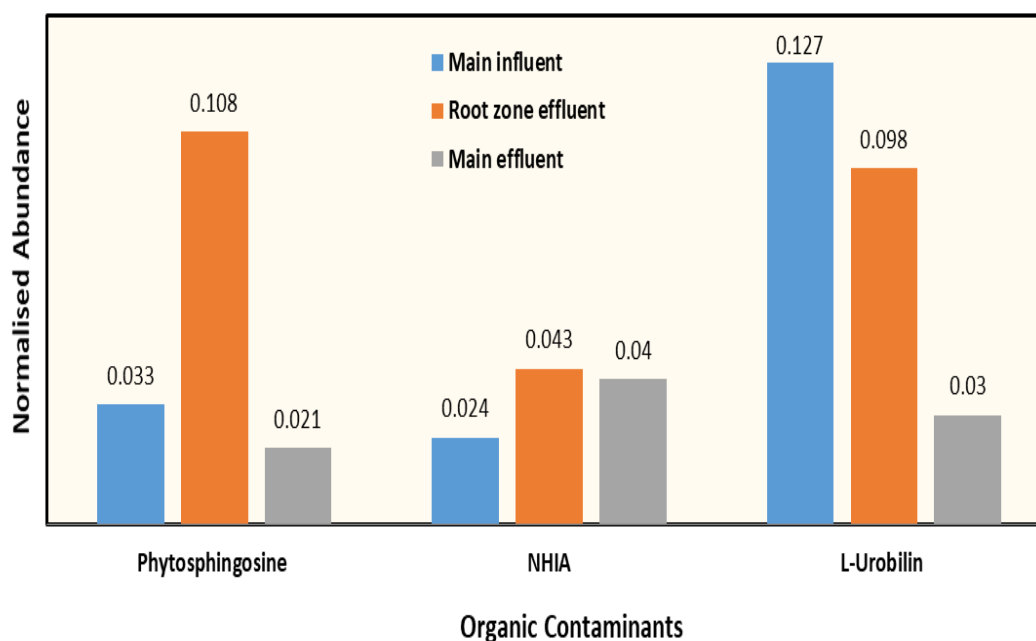
Figure 5.4. Organic contaminants observed in all wastewater phases of the AI WWTP.
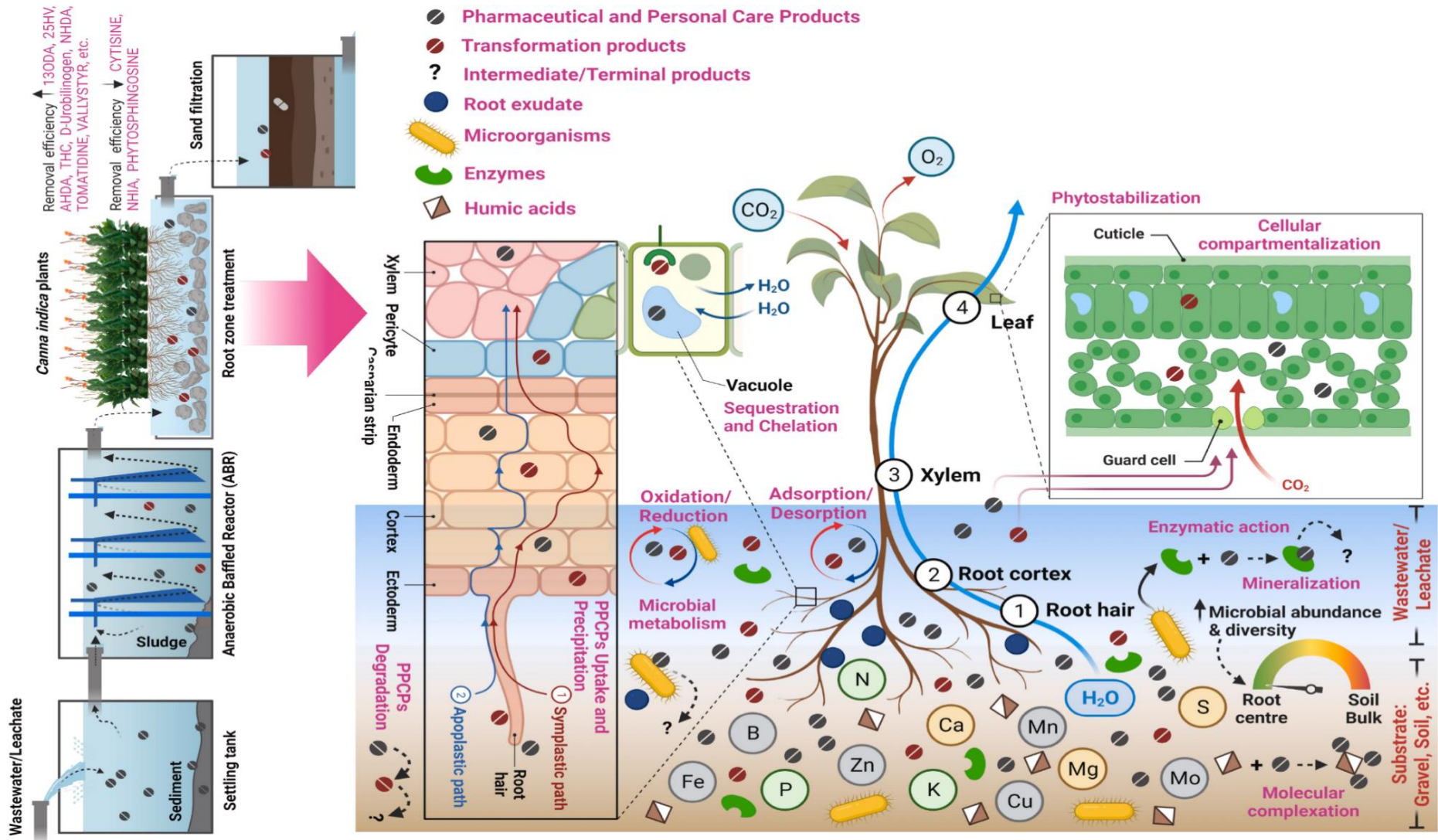
Figure 5.5. Process diagram depicting the facts and governing features of the observations made in the study.

5.3.3 Process diagram & applicability for leachate

The process diagram [Figure **5.5**] depicts the RZT/CW macrocosm which is further zoomed in to show the uptake and accumulation of PPCPs from the wastewater by C. indica plants. The various interactions of PPCPs and TPs in such CWs viz., root microbial actions (mineralization, oxidation, reduction, enzymatic action), complexation, compartmentalization by the plant cells, etc. are represented in detail. The uptake of PPCPs is plant species-specific and also depends on the physicochemical characteristics of the compound and the microenvironment. The diagram briefs the complex web of PPCPs pathways in the phyto environment. In subsequent stages of treatments, we found PPCPs that weren't in the WWTP influent. One pertinent observation has been the appearance of some PPCPs in the effluents without having their presence in the influents of a particular system or steps. This is likely due to conjugated PPCP metabolites in the influent that were deconjugated during biological wastewater treatment. In addition, after repeated sampling, we discovered the potential release of previously absorbed PPCPs in the system. This is because some PPCPs, up to a certain limit, attached to the root zone and became stable there based on the conditions of the surrounding environment; however, when their concentration exceeds the solubility concentration of the product, they are released.

The disposal of municipal solid waste in landfills is one of the most prevalent practices in the majority of countries. When excess rainwater percolates through the waste layers of a landfill, leachate is produced. Leachate from landfills is a water-based pollution comprising four classes of contaminants (dissolved organic matter, heavy metals, inorganic macro-components, and xenobiotic organic compounds). The most significant possible environmental effects of landfill leachate are surface water and groundwater contamination (Maiti et al., 2016). RZT is a natural, maintenance-free method where wetland plants purify sewage wastewater. This technology is one of the low-cost wastewater treatment solutions. This approach allows us to treat point Sources such as landfill leachate with optimal outcomes. Numerous types of PPCPs reach the landfill, and through the landfill, they reach leachate water (Reshadi et al., 2021). This research proposed that RZT technology can also be employed for leachate PPCPs treatment if the leachate BOD and COD values are first reduced using anaerobic digestion. The BOD and COD values of leachate are extremely high; hence, we cannot immediately treat it with RZT because its surface may become blocked.

5.4 Summary

The abundance of various organic contaminants in the RZT/CW-based WWTP at various stages was studied. In the current study, PPCPs detected in the various phases of the wastewater plant were found to be different from the PPCPs frequently reported in the WWTPs in previous literature. The RZT plant founds to be effective in removing most of the organic contaminants present in the main influent, but certain PCPs and other organic contaminants such as Phytosphingosine, L-Urobilin, and N-(2-hydroxyethyl)icosanamide found to be resistant to treatments in the plant. The PPCPs normalized abundances range between 0.037-0.012, 0.108-0.009, 0.208-0.005 in main influent, root zone effluent, and main effluent, respectively whereas -200% to ~100% removal rates for PPCPs were observed at RZT stage in the WWTP.

One of the key observations during the study was the presence of dextroamphetamine pharmaceutical in maximum abundance in the wastewater effluent, despite its absence in the influent and root zone effluent in the WWTP. The sudden presence of certain PPCPs and other contaminants in the root zone and main effluent instead of their absence in the influent may be due to (i) deconjugation of their metabolites present in the influent to parent compound form during treatment phases and (ii) release of earlier absorbed organic contaminants in wastewater by RZT system (roots of *Canna indica* plant and gravel substrate) and pressure filter system (filter media) during current treatment, (iii) decomposition of previous harvest/organic matter of *Canna indica*, and (iv) sorption-desorption in sludge due to change in log D values of transformation products from their parent compounds. However, continuous analysis is required to ascertain these findings, as analysis of the grab samples done in the current study for PPCPs abundance and fate during the treatment in the WWTP will only portray the partial snapshot results and implications. Thus, a composite sampling, i.e., consisting of multiple grab samples taken over the time period at various stages can prove to be much better in portraying the exact picture of PPCPs abundance and fate in RZT-based WWTP. RZT has high potential to be a promising and eco-friendly method for the removal of emerging concern of PPCPs, not only for domestic wastewater but for municipal landfill leachates. The promising results of this study along with supported literature, certainly vouch for having a CW/RZT around the buffer zones of landfill leachates as a future prospect.

CHAPTER 6: INVESTIGATION OF VARIOUS WASTE MATERIALS-BASED BIOCHAR FOR REMOVAL OF PPCPs IN AQUEOUS SOLUTION

6.1 Overview

This chapter focuses on the application of biochars derived from sawdust, and sawdust and plastic waste agglomerate (40% and 60% w/w) for the removal of PPCPs, known to be persistent in wastewater effluents. The PPCPs targeted in the study are major antibiotics, which include CFX (synthetic antibiotic) and SMX (human and veterinary antibiotic). These PPCPs are considered for the study owing to their widespread usage, potential of negatively affecting surface water and groundwater, bioaccumulating in aquatic organisms, and inducing antibiotic-resistant genes in various organisms (Ahmed et al., 2017; Ashiq et al., 2019; Huang et al., 2020; Li et al., 2018). Additionally, in the current work (Chapter 5) CFX and SMX were found to have low removal rates in the studied WWTPs (conventional treatments).

In general, the production of biochar, a carbon-rich material, involves the pyrolysis of biomass or carbonaceous waste such as agricultural waste and food residues (Adeniyi et al., 2023; Sun et al., 2015). Sawdust, a common waste generated from sawmill operations, is known to release significant amounts of carbon dioxide when burned, contributing to environmental pollution. As a result, there has been growing scientific interest in utilizing sawdust as a raw material for biochar production through pyrolysis (Adegoke et al., 2022; Liu et al., 2020). However, the presence of lignin, a complex and cross-linked polymer found in sawdust (approximately 30% content), can hinder the development of a high surface area in the resulting biochar (Antar et al., 2021). Lignin acts as a binder, limiting the formation of pores and voids and reducing the overall surface area. Therefore, the concept of co-pyrolysis, which allows for the utilization of different feedstocks, has gained significant attention (Ahmed et al., 2020; Li et al., 2022). Various researchers have explored the co-pyrolysis of biomass with plastic waste, such as bamboo waste with polystyrene (Oyedun et al., 2014); sugarcane bagasse pith with polyethylene terephthalate (Ghorbannezhad et al., 2020); cellulose/Douglas fir sawdust with plastics (Zhang et al., 2016) considering the high carbon content of the latter. The co-pyrolysis of sawdust with plastic waste from food packaging materials, spoons, and bottles for biochar production has not been reported in any of the mentioned studies. Furthermore, the use of this

specific type of biochar for the removal of CFX and SMX from aqueous solutions has not been explored before. Therefore, the present chapter aimed to investigate the co-pyrolysis of sawdust with plastic waste, driven by various factors such as increased porosity, surface chemistry, heating value, hydrophobicity, stability, and waste management considerations (Rago et al., 2020; Wang et al., 2019). The addition of plastic waste alongside the sawdust biomass is expected to disrupt the lignin binding action and potentially result in biochar with a higher surface area (Adeniyi et al., 2023). This approach not only addresses the disposal concerns of both types of waste and provides waste management solutions but also contributes synergistically to the achievement of SDGs (Hoang et al., 2022; Uday et al., 2022).

Herein the biochars investigated for the removal of targeted PPCPs in the study have been rarely explored and promise to report pertinent results. Important adsorption-related properties (crystallographic structure, functionality, pH) of the biochars through various techniques were evaluated. Then, batch adsorption tests were performed to assess the capacity of biochars for the removal of these compounds from the aqueous solution. Adsorption mechanisms and kinetics controlling interaction between PPCPs and biochars were elucidated. The results from the current study can suggest the incorporation of these biochars as filter media in the WWTPs for the efficient removal of such emerging contaminants from the wastewater.

6.2 Materials and Methods

6.2.1 Targeted adsorbates
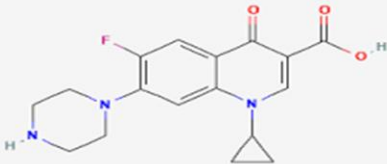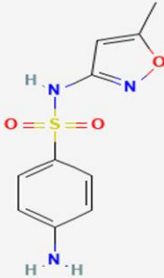
Two pharmaceuticals, CFX and SMX were targeted in the study. Standards of both antibiotics and HPLC grade organic solvents were procured from Sigma–Aldrich, USA. The physicochemical properties of the PPCPs are listed in Table **6.1**.

6.2.2 Adsorbents (Biochar)

Biochars produced from the pyrolysis of sawdust (S) and agglomerate of sawdust and plastic waste (SP, 40%:60% w/w) were studied to evaluate their adsorption potentials for antibiotics in aqueous solution. Plastic waste used as a raw material comprises a mixture of food packaging, plastic spoon, polythene, and plastic bottle. A small-scale batch-type reactor has been used for the pyrolysis of the waste. Prior to analysis, all feedstocks were air-dried, ground, and sieved through a 4 mm size sieve. Afterward, 1 kg of sieved waste was pyrolyzed slowly

at a low heating rate (10 °C per min) and a temperature of 500 °C for 4 h. In the process, the vapor produced from the reactor passes through the condenser and gets condensed at 6 °C temperature to convert into liquid form. In contrast, uncondensed gases pass through the vent pipe to the atmosphere. After that, biochar is produced as a solid residue at the bottom of the reactor. The prepared biochars are herein referred to as SB and SPB. In order to minimize water absorption, SP and SPB were later stored in a desiccator.

Table 6.1. Physicochemical properties and structures of the targeted PPCPs (antibiotics).

Compound	CFX	SMX
CAS Number	85721-33-1	723-46-6
Molecular formula	$C_{17}H_{18}FN_3O_3$	$C_{10}H_{11}N_3O_3S$
Molecular weight (gmol^{-1})	331.35	253.28
Water solubility (mgL^{-1} at 25°C)	35000	281
pK$_a$	6.38[a]	5.7 [a]
Log K$_{ow}$	0.28[b]	0.89[b]
Structure		

Source: PubChem
[a]Mohapatra et al. (2016)
[b]Wang & Wang (2016)

6.2.3 Biochar characterization

1. pH analysis

The pH of the biochars was evaluated using an altered method by Ndoun et al. (2021). The samples were mixed with Mill-Q water in a 1:20 ratio (1 g biochar + 20 mL water). Subsequently, a mechanical shaker was used to shake the mixture for 1 h, and the pH was measured by the potentiometric method.

2. Fourier-transform infrared spectroscopy (FTIR) analysis

The surface functional groups of the biochars were identified using a Fourier transform infrared (Frontier FTIR; Perkin Elmer) spectrometer equipped with deuterated triglycine sulfate (DTGS) detectors with an optional mercury cadmium telluride (MCT) detector (cooled with liquid nitrogen). The sample was prepared by mixing it with potassium bromide (KBr) in a mortar pestle, and about 1 to 2 mg of the sample is blended with the 200 mg of KBr powder. The blended sample was placed in a stainless-steel sample cup assembly (3 mm diameter), and an average of total 20 scans per spectrum was done at 4 cm^{-1} resolution with a scanning range between 4000-400 cm^{-1}.

3. X-Ray diffraction (XRD) analysis

The crystallographic structure and chemical composition of the biochars (SB and SPB) were characterised using an XRD instrument (D8 Advance Eco; Bruker).

6.2.4 Batch adsorption experiments

The tests were carried out to calculate the rate at which an equilibrium state can be achieved during the adsorption of the antibiotics onto the biochars. Stock solutions of concentration 200 mgL^{-1} for CFX and SMX were initially prepared. Afterward, these solutions were used to prepare antibiotics with initial concentrations of 10 to 20 mgL^{-1}. The initial concentration chosen for batch adsorption experiments in this study is comparatively higher than typical wastewater effluent concentrations to ensure the concentrations after the post-adsorption process should be above the detection limit (Ndoun et al., 2021). Batch adsorption experiments were performed with the prepared mixtures and were vigorously mixed at 250 rpm through a mechanical shaker in the laboratory. 10 mL aliquots (mixture) were collected after 5, 10, 15, 30, 60, 120, and 180 min contact times. Batch adsorption experiments incorporated duplicates to assure accuracy and precision. The samples were filtered through 0.2 μm filters and analysed by HPLC to determine CFX and SMX in aqueous solutions. The antibiotic removal efficiency (%) and quantity adsorbed (q$_t$, mgg^{-1}) on biochar were determined using the following equations:

CFX and SMX removal % $= \frac{(C_0 - C_t)}{C_0} \times 100$ %----(Eq. 1)

CFX and SMX adsorption capacity (q$_t$) $= \frac{(C_0 - C_t) \times (V)}{m}$ ---- (Eq. 2)

where, C_o= antibiotics initial concentration in solution (mgL^{-1}),

C_t= antibiotics concentration (mgL^{-1}) at time t (5, 10, 15, 30, 60, 120, and 180 min),

V= solution volume (L),

M= biochar mass (g).

6.2.5 HPLC analytical methodology

C18 column (4.6 mm × 250 mm, 5 μm) and a photodiode array (PDA) detector equipped HPLC were used for the chromatographic analysis. The constant flow rates of 1 mLmin^{-1} for 5 min and 0.75 mLmin^{-1} for 8 min were maintained for CFX and SMX, respectively. The mobile phase was 0.05 M phosphoric acid (PA): acetonitrile (AN) (30:70 v/v), and the detector wavelength was positioned at 278 nm for CFX. On the other hand, the mobile phase was 5 mM PA: AN (50:50 v/v), and the detector wavelength was 257 nm for SMX. CFX and SMX were eluted from the column at 2.2 min and 5.2 min, respectively. Blanks were run during both the calibration and sample analyses. Standards were run along with the samples to track any deviation in retention time, and five-point calibration curves were prepared for CFX and SMX.

6.2.6 Adsorption kinetic and isotherm studies

The adsorption kinetics were assessed using the pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion models. Two types of biochar (5 gL^{-1}) were equilibrated with the aqueous solutions of CFX and SMX in the concentration range of 10 to 20 mgL^{-1} by agitating for 0 to 180 min at 250 rpm to understand the rate of adsorption process. From these obtained results, the equilibrium data were used to calculate the Langmuir and Freundlich isotherm parameters (Table **6.3**).

6.3 Results and Discussion

6.3.1 Characterization of the biochars

6.3.1.1 pH

The biochar samples were found to be alkaline in nature. SB was found to be more alkaline (pH=9.6) compared to SPB (pH=8.9). The conversion of carbon into ash during the pyrolysis

process and the separation of alkali salts from the organic complex might be the potential reasons for the basic nature and increase in pH of the biochars (Cao & Harris, 2010).

6.3.1.2 FTIR

The surface functional groups on the biochars were characterised through their FTIR spectra. All spectrums comprise the -OH, C=C, and O=C=O groups, bonds stretching at 3200-3550 cm^{-1}, 1566-1650 cm^{-1}, and 2349 cm^{-1}, respectively. SB and SPB spectrums confirmed the presence of -OH through peaks at 3361.98 cm^{-1} and 3434.84 cm^{-1}, respectively. On the other hand, SB and SPB spectrums confirmed the presence of C=C (cyclic alkene) through peaks at 1587.20 cm^{-1} and 1623.38 cm^{-1}, respectively. In addition, C=C (cyclic alkene) groups in the biochars confirmed the presence of aromatic rings in their structure. The FTIR spectrums for the biochars with all identified surface functional groups are shown in Figure **6.1**.
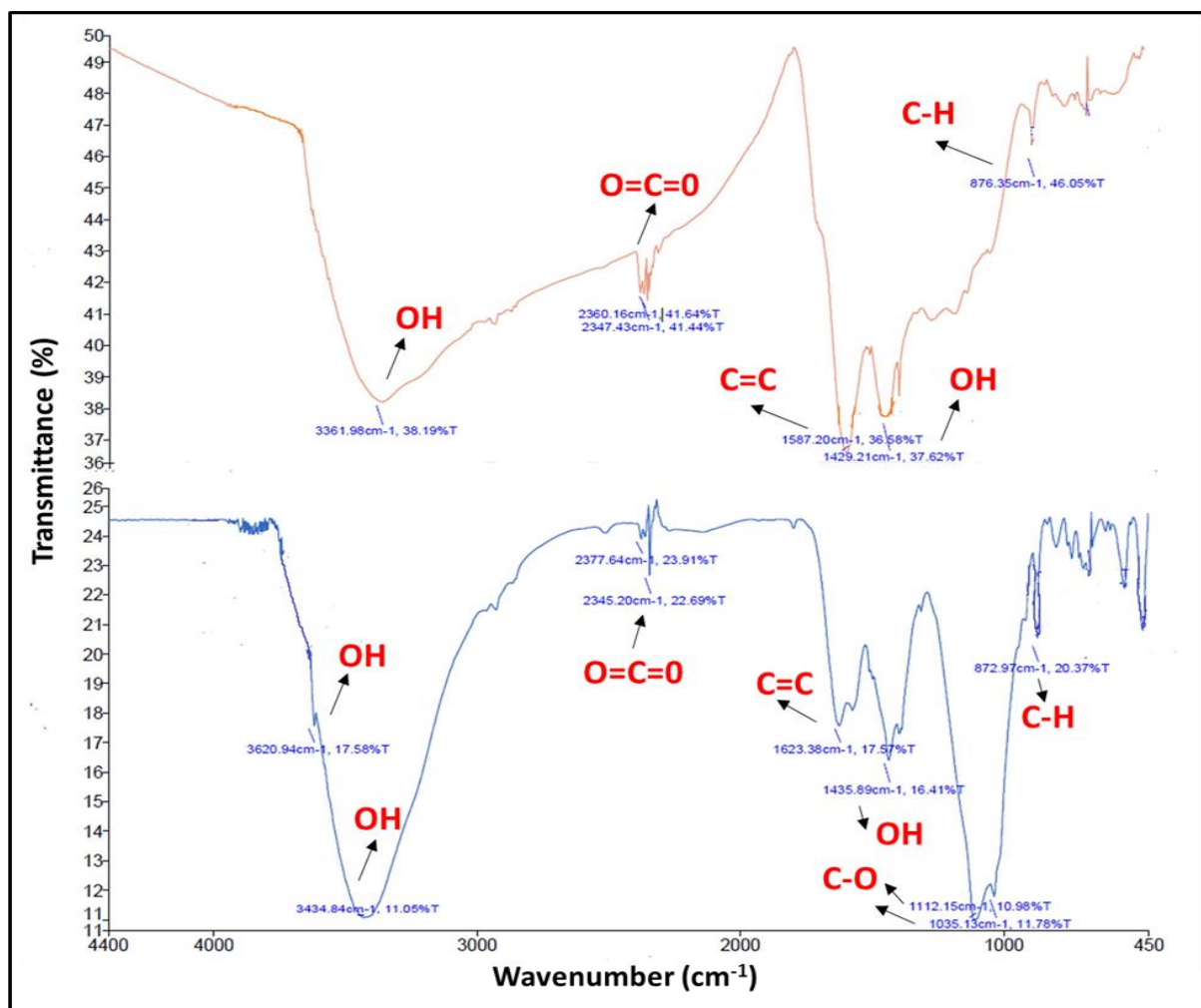
Figure 6.1. FT-IR spectra of SB (red line curve, top) and SPB (blue line curve, bottom), representing various surface functional groups of the biochars.

6.3.1.3 XRD

The crystallographic structure and chemical composition of the biochars were analysed using XRD plots. XRD pattern of SB showed the presence of broad humped peaks and the absence of distinct/clear peaks, which implies the amorphous nature of SB. The amorphous nature generally facilitates the adsorptive capacities of the biochar; hence SB is likely to show enhanced adsorption of antibiotics. On the other hand, the plot of SPB showed the presence of distinct and sharp peaks, which implies the crystallographic nature of the biochar. Henceforth, according to the results, SPB is likely to show less adsorptive capacity. The XRD plots/graphs for the various biochars are presented in Figure **6.2**.
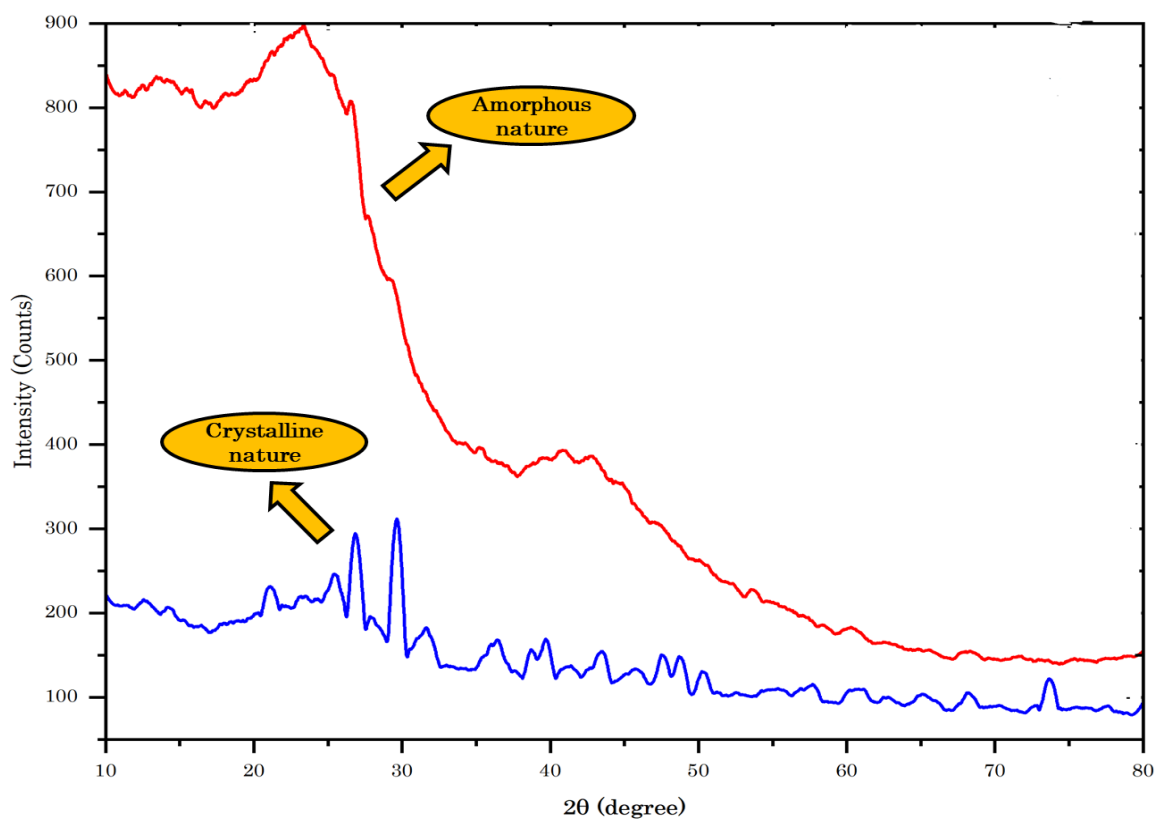
Figure 6.2. XRD patterns for the SB (red line curve, top) and SPB (blue line curve, bottom).

6.3.2 Antibiotics adsorption studies

6.3.2.1 CFX adsorption

The time-dependent concentration variation on the percentage removal and maximum adsorption of CFX on SB and SPB are shown in Figure **6.3(a-d),** respectively. Regarding

removal, the maximum removal of CFX by biochar was recorded with the SB (95.4%), whereas SPB showed maximum removal of 58.8% (Figure **6.3(a, b)**). The decreased CFX percentage removal for SB (88.5%) and SPB (50.5%) at higher initial concentration (20 mgL^{-1}) mainly suggested the saturation of the biochars sites. The equilibrium CFX adsorption capacity of SB and SPB was observed to be increased from 1.91 to 3.54 mgg^{-1} and 1.18 to 2.02 mgg^{-1}, respectively (Figure **6.3(c, d)**), mainly attributed to the higher driving force of CFX from solution to the adsorbent surface. A similar trend was noted for CFX removal by biochar derived from used tea leaves (Li et al., 2018).
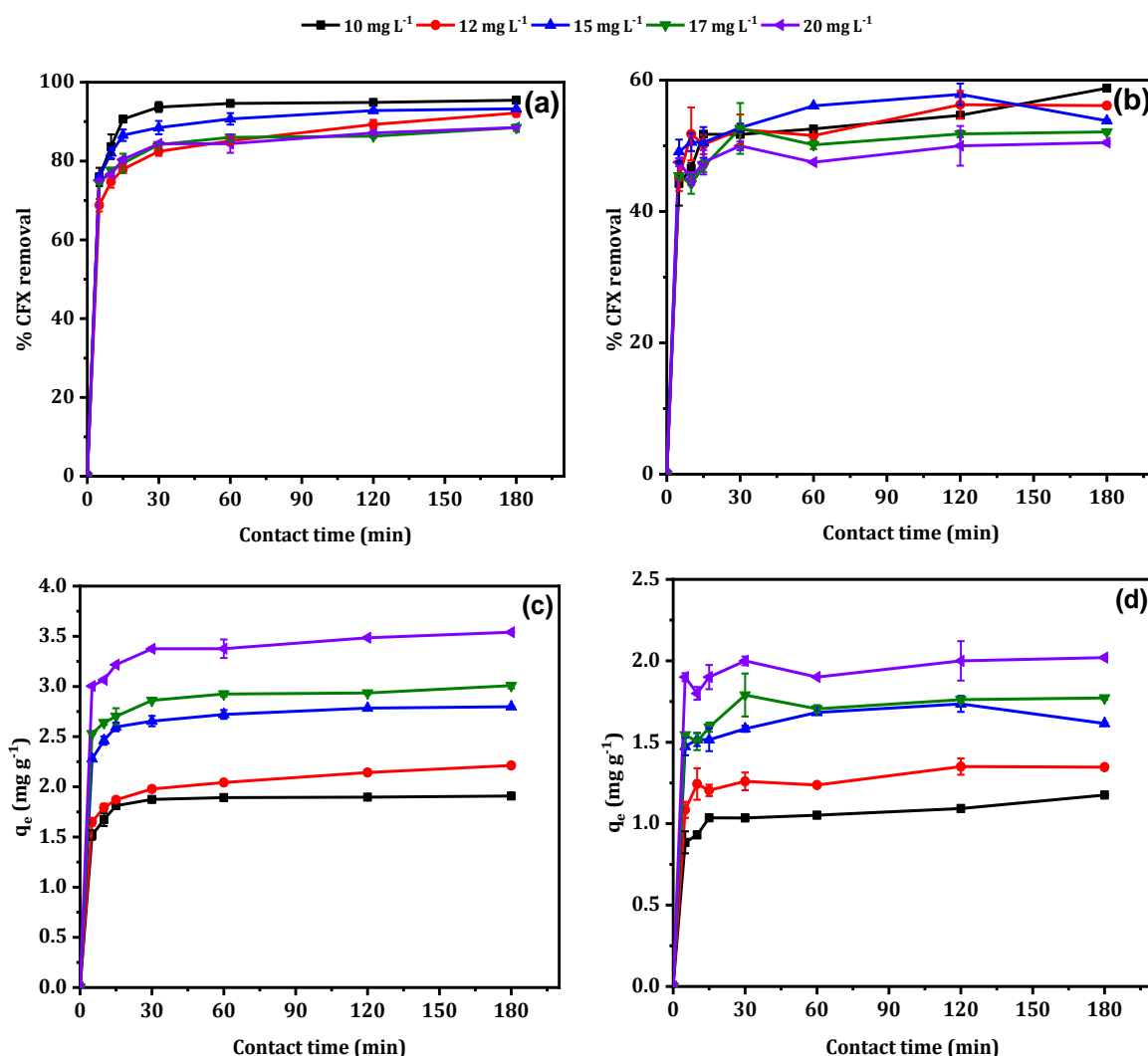
Figure 6.3. Effects of initial adsorbate concentration (10 to 20 mgL^{-1}) with varying contact time on the CFX removal percentage (a, b) using SB and SPB, respectively. The maximum adsorption capacity of SB (c) and SPB (d) for CFX with varying contact time and initial concentrations. (Conditions: pH= 7.0 ± 0.2; m= 5 gL^{-1}, temperature= 298 ± 2 K and stirring speed= 250 rpm).

It can be observed from Figure **6.3(a)** that SB showed almost 70% of CFX removal capacity within the first five minutes of the contact time. Whereas, for SPB the first five min contact brought only 50% of the CFX removal (Figure **6.3(b)**). In the case of SB, the equilibrium can be observed within 180 min which suggested that all the sites were occupied by the CFX molecules however, for SPB still some vacant sites were available resulting in the rising shaped curve for lower CFX concentrations. This observation suggested that it might be difficult for CFX to enter inside the porous structure of SPB at lower initial concentrations. For comparison purposes, 180 min contact time has been considered as the equilibrium for both the biochar adsorbents.
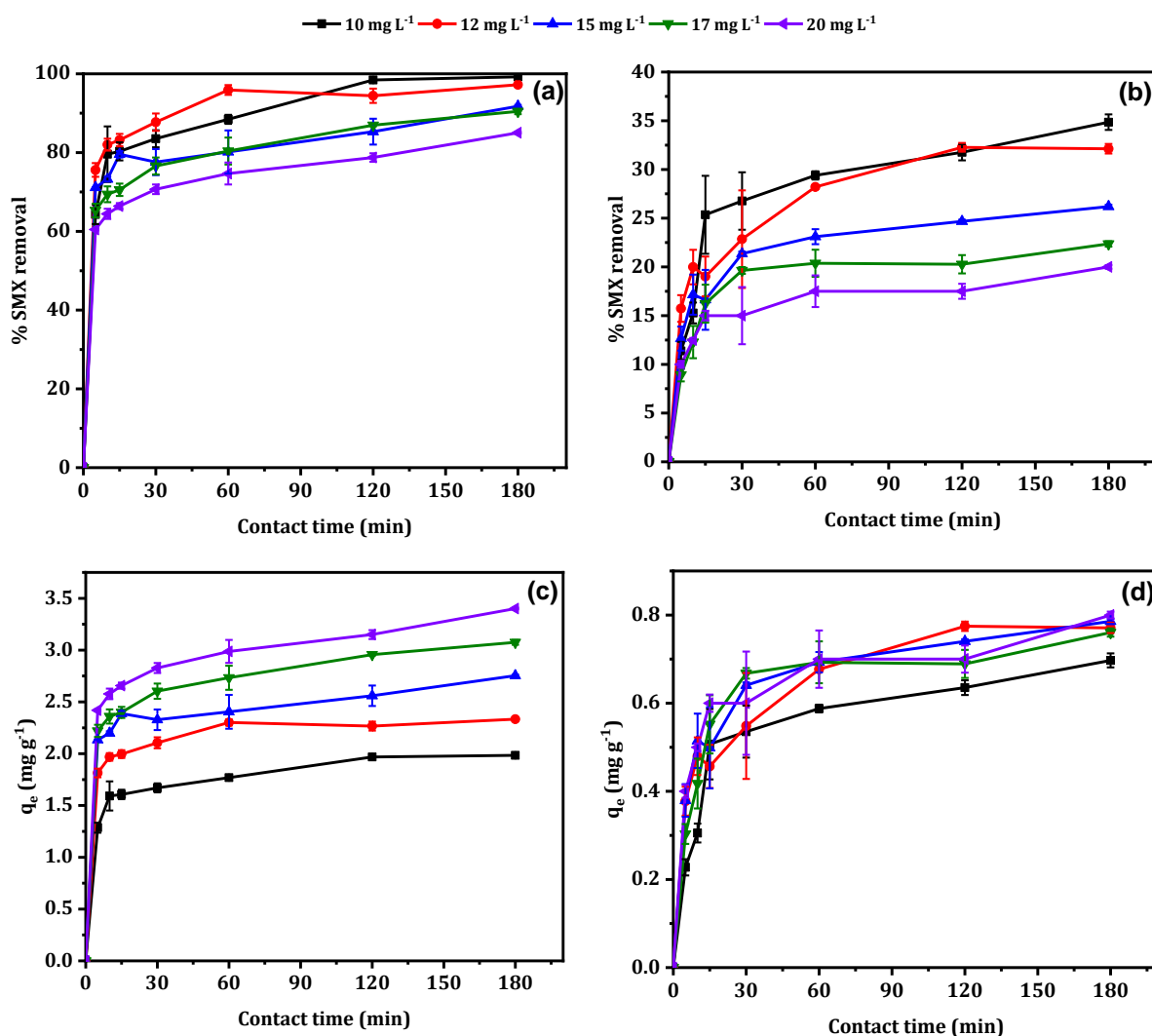
Figure 6.4. The SMX removal percentage (a, b) and maximum adsorption capacity (c, d) on SB and SPB, respectively against different time and SMX concentrations (Conditions: pH= 7.0 ± 0.2; m= 5 gL^{-1}, temperature= 298 ± 2 K and stirring speed= 250 rpm).

6.3.2.2 SMX adsorption

The effect of contact time and different initial SMX concentrations on its removal and maximum adsorption capacity by SB and SPB are shown in Figure **6.4(a-d)**, respectively. At initial SMX concentration of 10 mgL^{-1}, SB and SPB showed maximum removal of 99.2%, and 34.9%, respectively. However, with increasing concentration the removal capacity of SB and SPB for SMX was observed to be decreasing, and at maximum SMX concentration (20 mgL^{-1}), SB and SBF showed 85 and 20% removal efficiency, respectively. The higher SMX adsorption capacity of SB was attributed to its amicable surface structure and attractable surface functionality. With the increase in SMX concentration from 10 to 20 mgL^{-1}, the higher mass transfer and its driving force caused the increase in its maximum adsorption capacity on SB (~1.99 to 3.40 mgg^{-1}) and SPB (~0.69 to 0.80 mgg^{-1}). The equivalent results were earlier reported for SMX removal with raw bamboo and rice straw-derived biochar (Zheng et al., 2003; Huang et al., 2020).

SB showed a similar trend for removing CFX and SMX (>95% removal) from an aqueous solution. In contrast, SPB showed distinct trends for the removal of CFX and SMX from aqueous solution. SPB exhibits higher removal rates (58.8%) for CFX, whereas lower removal rates (34.8%) for SMX. Henceforth, SB can be considered effective in removing both antibiotics (CFX and SMX).

6.3.3 Adsorption kinetics modelling

Adsorption kinetic models primarily quantify the adsorbate (antibiotic) removal rate and the equilibrium adsorbate amount adsorbed by adsorbents (biochar) during the adsorption process. This helps determine the contact time required to remove a desired antibiotic during water treatment. Three kinetic rate models namely, PFO, PSO, and intraparticle diffusion were used to evaluate the obtained experimental data (Figure **6.5(a-d)**). However, only the PSO kinetic model showed a better fit since the R^2 (regression coefficient) values were observed to be higher (Table **6.2**). Lower R^2 values were observed for the PFO model. Higher R^2 values (>0.8) for the PSO model were observed for all the biochars and antibiotics. Hence PSO model could be used to elucidate the adsorption processes. The experimental values of q_e for CFX and SMX adsorption by the solutions biochars were close to the q_e values determined by the PSO kinetic model, which further supports that the adsorption processes followed the PSO model. The PSO kinetic model better fits the data, which portrays that the adsorption of CFX and SMX onto SB

and SPB is controlled by chemical adsorption/chemisorption as a rate-limited process, where the adsorbent adsorption capacity governs the adsorption rate and not by the adsorbate concentration, and which involves electrons sharing/exchange between biochars and pharmaceuticals (Chauhan et al., 2023; Ndoun et al., 2021).

In the same context, the PSO model governed the adsorption of sulfapyridine, docusate, and erythromycin by guayule bagasse and cotton gin waste biochars (Ndoun et al., 2021). Similarly, in another study, the PSO model-controlled sulfonamide adsorption by functionalised biochar (Ahmed et al. 2017). Also, SMX removal by magnetised pine sawdust biochar fitted the PSO model (Reguyal et al., 2017). Henceforth, the kinetic results of our study were found to be concordant with other previous literature.
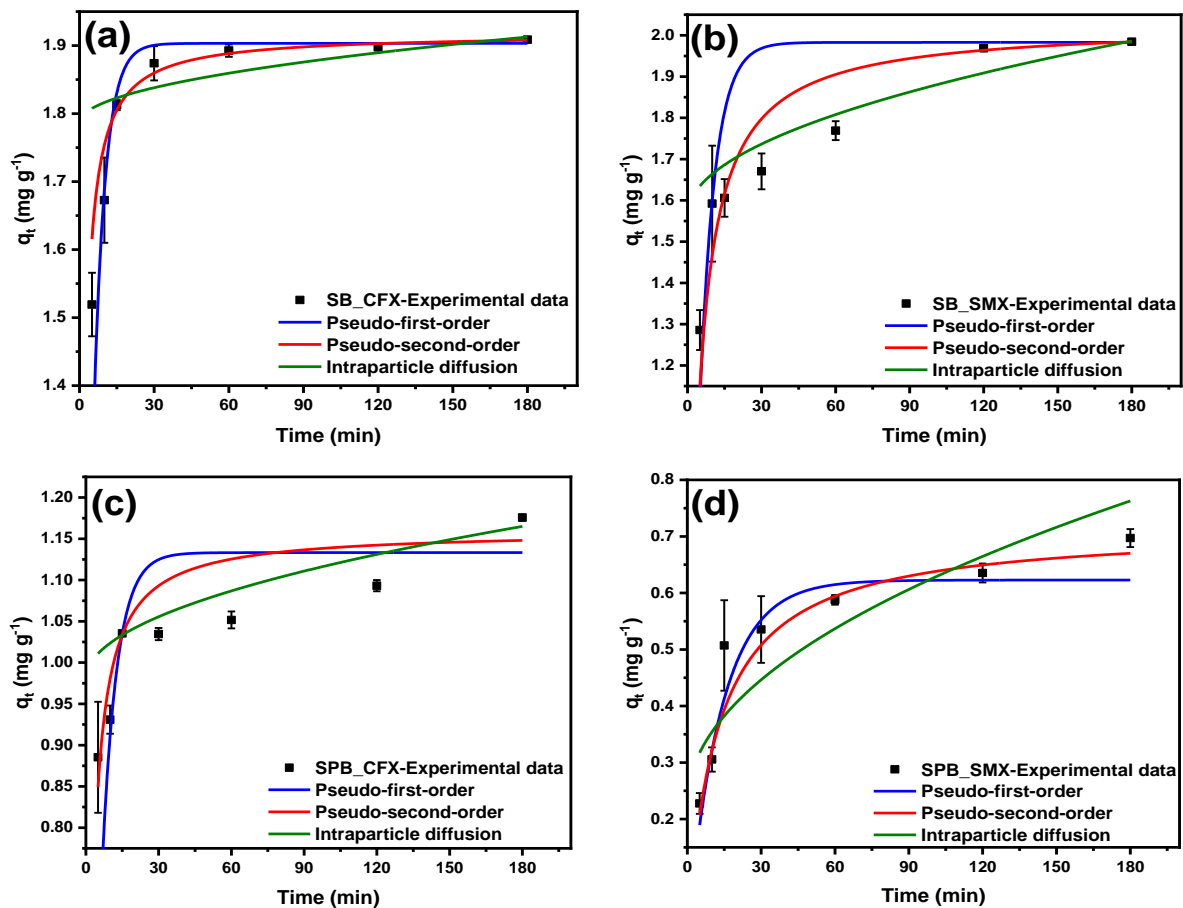
Figure 6.5. Non-linear kinetic plots for the adsorption of CFX (a, c) and SMX (b, d) on SB and SPB adsorbents, respectively (Conditions: pH= 7.0 ± 0.2; m= 5 gL^{-1}, temperature= 298 ± 2 K and stirring speed= 250 rpm).

6.3.4 Adsorption isotherm study

The equilibrium (at 180 min) experimental data (q_e) for the adsorption of CFX and SMX on SB and SPB are plotted (refer Figure **6.6(a-d)**) against the equilibrium adsorbate concentration to identify the suitability of the two parameters isotherm models (Langmuir and Freundlich). The calculated isotherm parameters and constants together with the regression coefficient values (R^2) are mentioned in Table **6.3**. The higher R^2 value of the Freundlich isotherm model for the adsorption of SMX onto SB suggested its heterogeneous multilayer adsorption process. The obtained values of the Freundlich constant (n) suggested the good physical adsorption of the process of antibiotics onto biochar adsorbents.
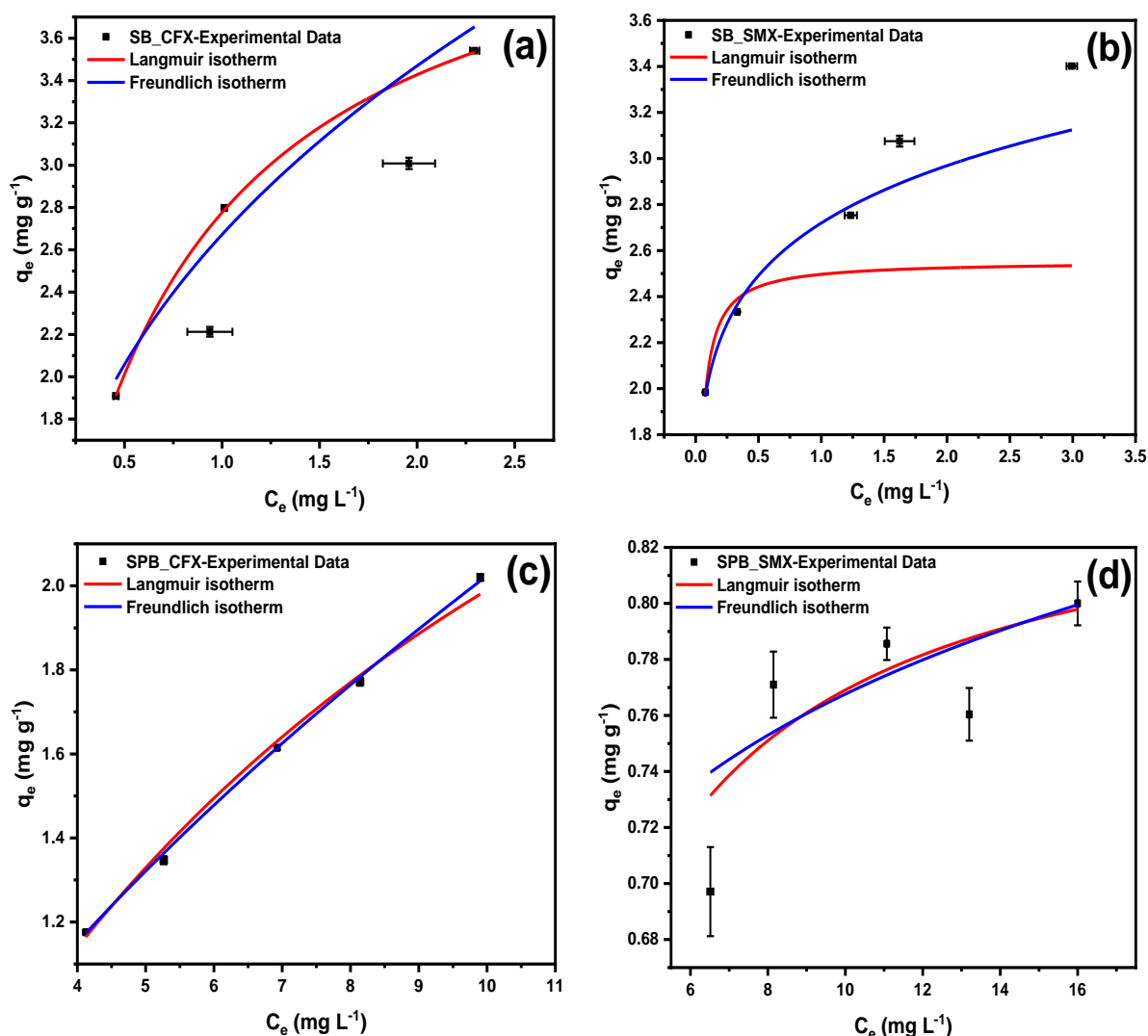
Figure 6.6. Adsorption isotherm curves with non-linear fitting for CFX (a, c) and SMX (b, d) on SB and SPB adsorbents, respectively. (Conditions: pH= 7.0 ± 0.2; m= 5 gL^{-1}, time= 180 min; temperature= 298 ± 2 K and stirring speed= 250 rpm).

For CFX adsorption onto SB and SPB, the consistently obtained higher R^2 values for the Langmuir isotherm model confirmed its suitability with the experimental data. It further suggested the monolayer adsorption of CFX molecules on the homogenous surface of the biochars, which occurred favorably as confirmed by the values of the separation factor ($0 < R_L < 1$) mentioned in Table **6.4**. The calculated Langmuir adsorption capacity (q_m) for CFX with SB and SPB was 4.48 and 3.96 mgg^{-1}. Whereas, in the case of SMX, SB showed moderate adsorption capacity (2.55 mgg^{-1}) but, very low capacity (0.85 mgg^{-1}) offered by the SPB. In addition, a comparison of the adsorption results of the present study with the earlier reported literature for CFX and SMX adsorptions onto biochar is summarized in Table **6.5**.

6.3.5 CFX and SMX adsorption mechanism

The adsorption of CFX and SMX by the biochars (SB and SPB) can be explained by physisorption and chemisorption processes. Biochar generally consists of oxygen-containing functional groups which facilitate the adsorption of PPCPs through hydrogen bonding and electrostatic mechanism/surface complexation (Rajapaksha et al., 2019; Chaturvedi et al., 2021). As per the FTIR results, the biochars (SB and SPB) are comprised of -OH (oxygen-containing functional group), which can form hydrogen bonding with the oxygen and hydroxyl functional groups of CFX and SMX.

Both the antibiotics get adsorbed onto oxygen-containing functional groups present in SB and SPB through an electrostatic interaction mechanism. Moreover, their sorption by SB and SPB can be elucidated by π–π electron donor-acceptor (EDA) interactions. Pharmaceuticals consisting of aromatic rings can interact with aromatic biochar rings through π-π EDA interactions (Rajapaksha et al., 2019). The N and/or hetero-aromatic rings and amine group present in CFX and SMX enable the compounds to act as a π-electron acceptors (Ndoun et al., 2021). SB and SPB enhanced with OH, C=C functional groups behave as strong electron donors. This promotes the π–π EDA interactions, leading to the removal of CFX and SMX from the aqueous solution. Therefore, the adsorption of CFX and SMX by the biochars primarily occurs through hydrogen bonding (physisorption), electrostatic, and π-π EDA interactions (chemisorption) mechanisms. In the same context, the interaction mechanism between the antibiotics (CFX and SMX) and the biochars is depicted in Figure **6.7**.

Table 6.2. The kinetic rate constants for the adsorption of CFX and SMX on SB and SPB.

Adsorbents		SB				SPB			
Pseudo-first-order constants	**Adsorbates**	$q_{e(exp)}$ (mgg^{-1})	$q_{e(cal)}$ (mgg^{-1})	k_1 (min^{-1})	R^2	$q_{e(exp)}$ (mgg^{-1})	$q_{e(cal)}$ (mgg^{-1})	k_1 (min^{-1})	R^2
	CFX	3.54	1.90	0.22	0.81	2.02	1.13	0.16	0.72
	SMX	3.40	1.98	0.16	0.59	0.80	0.62	0.07	0.93
Pseudo-second-order constants	**Adsorbates**	$q_{e(exp)}$ (mgg^{-1})	$q_{e(cal)}$ (mgg^{-1})	k_2 $(gmg^{-1}min^{-1})$	R^2	$q_{e(exp)}$ (mgg^{-1})	$q_{e(cal)}$ (mgg^{-1})	k_2 $(gmg^{-1}min^{-1})$	R^2
	CFX	3.54	1.92	0.56	0.96	2.02	1.16	0.47	0.83
	SMX	3.40	2.02	0.13	0.88	0.80	0.72	0.11	0.98
Intra-particle diffusion constants	**Adsorbates**	K_{id} $(mgg^{-1}min^{-1/2})$		I (mgg^{-1})	R^2	K_{id} $(mgg^{-1}min^{-1/2})$		I (mgg^{-1})	R^2
	CFX	0.01		1.79	0.71	0.01		0.98	0.93
	SMX	0.03		1.56	0.70	0.04		0.23	0.84

Table 6.3. The calculated Langmuir and Freundlich isotherm parameters for the adsorption of CFX and SMX on SB and SPB.

Isotherm Model	Isotherm Parameters	SB		SPB	
		CFX	SMX	CFX	SMX
Langmuir Isotherm	q_m (mgg^{-1})	4.48	2.55	3.96	0.85
	k_L (Lg^{-1})	1.63	43.9	0.10	0.94
	R^2	0.99	0.76	0.99	0.54
Freundlich isotherm	K_F (mg$^{1-1/n}$L$^{1/n}$g^{-1})	2.67	2.72	0.49	0.63
	n	2.63	7.69	1.61	1.15
	1/n	0.38	0.13	0.62	0.87
	R^2	0.96	0.97	0.99	0.48

Table 6.4. The values of the separation factor at different initial concentrations for the adsorption of CFX and SMX on SB and SPB.

Separation factor (R_L)	SB		SPB	
	CFX	SMX	CFX	SMX
10	0.06	0.02	0.52	0.11
12	0.05	0.01	0.48	0.09
15	0.04	0.01	0.42	0.07
17	0.04	0.01	0.39	0.07
20	0.03	0.01	0.35	0.06

Table 6.5. Collation of the CFX and SMX adsorption results of the current study with the previous literature.

PPCP	Feedstock	PPCP initial concentration (mgL^{-1})	Contact time (min)	Removal% (Adsorption capacity in mgg^{-1})	Kinetic model	Adsorption mechanism	Reference
CFX	Bamboo Sawdust	25	46.25	45.1%	PSO	Hydrogen bonding, π_π and electrostatic interactions	*Wakejo et al. (2022)*
	Bamboo Sawdust (Modified)	20	5-60 (46)	95.67% (78.43)	PSO	π-π interaction, hydrogen bonding, ion exchange, and electrostatic interaction	*Wakejo et al. (2022)*
	Used tea leaves	-	-	(238.1)	PSO		*Li et al. (2018)*
	Corncobs	-	-	(0.4)	PSO	π-π interaction, hydrogen bonding, and electrostatic interaction	*Dang et al. (2022)*
	Municipal solid waste	25	5-1440	(122.16)	PSO		*Ashiq et al. (2019)*
	SB and SPB	10-20	5-180	95.4% (4.48) and 58.8% (3.96)	PSO	Hydrogen bonding, π_π and electrostatic interactions	*Current study*
SMX	Sawdust	100–400	30–360	>95% (127.70-295.06)	PSO	π_π interaction and H-bonding	*Ahsan et al. (2018)*
	Ball milled Hickory chips	10	10.2-1440	83.3% (100.30)	Elovich	Hydrophobic interaction, π_π interaction, hydrogen bonding, and electrostatic interaction	*Huang et al. (2020)*
	Ball milled raw bamboo	-	120	(25.7)	Elovich	Hydrophobic interaction, π_π interaction, hydrogen bonding, and electrostatic interaction	*Huang et al. (2020)*
	Giant reed	0-80	-	(4.99)	PSO	Pore-filling and hydrophobic interactions	*Zheng et al. (2013)*
	Rice straw	5-200	1440	(1.83)	-	π_π interaction and surface complexation	*Han et al. (2013)*
	SB and SPB	10-20	5-180	>99% (2.55) and 34.9% (0.85)	PSO	Hydrogen bonding, π_π and electrostatic interactions	*Current study*
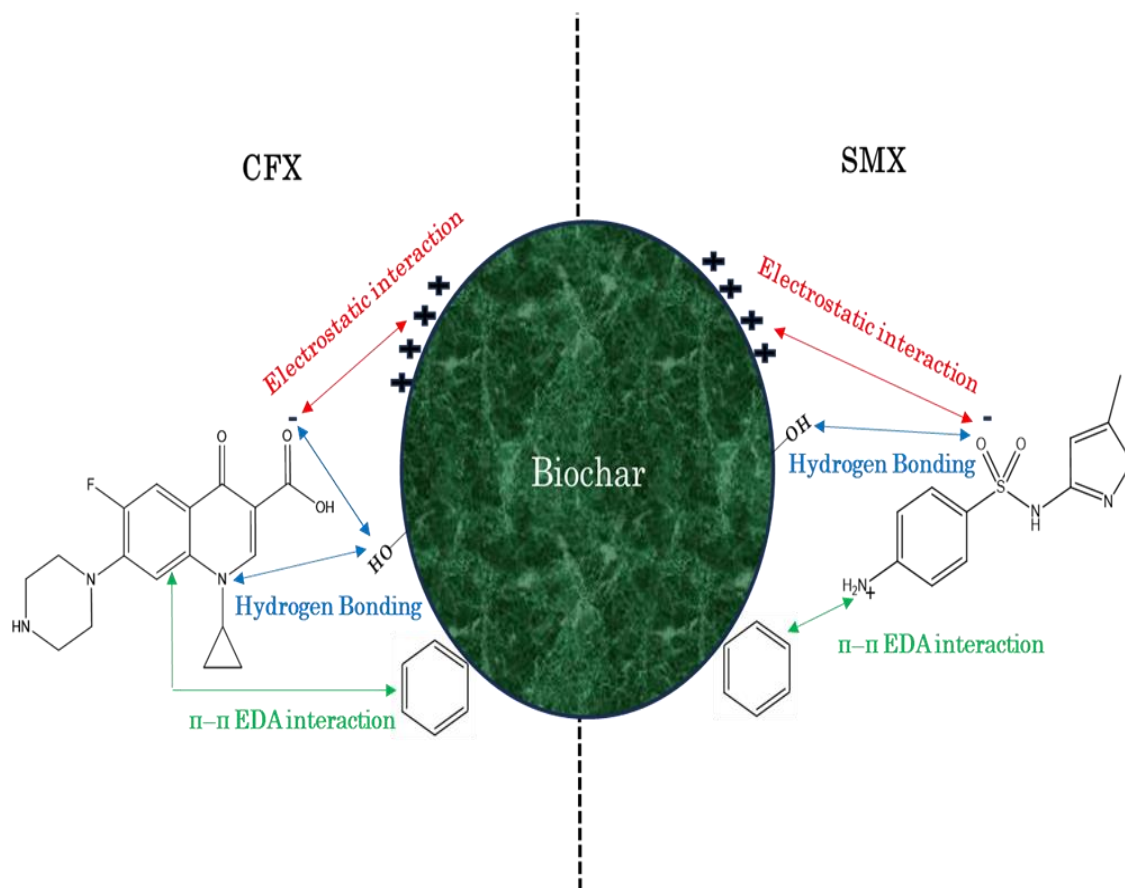
Figure 6.7. Adsorption mechanism of the antibiotics (CFX and SMX) onto the biochars.

6.4 Summary

Biochars produced from the pyrolysis of sawdust, and co-pyrolysis of sawdust and plastic waste exhibited substantial capacity to remove PPCPs from aqueous solution. Sawdust-based biochar showed far better removal of both the targeted PPCPs (antibiotics) from aqueous solution as compared to plastic-cum-biomass based biochars. This might be attributed to the more alkaline and amorphous nature of the sawdust biochar. Sawdust biochar reported ~95% and >95% removal efficiency for CFX and SMX, respectively. Mechanisms involved were hydrogen bonding, surface complexation, and π–π EDA interactions during the adsorption processes. Adsorption of both antibiotics onto biochars in aqueous solution primarily followed the PSO kinetic model, implying that adsorption was dominated by chemisorption via electron sharing or transfer. These results delineate the potential for waste materials-based biochar to serve as an economical additional treatment for reducing PPCPs in wastewater effluents. The findings from the current study suggest the incorporation of these biochars as filter media in the WWTPs for enhanced removal of such emerging contaminants from the wastewater.

CHAPTER 7: CONCLUSIONS, LIMITATIONS, AND FUTURE PROSPECTS

7.1 Summary

The research work presents a deep insight into the occurrence and monitoring of PPCPs and EDCs in major WWTPs of Dehradun city and evaluation of the effectiveness of the RZT/CW hybrid system and waste materials-based biochar for PPCPs removal from the water environment. The detailed findings of each targeted objective are mentioned in Chapter 4, Chapter 5, and Chapter 6.

Important findings of the current research work are as follows:

- Diclofenac and caffeine were detected in all influent samples of the studied WWTPs in Dehradun.
- Among the nine target compounds, the highest mean concentration in influents was found for estrone, a natural hormone, followed by caffeine and acetaminophen, an analgesic among the WWTPs.
- An astonishing concentration of 123.9 μgL^{-1} was recorded for the estrone in the influent, which is to date the highest ever recorded, worldwide.
- The total concentration of studied PPCPs in influent and effluent ranged from 1849 to 74187 ngL^{-1} and 22 to 64275 ngL^{-1}, respectively in the WWTPs.
- The correlation analysis indicated acetaminophen strong correlation with diclofenac (r=+0.77) and ketoprofen (r=+0.62), diclofenac profoundly linked with ketoprofen (r=+0.89) and ciprofloxacin was positively correlating with carbamazepine (r=+0.65).
- The tests for distribution showed a non-normal data distribution (p>0.05) for all wastewater PPCPs samples except for caffeine influents.
- PPCPs samples showed a significant variation between and within the influent and effluent samples (p<<<0.001), which shows highly decisive evidence for unequal means.
- The results of the analysed data for EDCs have shown a non-normal data distribution with bimodal variations as per the statistical studies performed.
- Seasonal variations showed mean total PPCPs concentrations in influents were higher in spring, followed by monsoon and summer seasons.

- The mean EDC concentrations in influents were higher during monsoon season indicating a significant run-off component in the area.
- The average removal efficiency of total PPCPs was observed highest in aeration and fluidized media oxidation treatment, followed by C-Tech and SBR treatments.
- The PPCPs and EDCs removal in the WWTPs were observed in the ranges of -293% to 100%.
- Acetaminophen, ketoprofen, and triclosan showed maximum removals among different WWTPs.
- The negative removal rates were recorded for ciprofloxacin, caffeine, carbamazepine, and estrone in the WWTPs.
- Hyperaccumulation of estrone in WWTP effluents is an emerging future threat in the area.
- Several PPCPs present in influent increases along the *in-situ* RZT/CW-based wastewater treatment system.
- Deconjugation of conjugated forms/metabolites may be the probable reason for the negative removal and abrupt presence of PPCPs at later stages of RZT-based WWTP.
- Phytosphingosine, L-Urobilin, and N-(2-hydroxyethyl)icosanamide were the organic pollutants found at all stages in the plant.
- The PPCPs normalized abundances range between 0.037-0.012, 0.108-0.009, 0.208-0.005 in main influent, root zone effluent, and main effluent, respectively whereas -200% to ~100% removal rates for PPCPs were observed at RZT stage in the WWTP.
- RZT-based WWTP is found to be effective in removal of the majority of PPCPs with a ~100% removal rate.
- The study suggests RZT as an additional unit could be incorporated in the Dehradun WWTPs for the removal of PPCPs from wastewater.
- It also suggests RZT to be appraised for PPCPs *in-situ* remediation from landfill leachates, an underestimated source of PPCPs intrusion in the environment.
- Sawdust-based biochar (SB) showed far better removal of targeted antibiotics from aqueous solution as compared to plastic-cum-sawdust based biochar.
- SB reported ~95% and >95% removal efficiency for CFX and SMX, respectively in aqueous solution.
- Sorption of CFX and SMX by the biochars in the aqueous solution is governed by hydrogen bonding, electrostatic, and $\pi-\pi$ EDA interactions/mechanisms.

- Adsorption of CFX and SMX onto various biochars in aqueous solution majorly followed PSO kinetic model, portraying chemisorption as the dominant adsorption process.
- The study suggests SB as an additional filter media could be incorporated in the filters of WWTPs for assessing its *in-situ* feasibility and suitability for ECs removal.

7.2 Limitations

The current work encompasses all the aspects, but there were certain potential limitations. The limitations of the study are as follows:

- Sampling limitations: Grab samples were taken from the RZT-based WWTP and analysed in the current study for PPCPs abundance and fate during the treatment, which portrayed the partial snapshot results and implications. However, composite sampling and continuous analysis can prove to be much better in portraying the exact and deep picture of PPCPs abundance and fate at various stages in RZT-based WWTP. In essence, the study showed that RZT-based WWTP was efficient in eliminating PPCPs and other organic pollutants. Nevertheless, the results highlight the importance of conducting further comprehensive research on RZT system to accurately determine the removal and fate of PPCPs during treatment in the system.

- Real-world environmental effects: Investigation of the various waste materials-derived biochar (sawdust and sawdust-plastic biochar) for the removal of PPCPs was conducted in laboratory-prepared aqueous solution, where matrix effects on the adsorption process were not considered. The study delineated the biochars adsorption capacity in ideal conditions, where interference and interaction of other contaminants during the adsorption processes in solution were neglected. However, field wastewater samples for batch adsorption studies can prove to be much better for comprehensively delineating the exact picture of biochar efficiency for PPCPs removal.

7.3 Future Prospects

Based on the current study results, future work could be attempted to conclude the deeper aspects of PPCPs contamination in the area. Also, explored remediation approaches could be extended to field conditions for evaluating their *in-situ* feasibility and suitability for ECs removal from wastewater.

Henceforth the future scope of work could include:

- Riverbed sediments and groundwater monitoring in nearby areas of the studied WWTPs could be conducted in Dehradun city to assess the exact extent of PPCPs contamination in these compartments and possible environmental threats. This would primarily appraise the groundwater quality of the area in deeper aspects and provide a base for protection of groundwater basin from such future anthropogenic contamination, especially by local people and policy makers in the area.

- This study suggests that RZT/CW technology can be a viable option for leachate PPCPs treatment, provided that the leachate BOD and COD levels are first lowered through anaerobic digestion. Due to the significantly elevated BOD and COD levels in leachate, direct application of RZT treatment is not feasible initially, as it may lead to potential blockage of the RZT system surface. Henceforth, as a current research gap, RZT could be appraised for PPCPs *in-situ* remediation from landfill leachates.

- This study proposes the integration of sawdust-derived biochar as a filter media within WWTPs to enhance the removal of ECs (particularly PPCPs) from wastewater. Therefore, saw dust-derived biochar as an additional filter media could be incorporated in WWTPs for assessing its *in-situ* feasibility and suitability for PPCPs removal.

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APPENDICES

Appendix A1

The targeted PPCPs concentrations in influents of the studied WWTPs. Concentrations are expressed in ngL^{-1}.

S.No.	WWTP_month	Ciprofloxacin	Acetaminophen	Diclofenac	Ketoprofen	Sulfamethoxazole	Caffeine	Carbamazepine
1	WWTP-I_Mar	7363.99	7340.37	624.03	BDL	BDL	29832.62	7.73
2	WWTP-I_Apr	1335.48	9078.84	205.73	94.45	BDL	40038.22	19.12
3	WWTP-I_May	365.22	9658.72	318.79	315.17	13.44	9034.20	51.01
4	WWTP-I_Jun	12.48	BDL	651.11	148.97	18.07	6313.04	11.90
5	WWTP-I_Jul	41.67	5785.09	465.15	1023.78	42.97	55247.99	BDL
6	WWTP-I_Aug	BDL	12102.29	103.83	5.53	BDL	39814.51	BDL
7	WWTP-II_Mar	4212.14	4164.85	590.38	1345.24	24.08	46135.90	33.22
8	WWTP-II_Apr	127.64	8851.75	1108.11	604.54	32.59	44472.24	17.58
9	WWTP-II_May	130.82	3337.03	335.29	325.06	BDL	3825.05	13.67
10	WWTP-II_Jun	500.84	444.64	91.76	0.18	BDL	8267.92	BDL
11	WWTP-II_Jul	275.09	65.67	230.51	BDL	BDL	37165.23	9.47
12	WWTP-II_Aug	120.45	BDL	81.31	BDL	BDL	15021.63	BDL
13	WWTP-III_Mar	16931.81	1695.23	672.76	700.82	BDL	38208.89	4.04
14	WWTP-III_Apr	6424.93	8725.61	951.70	BDL	BDL	53424.97	BDL
15	WWTP-III_May	12.98	679.16	489.13	381.40	69.55	22410.30	1.93
16	WWTP-III_Jun	50.86	BDL	272.13	2.35	672.73	851.45	0.14
17	WWTP-III_Jul	1877.36	175.55	364.25	3.84	112.20	71653.59	0.73
18	WWTP-III_Aug	45.03	7424.03	58.86	BDL	BDL	49809.01	7.50
19	WWTP-IV_Mar	1885.79	9719.78	1651.77	1974.45	BDL	49399.72	0.15
20	WWTP-IV_Apr	1176.01	5344.68	588.89	181.24	BDL	58171.16	16.56
21	WWTP-IV_May	83.19	99.09	512.14	BDL	111.25	13869.85	BDL
22	WWTP-IV_Jun	131.39	6164.74	481.85	BDL	BDL	6656.35	14.03
23	WWTP-IV_Jul	BDL	BDL	60.92	BDL	176.10	38722.87	22.12
24	WWTP-IV_Aug	41.21	7267.35	31.67	20.79	BDL	52574.44	12.26

BDL represents below detection limit.

Appendix A2

The targeted PPCPs concentrations in effluents of the studied WWTPs. Concentrations are expressed in ngL^{-1}.

S.No.	WWTP_month	Ciprofloxacin	Acetaminophen	Diclofenac	Ketoprofen	Sulfamethoxazole	Caffeine	Carbamazepine
1	WWTP-I_Mar	409.70	196.55	80.06	BDL	BDL	23570.02	9.87
2	WWTP-I_Apr	568.62	471.63	81.25	28.24	BDL	14512.69	BDL
3	WWTP-I_May	394.16	BDL	228.77	BDL	2.56	5085.04	35.81
4	WWTP-I_Jun	BDL	148.51	190.38	BDL	BDL	6078.36	2.86
5	WWTP-I_Jul	15.35	BDL	166.38	105.73	BDL	39752.76	6.45
6	WWTP-I_Aug	BDL	164.92	BDL	BDL	BDL	35729.40	BDL
7	WWTP-II_Mar	2871.98	38.95	228.57	369.63	BDL	46295.53	42.99
8	WWTP-II_Apr	9.12	42.13	372.10	499.26	70.61	46501.17	BDL
9	WWTP-II_May	BDL	BDL	231.42	115.09	BDL	559.56	BDL
10	WWTP-II_Jun	211.25	25.93	34.80	BDL	BDL	5883.62	1.72
11	WWTP-II_Jul	84.60	BDL	159.53	BDL	BDL	8212.18	8.68
12	WWTP-II_Aug	BDL	BDL	BDL	BDL	BDL	11541.83	BDL
13	WWTP-III_Mar	622.62	286.64	131.20	140.18	BDL	18915.65	4.85
14	WWTP-III_Apr	1064.22	222.19	197.05	BDL	BDL	62792.13	BDL
15	WWTP-III_May	BDL	42.88	55.51	BDL	BDL	3677.54	BDL
16	WWTP-III_Jun	BDL	BDL	22.51	BDL	BDL	BDL	BDL
17	WWTP-III_Jul	BDL	BDL	34.95	BDL	BDL	56786.06	0.52
18	WWTP-III_Aug	75.90	BDL	23.93	BDL	BDL	24122.71	BDL
19	WWTP-IV_Mar	180.41	2688.65	1032.58	973.14	BDL	50548.21	BDL
20	WWTP-IV_Apr	582.54	1998.76	272.51	BDL	BDL	10709.34	BDL
21	WWTP-IV_May	65.46	BDL	8.31	BDL	118.32	BDL	BDL
22	WWTP-IV_Jun	103.32	BDL	202.28	BDL	BDL	89.48	12.85
23	WWTP-IV_Jul	BDL	BDL	36.86	BDL	BDL	7771.24	8.30
24	WWTP-IV_Aug	BDL	BDL	8.82	BDL	BDL	24426.77	2.56

BDL represents below detection limit.

The targeted EDCs concentrations in influents and effluents of the studied WWTPs. Concentrations are expressed in ngL^{-1}.

			Influent						Effluent					
			Spring		Summer		Monsoon		Spring		Summer		Monsoon	
			March	April	May	June	July	August	March	April	May	June	July	August
S.No.	Compound	WWTP												
1.	TCS	WWTP-I	37.68	BDL	55.84	BDL	136.16	BDL	BDL	1.10	8.62	BDL	26.51	BDL
		WWTP-II	30.57	89.67	BDL	BDL	44.31	BDL	BDL	47.86	BDL	BDL	23.87	BDL
		WWTP-III	68.91	135.74	73.61	71.14	107.72	BDL	BDL	103.08	BDL	BDL	66.86	BDL
		WWTP-IV	8.38	48.57	BDL	16.26	29.06	214.37	BDL	BDL	BDL	15.35	BDL	159.17
2.	Estrone	WWTP-I	35619.73	40554.07	4576.91	15282.61	62731.30	96628.61	25246.81	34534.25	BDL	8695.03	29985.92	36154.05
		WWTP-II	34833.36	48016.52	868.18	1261.49	29281.80	64507.78	73573.77	42126.45	BDL	BDL	27275.14	10458.79
		WWTP-III	28623.11	39052.59	102395.19	BDL	116210.00	123951.42	32572.87	35965.20	2604.84	BDL	48633.81	60504.24
		WWTP-IV	46148.09	39902.05	14106.01	4677.25	22967.56	107872.04	51639.59	60053.02	5461.91	18403.02	19808.38	81766.67

BDL represents below detection limit.

Appendix A4

Triclosan:

Case 1. Influents Vs. Effluents (Overall)

    1.   **One-way ANOVA**

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)
Between groups:	10667.5	1	10667.5	4.556	0.03816
Within groups:	107700	46	2341.31	Permutation p (n=99999)	
Total:	118368	47	0.03664		

Components of variance (only for random effects):

Var(group):   346.925 Var(error):   2341.31 ICC: 0.129053

omega2: 0.06898

Levene´s test for homogeneity of variance, from means   p (same): 0.07615

Levene´s test, from medians   p (same): 0.05059

Welch F test in the case of unequal variances: F=4.556, df=41.34, p=0.03878

Bayes factor: 1.24 (no evidence for either equal or unequal means

    2.   **Effects**

	INF	EFF
INF		1.699; 57.93
EFF	-57.93; -1.699	

    3.   **Tukey's pairwise Analysis**

	INF	EFF
INF		0.03816
EFF	3.019	

    4.   **Residuals**
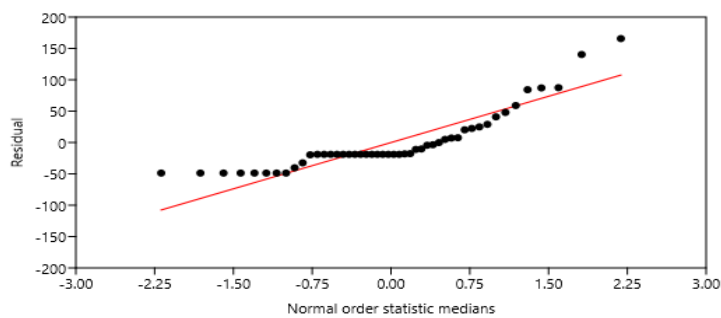
5. Kruskal-Wallis

Kruskal-Wallis test for equal medians

H (chi2): 5.051

Hc (tie corrected): 5.675

p (same): 0.01721

There is a significant difference between sample medians

6. Mann-Whitney Pairwise

	INF	EFF
INF		0.01773
EFF	0.01773	

7. Dunn's Post hoc

	INF	EFF
INF		0.01721
EFF	0.01721	

8. Test for Normal Distribution

	INF	EFF
N	24	24
Shapiro-Wilk W	0.8362	0.564
p(normal)	0.001224	2.51E-07
Anderson-Darling A	1.211	4.352
p(normal)	0.002933	3.60E-11
p(Monte Carlo)	0.0029	0.0001
Lilliefors L	0.1921	0.3403
p(normal)	0.02196	0.0001
p(Monte Carlo)	0.0223	0.0001
Jarque-Bera JB	8.64	52.84
p(normal)	0.0133	3.35E-12
p(Monte Carlo)	0.014	0.0003

9. Normal Probability Test

NOSM	INF	NOSM	EFF
-1.9038	0	-1.9038	0
-1.48287	0	-1.4829	0
-1.22602	0	-1.226	0
-1.03156	0	-1.0316	0
-0.86989	0	-0.8699	0
-0.72827	0	-0.7283	0
-0.59996	0	-0.6	0
-0.48086	0	-0.4809	0
-0.36823	8.38	-0.3682	0
-0.2601	16.26	-0.2601	0
-0.15494	29.06	-0.1549	0
-0.05146	30.57	-0.0515	0
0.051461	37.68	0.0515	0
0.154935	44.31	0.1549	0

0.260099	48.57	0.2601	0
0.368229	55.84	0.3682	1.1
0.480858	68.91	0.4809	8.62
0.59996	71.14	0.6	15.35
0.728271	73.61	0.7283	23.87
0.869886	89.67	0.8699	26.51
1.03156	107.72	1.0316	47.86
1.22602	135.74	1.226	66.86
1.48287	136.16	1.4829	103.08
1.9038	214.37	1.9038	159.17

10. Univariate Statistics

	INF	EFF
N	24	24
Min	0	0
Max	214.37	159.17
Sum	1167.99	452.42
Mean	48.66625	18.85083
Std. error	11.41476	8.050634
Variance	3127.124	1555.505
Stand. dev	55.92069	39.43989
Median	34.125	0
25 prcntil	0	0
75 prcntil	72.9925	21.74
Mode	0	0
Skewness	1.397895	2.620016
Kurtosis	1.962046	6.97395
Geom. mean	0	0
Coeff. var	114.9065	209.2209

Case 2. Seasonal Influents (Spring, Summer and Monsoon)

1. One-way ANOVA

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)

Between groups: 6363.09 2   3181.55 1.019   0.3781

Within groups: 65561   21   3121.95 Permutation p (n=99999)

Total: 71924.1 23   0.3867

Components of variance (only for random effects):

Var(group):   7.44923 Var(error):   3121.95 ICC: 0.0023804

omega2: 0.001588

Levene´s test for homogeneity of variance, from means   p (same): 0.03626

Levene´s test, from medians   p (same): 0.2561

Welch F test in the case of unequal variances: F=1.275, df=12.95, p=0.3124

Bayes factor: 0.2185 (substantial evidence for equal means)

2. **Effects**

	SPRING	SUMMER	MONSOON
SPRING		-47.34; 98.01	-86.69; 58.66
SUMMER	-98.01; 47.34		-112; 33.33
MONSOON	-58.66; 86.69	-33.33; 112	

3. **Tukey's pairwise Analysis**

	SPRING	SUMMER	MONSOON
SPRING		0.6421	0.8714
SUMMER	1.282		0.3548
MONSOON	0.7092	1.992	

4. **Residuals**
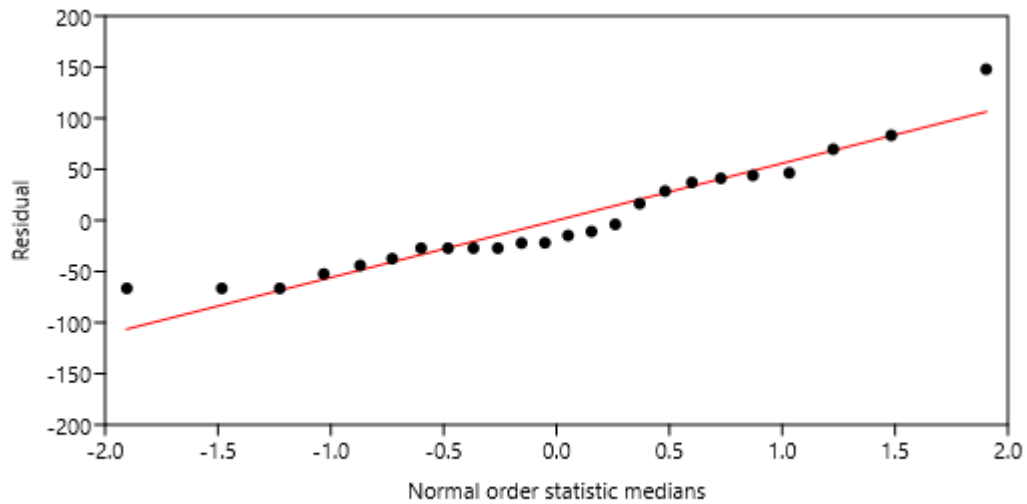
5. **Kruskal-Wallis**

Kruskal-Wallis test for equal medians

H (chi2): 1.399

Hc (tie corrected): 1.452

p (same): 0.4839

There is no significant difference between sample medians

6. **Mann-Whitney Pairwise**

	SPRING	SUMMER	MONSOON
SPRING		0.263	0.9157
SUMMER	0.263		0.4109
MONSOON	0.9157	0.4109	

7. Dunn's Post hoc

	SPRING	SUMMER	MONSOON
SPRING		0.2565	0.8289
SUMMER	0.2565		0.3584
MONSOON	0.8289	0.3584	

8. Test for Normal Distribution

	SPRING	SUMMER	MONSOON
N	8	8	8
Shapiro-Wilk W	0.9476	0.7569	0.8503
p(normal)	0.6867	0.009733	0.096
Anderson-Darling A	0.2248	0.8829	0.5268
p(normal)	0.7322	0.01255	0.1207
p(Monte Carlo)	0.7797	0.0101	0.1296
Lilliefors L	0.1595	0.2889	0.2355
p(normal)	0.7918	0.04684	0.211
p(Monte Carlo)	0.7961	0.0465	0.2157
Jarque-Bera JB	0.6697	1.182	1.067
p(normal)	0.7154	0.5536	0.5864
p(Monte Carlo)	0.4745	0.1273	0.1656

9. Normal Probability Test

NOSM	SPRING	NOSM	SUMMER	NOSM	MONSOON
-1.3852	0	-1.3852	0	-1.3852	0
-0.83757	8.37907	-0.83757	0	-0.83757	0
-0.46579	30.5705	-0.46579	0	-0.46579	0
-0.15039	37.6833	-0.15039	0	-0.15039	29.0616
0.150393	48.5733	0.150393	16.2606	0.150393	44.3068
0.465794	68.9092	0.465794	55.8402	0.465794	107.717
0.837572	89.6702	0.837572	71.1449	0.837572	136.158
1.3852	135.743	1.3852	73.6089	1.3852	214.371
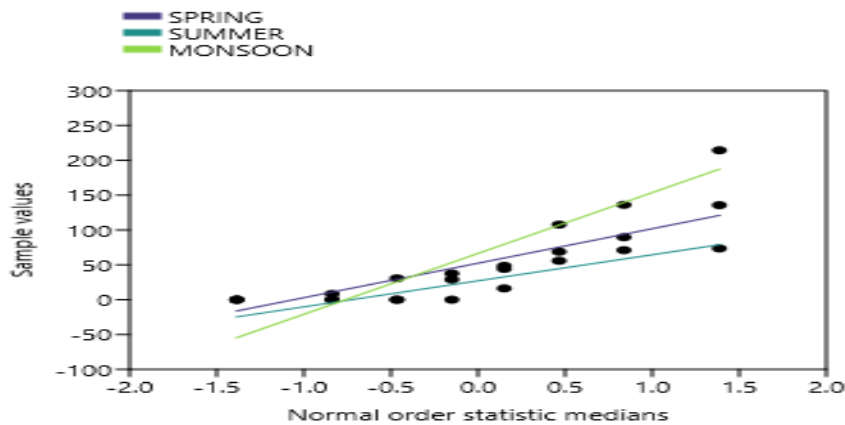
10. Univariate Statistics

	SPRING	SUMMER	MONSOON
N	8	8	8
Min	0	0	0

Max	135.7429	73.60886	214.3708
Sum	419.5284	216.8546	531.615
Mean	52.44105	27.10682	66.45188
Std. error	15.81082	11.94045	27.8958
Variance	1999.857	1140.594	6225.405
Stand. dev	44.71976	33.77268	78.90124
Median	43.1283	8.130312	36.68423
25 prcntil	13.92691	0	0
75 prcntil	84.47997	67.31873	129.0482
Mode	NA	0	0
Skewness	0.831949	0.636584	1.047783
Kurtosis	0.394089	-1.924	0.106647
Geom. mean	0	0	0
Coeff. var	85.27626	124.5911	118.7344

Case 3. Seasonal Effluents (Spring, Summer and Monsoon)

1. **One-way ANOVA**

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)
Between groups:	3983.41	2	1991.7	1.316	0.2896
Within groups:	31794.4	21	1514.02	Permutation p (n=99999)	
Total:	35777.8	23		0.2842	

Components of variance (only for random effects):

Var(group): 59.7108 Var(error): 1514.02 ICC: 0.0379422

omega2: 0.02562

Levene´s test for homogeneity of variance, from means   p (same): 0.03157

Levene´s test, from medians   p (same): 0.2279

Welch F test in the case of unequal variances: F=1.824, df=9.649, p=0.2128

Bayes factor: 0.2751 (substantial evidence for equal means)

2. **Effects**

	SPRING	SUMMER	MONSOON
SPRING		-34.6; 66.62	-66.16; 35.06
SUMMER	-66.62; 34.6		-82.17; 19.05
MONSOON	-35.06; 66.16	-19.05; 82.17	

3. **Tukey's pairwise Analysis**

	SPRING	SUMMER	MONSOON
SPRING		0.6933	0.7077
SUMMER	1.164		0.2587

MONSOON 1.13 2.294

4. Residuals
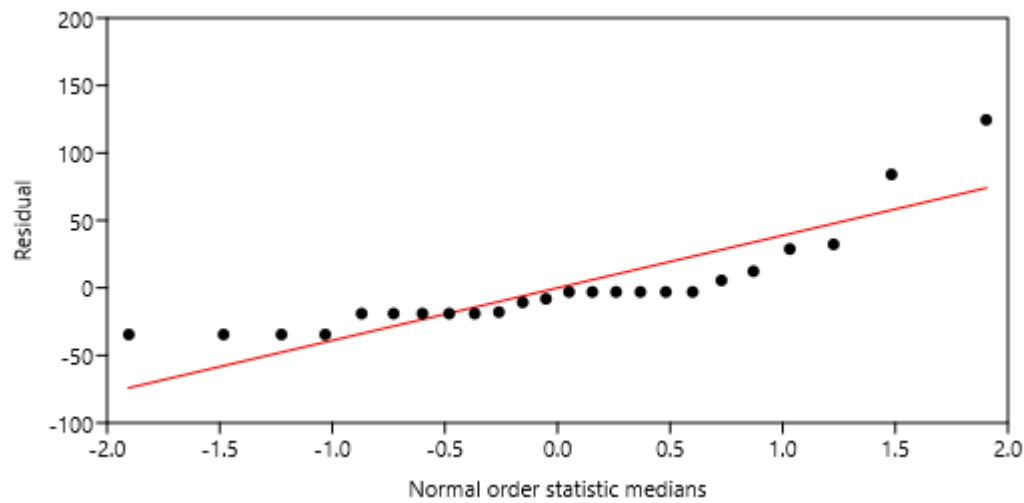
5. Kruskal-Wallis

Kruskal-Wallis test for equal medians

H (chi2): 1.445

Hc (tie corrected): 1.91

p (same): 0.3848

There is no significant difference between sample medians

6. Mann-Whitney Pairwise

	SPRING	SUMMER	MONSOON
SPRING		0.5656	0.6025
SUMMER	0.5656		0.1652
MONSOON	0.6025	0.1652	

7. Dunn's Post hoc

	SPRING	SUMMER	MONSOON
SPRING		0.4896	0.4896
SUMMER	0.4896		0.167
MONSOON	0.4896	0.167	

8. Test for Normal Distribution

	SPRING	SUMMER	MONSOON
N	8	8	8
Shapiro-Wilk W	0.6021	0.6062	0.7079
p(normal)	0.000168	0.000188	0.002765
Anderson-Darling A	1.564	1.586	1.023
p(normal)	0.000162	0.00014	0.005106

p(Monte Carlo)		0.0001	0.0001		0.0047
Lilliefors L		0.4319	0.4463		0.3076
p(normal)		0.0001	0.0001		0.02548
p(Monte Carlo)		0.0001	0.0001		0.0263
Jarque-Bera JB		3.933	2.94		4.019
p(normal)		0.14	0.2299		0.134
p(Monte Carlo)		0.013	0.0243		0.0121

9. Normal Probability Test

NOSM	SPRING	NOSM	SUMMER	NOSM	MONSOON
-1.3852	0	-1.3852	0	-1.3852	0
-0.83757	0	-0.83757	0	-0.83757	0
-0.46579	0	-0.46579	0	-0.46579	0
-0.15039	0	-0.15039	0	-0.15039	0
0.150393	0	0.150393	0	0.150393	23.8681
0.465794	1.1004	0.465794	0	0.465794	26.5119
0.837572	47.8648	0.837572	8.6187	0.837572	66.8649
1.3852	103.081	1.3852	15.3493	1.3852	159.171
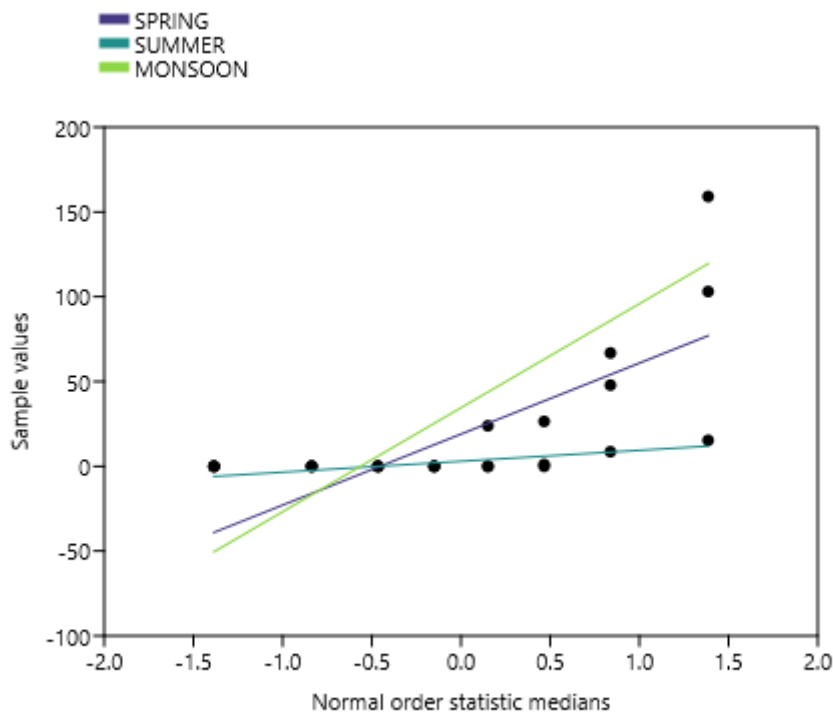
10. Univariate Statistics

	SPRING	SUMMER	MONSOON
N	8	8	8
Min	0	0	0
Max	103.0806	15.34927	159.1711
Sum	152.0458	23.96796	276.4159
Mean	19.00573	2.995995	34.55199
Std. error	13.38184	2.061873	19.60694

Variance	1432.589	34.01057	3075.456
Stand. dev	37.84956	5.831858	55.45679
Median	0	0	11.93405
25 prcntil	0	0	0
75 prcntil	36.17368	6.464023	56.77662
Mode	0	0	0
Skewness	2.031333	1.82612	2.012842
Kurtosis	3.689133	2.442147	4.089237
Geom. mean	0	0	0
Coeff. var	199.1482	194.6551	160.5025

Case 4. Seasonal Treatments (Spring, Summer and Monsoon)

1. **One-way ANOVA**

Test for equal means

        Sum of sqrs   df   Mean square   F   p (same)

Between groups: 21014   5   4202.79 1.813   0.1311

Within groups: 97355.4 42   2317.99 Permutation p (n=99999)

Total: 118369 47   0.1214

Components of variance (only for random effects):

Var(group):   235.601 Var(error):   2317.99 ICC: 0.0922627

omega2: 0.07809

Levene´s test for homogeneity of variance, from means   p (same): 0.002387

Levene´s test, from medians p (same): 0.1055

Welch F test in the case of unequal variances: F=3.721, df=16.85, p=0.01876

Bayes factor: 0.2607 (substantial evidence for equal means)

2. **Effects**

	INFL	EFFL	INFL	EFFL	INFL	EFFL
INFL		-41.49; 108.4	-49.59; 100.3	-25.48; 124.4	-88.94; 60.91	-57.04; 92.81
EFFL	-108.4; 41.49		-83.03; 66.82	-58.92; 90.93	-122.4; 27.48	-90.47; 59.38
INFL	-100.3; 49.59	-66.82; 83.03		-50.81; 99.04	-114.3; 35.58	-82.37; 67.48
EFFL	-124.4; 25.48	-90.93; 58.92	-99.04; 50.81		-138.4; 11.47	-106.5; 43.37
INFL	-60.91; 88.94	-27.48; 122.4	-35.58; 114.3	-11.47; 138.4		-43.02; 106.8
EFFL	-92.81; 57.04	-59.38; 90.47	-67.48; 82.37	-43.37; 106.5	-106.8; 43.02	

3. **Tukey's pairwise Analysis**

	INFL	EFFL	INFL	EFFL	INFL	EFFL
INFL		0.7333	0.897	0.3306	0.9917	0.9752
EFFL	1.964		0.9994	0.9848	0.3756	0.9867
INFL	1.488	0.4759		0.9148	0.5812	0.9996
EFFL	2.905	0.9405	1.416		0.1109	0.7774
INFL	0.8231	2.787	2.311	3.728		0.7696
EFFL	1.051	0.9133	0.4374	1.854	1.874	

4. Residuals
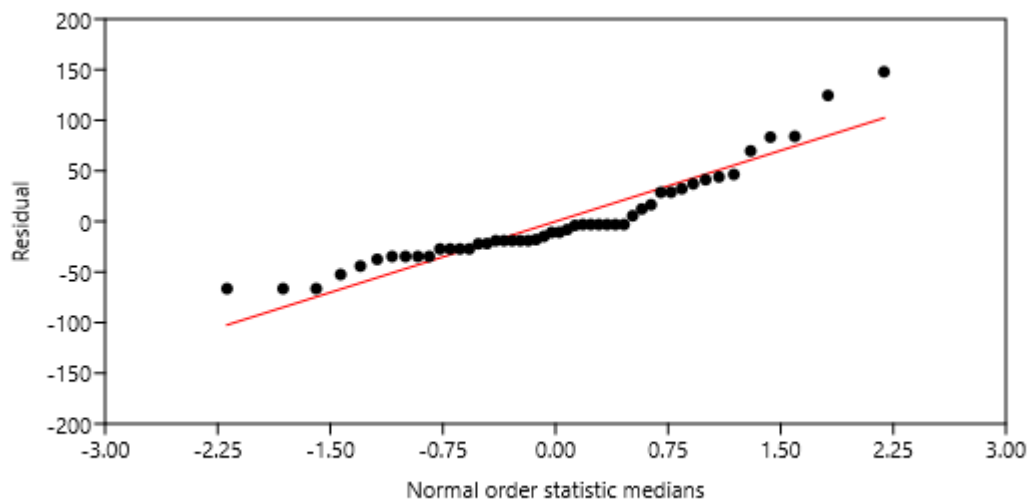
5. Kruskal-Wallis

Kruskal-Wallis test for equal medians

H (chi2): 8.093

Hc (tie corrected): 9.092

p (same): 0.1055

There is no significant difference between sample medians

6. Mann-Whitney Pairwise

	INFL	EFFL	INFL	EFFL	INFL	EFFL
INFL		0.06678	0.263	0.007232	0.9157	0.1827
EFFL	0.06678		0.6025	0.5656	0.2172	0.6025
INFL	0.263	0.6025		0.1652	0.4109	0.9553
EFFL	0.007232	0.5656	0.1652		0.0562	0.1652
INFL	0.9157	0.2172	0.4109	0.0562		0.4109
EFFL	0.1827	0.6025	0.9553	0.1652	0.4109	

7. Dunn's Post hoc

	INFL	EFFL	INFL	EFFL	INFL	EFFL
INFL		0.05354	0.1852	0.008517	0.6361	0.173
EFFL	0.05354		0.5447	0.4837	0.145	0.5702
INFL	0.1852	0.5447		0.1916	0.3944	0.9698
EFFL	0.008517	0.4837	0.1916		0.03095	0.2048
INFL	0.6361	0.145	0.3944	0.03095		0.3737
EFFL	0.173	0.5702	0.9698	0.2048	0.3737	

8. Test for Normal Distribution

	INFL	EFFL	INFL	EFFL	INFL	EFFL
N	8	8	8	8	8	8
Shapiro-Wilk W	0.9476	0.6021	0.7569	0.6062	0.8503	0.7079
p(normal)	0.6867	0.000168	0.009733	0.000188	0.096	0.002765
Anderson-Darling A	0.2248	1.564	0.8829	1.586	0.5268	1.023
p(normal)	0.7322	0.000162	0.01255	0.00014	0.1207	0.005106
p(Monte Carlo)	0.7849	0.0002	0.0126	0.0002	0.133	0.0054
Lilliefors L	0.1595	0.4319	0.2889	0.4463	0.2355	0.3076
p(normal)	0.7918	0.0001	0.04684	0.0001	0.211	0.02548
p(Monte Carlo)	0.7975	0.0001	0.0471	0.0001	0.2124	0.0267
Jarque-Bera JB	0.6697	3.933	1.182	2.94	1.067	4.019
p(normal)	0.7154	0.14	0.5536	0.2299	0.5864	0.134
p(Monte Carlo)	0.4716	0.0132	0.1332	0.0249	0.1626	0.0135

9. Normal Probability Test

NOSM	INFL	NOSM	EFFL	NOSM	INFL	NOSM	EFFL	NOSM	INFL	NOSM	EFFL
-1.3852	0	-1.3852	0	-1.3852	0	-1.3852	0	-1.3852	0	-1.3852	0
-0.83757	8.37907	-0.83757	0	-0.83757	0	-0.83757	0	-0.83757	0	-0.83757	0
-0.46579	30.5705	-0.46579	0	-0.46579	0	-0.46579	0	-0.46579	0	-0.46579	0
-0.15039	37.6833	-0.15039	0	-0.15039	0	-0.15039	0	-0.15039	29.0616	-0.15039	0
0.150393	48.5733	0.150393	0	0.150393	16.2606	0.150393	0	0.150393	44.3068	0.150393	23.8681
0.465794	68.9092	0.465794	1.1004	0.465794	55.8402	0.465794	0	0.465794	107.717	0.465794	26.5119
0.837572	89.6702	0.837572	47.8648	0.837572	71.1449	0.837572	8.6187	0.837572	136.158	0.837572	66.8649
1.3852	135.743	1.3852	103.081	1.3852	73.6089	1.3852	15.3493	1.3852	214.371	1.3852	159.171

10. Univariate Statistics

	INFL-SPRING	INFL-SUMMER	INFL-MONSOON	EFFL-SPRING	EFFL-SUMMER	EFFL-MONSOON
N	8	8	8	8	8	8
Min	28.62311	1.00E-07	22.96756	25.24681	0	10.45879
Max	48.01652	102.3952	123.9514	73.57377	18.40302	81.76667
Sum	312.7495	143.1676	624.1505	355.712	35.1648	314.587
Mean	39.09369	17.89596	78.01881	44.464	4.3956	39.32337
Std. error	2.203979	12.24771	13.77634	5.714766	2.300318	8.230104
Variance	38.86019	1200.052	1518.301	261.2684	42.33171	541.8769
Stand. dev	6.233794	34.64176	38.96538	16.1638	6.506283	23.27825
Median	39.47732	4.627077	80.56819	39.04582	1.302418	33.06998
25 prcntil	35.02995	0.966511	37.64418	33.06321	0	21.67507
75 prcntil	44.74959	14.98846	114.1255	57.94966	7.886748	57.53663
Mode	NA	NA	NA	NA	0	NA
Skewness	-0.15888	2.672678	-0.33156	0.831749	1.717604	0.7956783
Kurtosis	-0.06067	7.314851	-1.56732	-0.12286	2.819001	0.1464766
Geom. mean	38.64367	0.690625	67.05248	42.07255	0	33.19396
Coeff. var	15.94578	193.5731	49.94356	36.35256	148.0181	59.19698

Case 5. WWTP Treatment Eff. Percentage Removal (Triclosan)

1. One-way ANOVA

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)
Between groups:	1.51359E19	3	5.04531E18	1	0.4133

Within groups: 1.00906E20   20   5.04531E18   Permutation p (n=99999)

Total: 1.16042E20   23   0.828

Components of variance (only for random effects):

Var(group):   -1.46845E10   Var(error):   5.04531E18   ICC: -2.91052E-09

omega2:   0

Levene´s test for homogeneity of variance, from means   p (same): 0.003613

Levene´s test, from medians   p (same): 0.4133

Welch F test in the case of unequal variances: F=0.3693, df=10.5, p=0.7768

Bayes factor: 0.1755 (substantial evidence for equal means)

2. Effects

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
WWTP-I		-5.63E09; 1.962E09	-5.63E09; 1.962E09	-5.63E09; 1.962E09
WWTP-II	-1.962E09; 5.63E09		-3.796E09; 3.796E09	-3.796E09; 3.796E09
WWTP-III	-1.962E09; 5.63E09	-3.796E09; 3.796E09		-3.796E09; 3.796E09
WWTP-IV	-1.962E09; 5.63E09	-3.796E09; 3.796E09	-3.796E09; 3.796E09	

3. Tukey's pairwise Analysis

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
WWTP-I		0.5054	0.5054	0.5054
WWTP-II	2		1	1
WWTP-III	2	5.59E-09		1
WWTP-IV	2	1.12E-08	5.57E-09	

4. Residuals
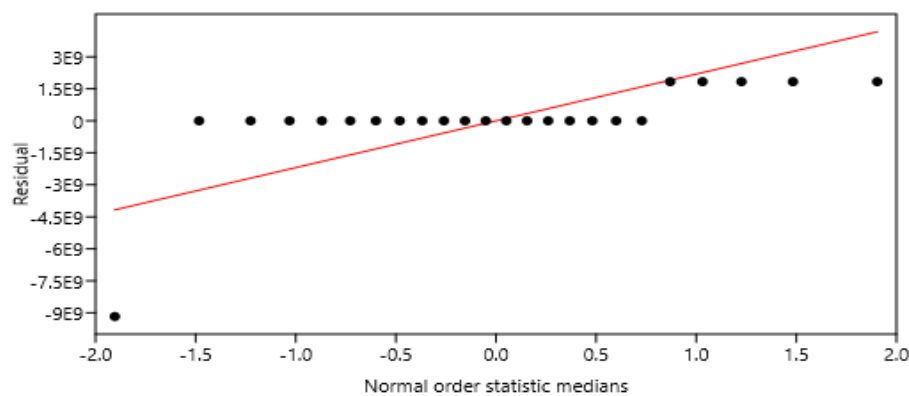
5. Kruskal-Wallis

Kruskal-Wallis test for equal medians

H (chi2): 0.2467

Hc (tie corrected):   0.3261

p (same): 0.9551

There is no significant difference between sample medians

6. Mann-Whitney Pairwise

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
WWTP-I		0.7888	0.7888	0.7888
WWTP-II	0.7888		0.775	0.775
WWTP-III	0.7888	0.775		0.9241
WWTP-IV	0.7888	0.775	0.9241	

7. Dunn's Post hoc

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
WWTP-I		0.5733	0.7425	0.8145
WWTP-II	0.5733		0.8145	0.7425
WWTP-III	0.7425	0.8145		0.9252
WWTP-IV	0.8145	0.7425	0.9252	

8. Test for Normal Distribution

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
N	6	6	5	6
Shapiro-Wilk W	0.9627	0.8461	0.9646	0.7669
p(normal)	0.8399	0.1464	0.8398	0.02898
Anderson-Darling A	0.2018	0.4584	0.2043	0.7062
p(normal)	0.7779	0.162	0.7336	0.03078
p(Monte Carlo)	0.8451	0.1754	0.8339	0.0294
Lilliefors L	0.1725	0.2368	0.1992	0.3093
p(normal)	0.833	0.3641	0.7423	0.07055
p(Monte Carlo)	0.8586	0.3831	0.7751	0.0738
Jarque-Bera JB	0.4201	0.8237	0.334	2.238
p(normal)	0.8105	0.6624	0.8462	0.3266
p(Monte Carlo)	0.7183	0.2059	0.8111	0.0154

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
N	6	6	6	6
Shapiro-Wilk W	0.4961	0.6422	0.681	0.6866
p(normal)	2.07E-05	0.001434	0.003874	0.004447
Anderson-Darling A	1.599	1.086	0.9842	0.9686
p(normal)	7.65E-05	0.002391	0.004733	0.005258
p(Monte Carlo)	0.0001	0.0009	0.004	0.0033
Lilliefors L	0.4918	0.4074	0.4058	0.4052
p(normal)	0.0001	0.001408	0.001733	0.001867
p(Monte Carlo)	0.0001	0.0024	0.0024	0.0022
Jarque-Bera JB	3.56	1.062	1.036	1.03
p(normal)	0.1686	0.5879	0.5956	0.5976
p(Monte Carlo)	0.0001	0.1062	0.116	0.1196

9. Normal Probability Test

NOSM	WWTP-I	NOSM	WWTP-II	NOSM	WWTP-III	NOSM	WWTP-IV
-1.23132	########	-1.23132	46.13	-1.23132	24.0618	-1.23132	5.6047
-0.630034	80.5287	-0.63003	46.6213	-0.63003	37.9256	-0.63003	25.7496
-0.198197	84.5654	-0.1982	100	-0.1982	100	-0.1982	100
0.198197	100	0.198197	100	0.198197	100	0.198197	100
0.630034	100	0.630034	100	0.630034	100	0.630034	100
1.23132	100	1.23132	100	1.23132	100	1.23132	100
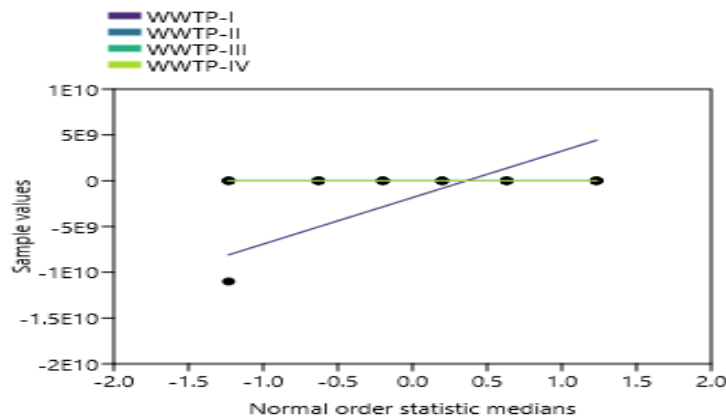
10. Univariate Statistics

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
N	6	6	6	6
Min	-1.10E+10	46.12997	24.06185	5.604699
Max	100	100	100	100
Sum	-1.10E+10	492.7513	461.9874	431.3543
Mean	-1.83E+09	82.12522	76.99791	71.89239
Std. error	1.83E+09	11.30518	14.65749	17.96605
Variance	2.02E+19	766.843	1289.051	1936.673
Stand. dev	4.49E+09	27.69193	35.90336	44.00764
Median	92.28271	100	100	100
25 prcntil	-2.75E+09	46.49849	34.45966	20.7134
75 prcntil	100	100	100	100
Mode	100	100	100	100
Skewness	-2.44949	-0.96838	-1.03265	-1.05842
Kurtosis	6	-1.87417	-1.48846	-1.33455
Geom. mean	0	77.40363	67.0981	49.34243
Coeff. var	-244.949	33.71916	46.62901	61.21322

Appendix A5

Estrone:
Case 1. Influents Vs. Effluents (Overall)

1. **One-way ANOVA**

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)
Between groups:	2923.5	1	2923.5	2.819	0.09992
Within groups:	47701.8	46	1037		Permutation p (n=99999)
Total:	50625.3	47	0.09963		

Components of variance (only for random effects):

Var(group):   78.6044   Var(error):   1037   ICC: 0.0704593

omega2: 0.03652

Levene´s test for homogeneity of variance, from means   p (same): 0.05595

Levene´s test, from medians   p (same): 0.1219

Welch F test in the case of unequal variances: F=2.819, df=38.74, p=0.1012

Bayes factor: 0.5763 (no evidence for either equal or unequal means)

2. **Effects**

	INF	EFF
INF		-3.103; 34.32
EFF	-34.32; 3.103	

3. **Tukey's pairwise Analysis**

	INF	EFF
INF		0.09992
EFF	2.375	

4. **Residuals**
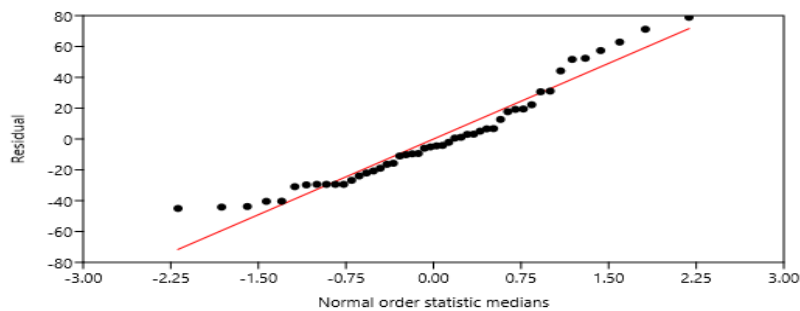
5. Kruskal-Wallis

Kruskal-Wallis test for equal medians

H (chi2): 1.796

Hc (tie corrected): 1.797

p (same): 0.18

There is no significant difference between sample medians

6. Mann-Whitney Pairwise

	INF	EFF
INF		0.1834
EFF	0.1834	

7. Dunn's Post hoc

	INF	EFF
INF		0.18
EFF	0.18	

8. Test for Normal Distribution

	INF	EFF
N	24	24
Shapiro-Wilk W	0.8909	0.9347
p(normal)	0.01389	0.1239
Anderson-Darling A	0.9213	0.4296
p(normal)	0.01602	0.2843
p(Monte Carlo)	0.0165	0.282
Lilliefors L	0.1772	0.1159
p(normal)	0.04792	0.5436
p(Monte Carlo)	0.0474	0.5366
Jarque-Bera JB	2.618	1.413
p(normal)	0.2701	0.4933
p(Monte Carlo)	0.0951	0.2744

9. Normal Probability Test

NOSM	INF	NOSM	EFF
-1.9038	1.00E-07	-1.9038	0
-1.48287	0.868185	-1.48287	0
-1.22602	1.26149	-1.22602	0
-1.03156	4.57691	-1.03156	0
-0.86989	4.67725	-0.86989	2.60484
-0.72827	14.106	-0.72827	5.46191
-0.59996	15.2826	-0.59996	8.69503
-0.48086	22.9676	-0.48086	10.4588
-0.36823	28.6231	-0.36823	18.403
-0.2601	29.2818	-0.2601	19.8084
-0.15494	34.8334	-0.15494	25.2468
-0.05146	35.6197	-0.05146	27.2751
0.051461	39.0526	0.051461	29.9859

0.154935	39.9021	0.154935	32.5729
0.260099	40.5541	0.260099	34.5343
0.368229	46.1481	0.368229	35.9652
0.480858	48.0165	0.480858	36.154
0.59996	62.7313	0.59996	42.1264
0.728271	64.5078	0.728271	48.6338
0.869886	96.6286	0.869886	51.6396
1.03156	102.395	1.03156	60.053
1.22602	107.872	1.22602	60.5042
1.48287	116.21	1.48287	73.5738
1.9038	123.951	1.9038	81.7667

10. Univariate Statistics

	INF	EFF
N	24	24
Min	1.00E-07	0
Max	123.9514	81.76667
Sum	1080.068	705.4638
Mean	45.00282	29.39432
Std. error	7.868776	4.949615
Variance	1486.023	587.9686
Stand. dev	38.54897	24.24806
Median	37.33616	28.63053
25 prcntil	14.40016	6.270191
75 prcntil	64.06366	47.00697
Mode	NA	0
Skewness	0.8046405	0.5232775
Kurtosis	-0.434928	-0.539042
Geom. mean	12.14074	0
Coeff. var	85.65901	82.49233

Case 2. Seasonal Influents (Spring, Summer and Monsoon)

1. One-way ANOVA

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)
Between groups:	14878	2	7439.02	8.094	0.002478

Within groups: 19300.5 21 919.071 Permutation p (n=99999)

Total: 34178.5 23 0.00293

Components of variance (only for random effects):

Var(group): 814.994 Var(error): 919.071 ICC: 0.469991

omega2: 0.3715

Levene´s test for homogeneity of variance, from means   p (same): 0.01557

Levene´s test, from medians   p (same): 0.04602

Welch F test in the case of unequal variances: F=5.133, df=9.851, p=0.0297

Bayes factor: 17.84 (strong evidence for unequal means)

2. **Effects**

	SPRING	SUMMER	MONSOON
SPRING		-18.23; 60.63	-78.36; 0.5064
SUMMER	-60.63; 18.23		-99.55; -20.69
MONSOON	-0.5064; 78.36	20.69; 99.55	

3. **Tukey's pairwise Analysis**

	SPRING	SUMMER	MONSOON
SPRING		0.3597	0.04535
SUMMER	1.978		0.001951
MONSOON	3.632	5.609	

4. **Residuals**
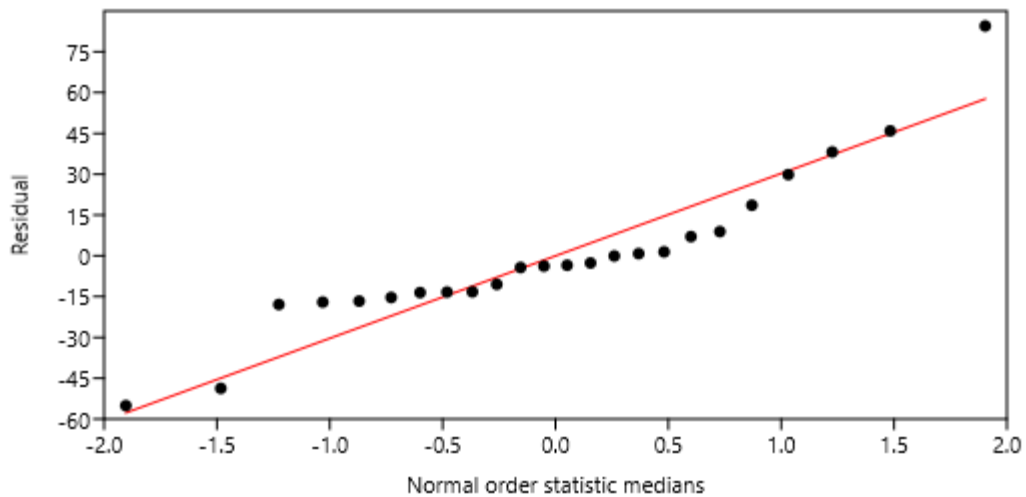
5. **Kruskal-Wallis**

Kruskal-Wallis test for equal medians

H (chi2): 11.47

Hc (tie corrected): 11.47

p (same): 0.003239

There is a significant difference between sample medians

6. **Mann-Whitney Pairwise**

	SPRING	SUMMER	MONSOON
SPRING		0.01359	0.08312
SUMMER	0.01359		0.005385

MONSOON   0.08312   0.005385

7. **Dunn's Post hoc**

	SPRING	SUMMER	MONSOON
SPRING		0.0403	0.1908
SUMMER	0.0403		0.0007829
MONSOON	0.1908	0.0007829	

8. **Test for Normal Distribution**

	SPRING	**SUMMER**	**MONSOON**
N	8	8	8
Shapiro-Wilk W	0.9678	0.563	0.9095
p(normal)	0.88	5.83E-05	0.3504
Anderson-Darling A	0.2029	1.622	0.3308
p(normal)	0.8099	0.000112	0.4179
p(Monte Carlo)	0.84	0.0001	0.4442
Lilliefors L	0.1574	0.4051	0.1835
p(normal)	0.8075	0.0001	0.5885
p(Monte Carlo)	0.8042	0.0004	0.5978
Jarque-Bera JB	0.1829	8.767	0.7598
p(normal)	0.9126	0.01248	0.6839
p(Monte Carlo)	0.9289	0.0001	0.3728

9. **Normal Probability Test**

NOSM	SPRING	NOSM	SUMMER	NOSM	MONSOON
-1.3852	28.6231	-1.3852	1.00E-07	-1.3852	22.9676
-0.837572	34.8334	-0.83757	0.868185	-0.83757	29.2818
-0.465794	35.6197	-0.46579	1.26149	-0.46579	62.7313
-0.150393	39.0526	-0.15039	4.57691	-0.15039	64.5078
0.150393	39.9021	0.150393	4.67725	0.150393	96.6286
0.465794	40.5541	0.465794	14.106	0.465794	107.872
0.837572	46.1481	0.837572	15.2826	0.837572	116.21
1.3852	48.0165	1.3852	102.395	1.3852	123.951
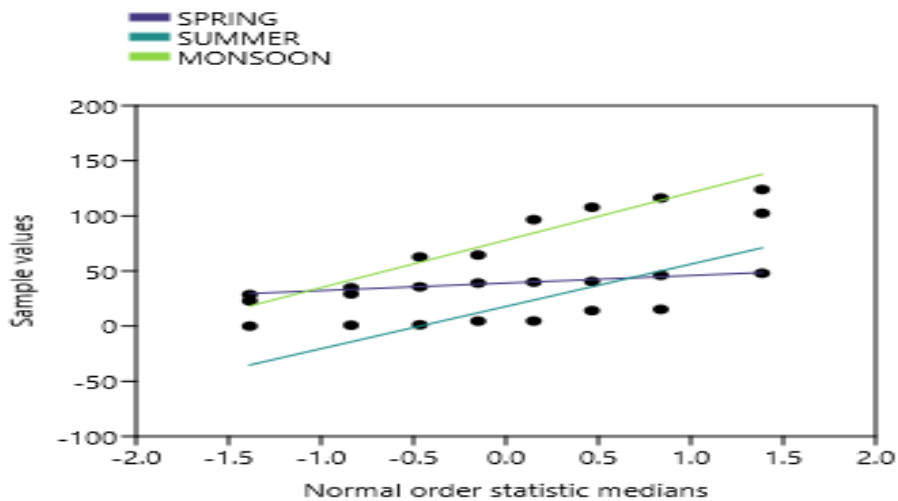
10. Univariate Statistics

	SPRING	SUMMER	MONSOON
N	8	8	8
Min	28.62311	1.00E-07	22.96756
Max	48.01652	102.3952	123.9514
Sum	312.7495	143.1676	624.1505
Mean	39.09369	17.89596	78.01881
Std. error	2.203979	12.24771	13.77634
Variance	38.86019	1200.052	1518.301
Stand. dev	6.233794	34.64176	38.96538
Median	39.47732	4.627077	80.56819
25 prcntil	35.02995	0.966511	37.64418
75 prcntil	44.74959	14.98846	114.1255
Mode	NA	NA	NA
Skewness	-0.15888	2.672678	-0.33156
Kurtosis	-0.06067	7.314851	-1.56732
Geom. mean	38.64367	0.690625	67.05248
Coeff. var	15.94578	193.5731	49.94356

Case 3. Seasonal Effluents (Spring, Summer and Monsoon)

1. One-way ANOVA

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)
Between groups:	7604.94	2	3802.47	13.49	0.0001705
Within groups:	5918.34	21	281.826	Permutation p (n=99999)	
Total:	13523.3	23	0.00023		

Components of variance (only for random effects):

Var(group):   440.08   Var(error):   281.826   ICC: 0.609609

omega2: 0.51

Levene´s test for homogeneity of variance, from means   p (same): 0.02481

Levene´s test, from medians   p (same): 0.09303

Welch F test in the case of unequal variances: F=25.58, df=11.17, p=6.763E-05

Bayes factor: 196.4 (decisive evidence for unequal means)

2. Effects

	SPRING	SUMMER	MONSOON
SPRING		18.23; 61.9	-16.69; 26.98
SUMMER	-61.9; -18.23		-56.76; -13.09
MONSOON	-26.98; 16.69	13.09; 56.76	

3. Tukey's pairwise Analysis

	SPRING	SUMMER	MONSOON
SPRING		0.0002904	0.815

SUMMER	6.751		0.001233
MONSOON	0.8661	5.885	

4. Residuals
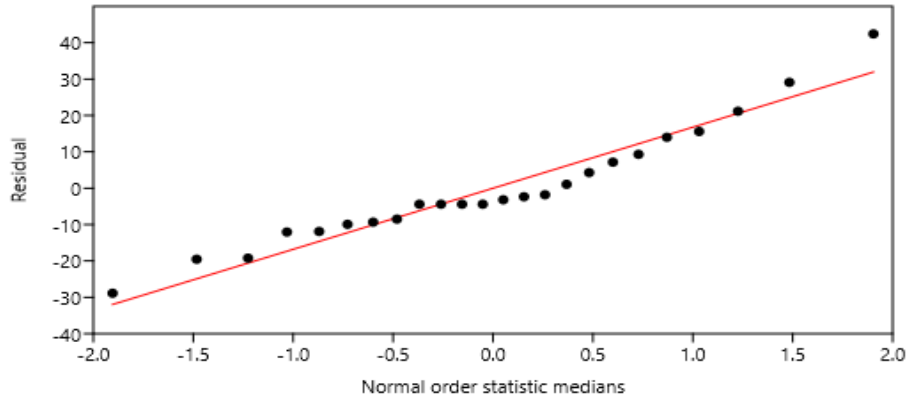
5. Kruskal-Wallis

Kruskal-Wallis test for equal medians

H (chi2): 15.1

Hc (tie corrected): 15.16

p (same): 0.0005103

There is a significant difference between sample medians.

6. Mann-Whitney Pairwise

	SPRING	SUMMER	MONSOON
SPRING		0.0008599	0.5635
SUMMER	0.0008599		0.001251
MONSOON	0.5635	0.001251	

7. Dunn's Post hoc

	SPRING	SUMMER	MONSOON
SPRING		0.0003453	0.6451
SUMMER	0.0003453		0.00182
MONSOON	0.6451	0.00182	

8. Test for Normal Distribution

	SPRING	SUMMER	MONSOON
N	8	8	8
Shapiro-Wilk W	0.9316	0.7582	0.9524

p(normal)	0.5304	0.01005	0.7359
Anderson-Darling A	0.309	0.8329	0.2336
p(normal)	0.4757	0.01728	0.6988
p(Monte Carlo)	0.5057	0.0161	0.7502
Lilliefors L	0.2005	0.2504	0.1791
p(normal)	0.4448	0.1446	0.6269
p(Monte Carlo)	0.4515	0.1466	0.6267
Jarque-Bera JB	0.7683	2.681	0.6614
p(normal)	0.681	0.2617	0.7184
p(Monte Carlo)	0.3634	0.0322	0.4781

9. Normal Probability Test

NOSM	SPRING	NOSM	SUMMER	NOSM	MONSOON
-1.3852	25.2468	-1.3852	0	-1.3852	10.4588
-0.837572	32.5729	-0.837572	0	-0.83757	19.8084
-0.465794	34.5343	-0.465794	0	-0.46579	27.2751
-0.150393	35.9652	-0.150393	0	-0.15039	29.9859
0.150393	42.1264	0.150393	2.60484	0.150393	36.154
0.465794	51.6396	0.465794	5.46191	0.465794	48.6338
0.837572	60.053	0.837572	8.69503	0.837572	60.5042
1.3852	73.5738	1.3852	18.403	1.3852	81.7667

Case 4. Seasonal Treatments (Spring, Summer and Monsoon)

1. One-way ANOVA

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)
Between groups:	25406.5	5	5081.3	8.463	1.323E-05
Within groups:	25218.8	42	600.448	Permutation p (n=99999)	
Total:	50625.3	47		2E-05	

Components of variance (only for random effects):

Var(group): 560.106 Var(error): 600.448 ICC: 0.482619

omega2: 0.4374

Levene´s test for homogeneity of variance, from means p (same): 0.001789

Levene´s test, from medians p (same): 0.01941

Welch F test in the case of unequal variances: F=26.4, df=18.61, p=7.662E-08

Bayes factor: 1836 (decisive evidence for unequal means)
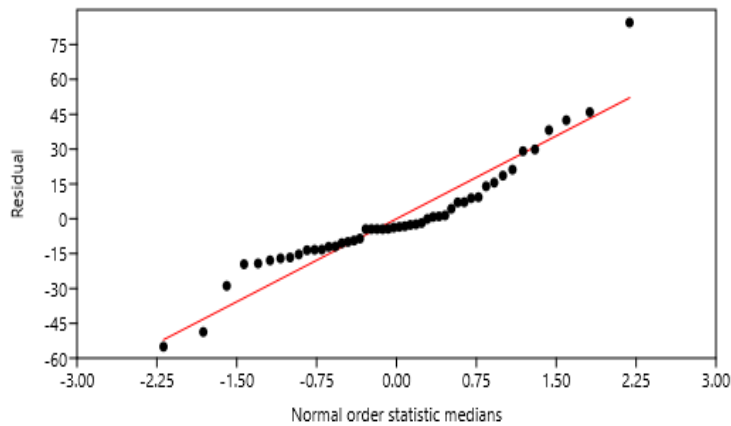
2. Effects

	INFL-SPRING	INFL-SUMMER	INFL-MONSOON	EFFL-SPRING	EFFL-SUMMER	EFFL-MONSOON
INFL-SPRING		-16.94; 59.33	-77.06; -0.7915	-43.5; 32.76	-3.436; 72.83	-38.36; 37.9

	INFL-SPRING	INFL-SUMMER	INFL-MONSOON	EFFL-SPRING	EFFL-SUMMER	EFFL-MONSOON
INFL-SUMMER	-59.33; 16.94		-98.26; -21.99	-64.7; 11.57	-24.63; 51.63	-59.56; 16.71
INFL-MONSOON	0.7915; 77.06	21.99; 98.26		-4.579; 71.69	35.49; 111.8	0.5618; 76.83
EFFL-SPRING	-32.76; 43.5	-11.57; 64.7	-71.69; 4.579		1.935; 78.2	-32.99; 43.27
EFFL-SUMMER	-72.83; 3.436	-51.63; 24.63	-111.8; -35.49	-78.2; -1.935		-73.06; 3.206
EFFL-MONSOON	-37.9; 38.36	-16.71; 59.56	-76.83; -0.5618	-43.27; 32.99	-3.206; 73.06	

3. Tukey's pairwise Analysis

	INFL-SPRING	INFL-SUMMER	INFL-MONSOON	EFFL-SPRING	EFFL-SUMMER	EFFL-MONSOON
INFL-SPRING		0.5204	0.03111	0.9978	0.07174	1
INFL-SUMMER	2.447		0.000198	0.2738	0.8778	0.5086
INFL-MONSOON	4.493	6.94		0.08861	5.54E-06	0.03262
EFFL-SPRING	0.6199	3.067	3.873		0.02448	0.9982
EFFL-SUMMER	4.005	1.558	8.498	4.625		0.0687
EFFL-MONSOON	0.02651	2.473	4.466	0.5934	4.032	

4. Residuals

5. Kruskal-Wallis

Kruskal-Wallis test for equal medians

H (chi2): 27.63

Hc (tie corrected): 27.64

p (same): 4.272E-05

There is a significant difference between sample medians.

6. Mann-Whitney Pairwise

	INFL-SPRING	INFL-SUMMER	INFL-MONSOON	EFFL-SPRING	EFFL-SUMMER	EFFL-MONSOON
INFL-SPRING		0.01359	0.08312	0.7929	0.0008599	0.7132
INFL-SUMMER	0.01359		0.005385	0.01359	0.2237	0.02395
INFL-MONSOON	0.08312	0.005385		0.1278	0.0008599	0.05203

EFFL-SPRING	0.7929	0.01359	0.1278		0.0008599	0.5635
EFFL-SUMMER	0.00086	0.2237	0.00086	0.00086		0.001251
EFFL-MONSOON	0.7132	0.02395	0.05203	0.5635	0.001251	

7. Dunn's Post hoc

	INFL-SPRING	INFL-SUMMER	INFL-MONSOON	EFFL-SPRING	EFFL-SUMMER	EFFL-MONSOON
INFL-SPRING		0.02557	0.2112	0.8582	0.001387	0.775
INFL-SUMMER	0.02557		0.000496	0.01589	0.3348	0.05154
INFL-MONSOON	0.2112	0.000496		0.2838	8.68E-06	0.1245
EFFL-SPRING	0.8582	0.01589	0.2838		0.0007357	0.6424
EFFL-SUMMER	0.001387	0.3348	8.68E-06	0.000736		0.003597
EFFL-MONSOON	0.775	0.05154	0.1245	0.6424	0.003597	

8. Test for Normal Distribution

	INFL-SPRING	INFL-SUMMER	INFL-MONSOON	EFFL-SPRING	EFFL-SUMMER	EFFL-MONSOON
N	8	8	8	8	8	8
Shapiro-Wilk W	0.9678	0.563	0.9095	0.9316	0.7582	0.9524
p(normal)	0.88	5.83E-05	0.3504	0.5304	0.01005	0.7359
Anderson-Darling A	0.2029	1.622	0.3308	0.309	0.8329	0.2336
p(normal)	0.8099	0.000112	0.4179	0.4757	0.01728	0.6988
p(Monte Carlo)	0.8467	0.0001	0.4435	0.5044	0.0154	0.7447
Lilliefors L	0.1574	0.4051	0.1835	0.2005	0.2504	0.1791
p(normal)	0.8075	0.0001	0.5885	0.4448	0.1446	0.6269
p(Monte Carlo)	0.8139	0.0005	0.5883	0.4513	0.1532	0.6249
Jarque-Bera JB	0.1829	8.767	0.7598	0.7683	2.681	0.6614
p(normal)	0.9126	0.01248	0.6839	0.681	0.2617	0.7184
p(Monte Carlo)	0.9307	0.0001	0.3707	0.363	0.0315	0.474

9. Normal Probability Test

NOSM	INFL-SPRING	NOSM	INFL-SUMMER	NOSM	INFL-MONSOON	NOSM	EFFL-SPRING	NOSM	EFFL-SUMMER	NOSM	EFFL-MONSOON
-1.3852	28.6231	-1.3852	1.00E-07	-1.3852	22.9676	-1.3852	25.2468	-1.3852	0	-1.3852	10.4588
-0.837572	34.8334	-0.83757	0.868185	-0.83757	29.2818	-0.837572	32.5729	-0.83757	0	-0.83757	19.8084
-0.465794	35.6197	-0.46579	1.26149	-0.46579	62.7313	-0.465794	34.5343	-0.46579	0	-0.46579	27.2751
-0.150393	39.0526	-0.15039	4.57691	-0.15039	64.5078	-0.150393	35.9652	-0.15039	0	-0.15039	29.9859
0.150393	39.9021	0.150393	4.67725	0.150393	96.6286	0.150393	42.1264	0.150393	2.60484	0.150393	36.154
0.465794	40.5541	0.465794	14.106	0.465794	107.872	0.465794	51.6396	0.465794	5.46191	0.465794	48.6338
0.837572	46.1481	0.837572	15.2826	0.837572	116.21	0.837572	60.053	0.837572	8.69503	0.837572	60.5042
1.3852	48.0165	1.3852	102.395	1.3852	123.951	1.3852	73.5738	1.3852	18.403	1.3852	81.7667

10. Univariate Statistics

	INFL-SPRING	INFL-SUMMER	INFL-MONSOON	EFFL-SPRING	EFFL-SUMMER	EFFL-MONSOON
N	8	8	8	8	8	8
Min	28.62311	1.00E-07	22.96756	25.24681	0	10.45879
Max	48.01652	102.3952	123.9514	73.57377	18.40302	81.76667
Sum	312.7495	143.1676	624.1505	355.712	35.1648	314.587
Mean	39.09369	17.89596	78.01881	44.464	4.3956	39.32337
Std. error	2.203979	12.24771	13.77634	5.714766	2.300318	8.230104
Variance	38.86019	1200.052	1518.301	261.2684	42.33171	541.8769
Stand. dev	6.233794	34.64176	38.96538	16.1638	6.506283	23.27825
Median	39.47732	4.627077	80.56819	39.04582	1.302418	33.06998
25 prcntil	35.02995	0.966511	37.64418	33.06321	0	21.67507
75 prcntil	44.74959	14.98846	114.1255	57.94966	7.886748	57.53663
Mode	NA	NA	NA	NA	0	NA
Skewness	-0.15888	2.672678	-0.33156	0.831749	1.717604	0.7956783
Kurtosis	-0.06067	7.314851	-1.56732	-0.12286	2.819001	0.1464766
Geom. mean	38.64367	0.690625	67.05248	42.07255	0	33.19396
Coeff. var	15.94578	193.5731	49.94356	36.35256	148.0181	59.19698

Case 5. WWTP Treatment Eff. Percentage Removal

1. One-way ANOVA

Test for equal means

	Sum of sqrs	df	Mean square	F	p (same)
Between groups:	25406.5	5	5081.3	8.463	1.323E-05
Within groups:	25218.8	42	600.448	Permutation p (n=99999)	
Total:	50625.3	47	2E-05		

Components of variance (only for random effects):

Var(group): 560.106 Var(error): 600.448 ICC: 0.482619

omega2: 0.4374

Levene´s test for homogeneity of variance, from means   p (same): 0.001789

Levene´s test, from medians   p (same): 0.01941

Welch F test in the case of unequal variances: F=26.4, df=18.61, p=7.662E-08

Bayes factor: 1836 (decisive evidence for unequal means)

2. Effects

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
WWTP-I		-121.1; 157.8	-136.1; 156.4	-46.36; 232.5
WWTP-II	-157.8; 121.1		-154.5; 138	-64.72; 214.2
WWTP-III	-156.4; 136.1	-138; 154.5		-63.3; 229.2
WWTP-IV	-232.5; 46.36	-214.2; 64.72	-229.2; 63.3	

3. Tukey's pairwise Analysis

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
WWTP-I		0.9796	0.9969	0.2357
WWTP-II	0.5482		0.9983	0.4142
WWTP-III	0.2883	0.2343		0.366
WWTP-IV	2.779	2.231	2.361	

4. Residuals
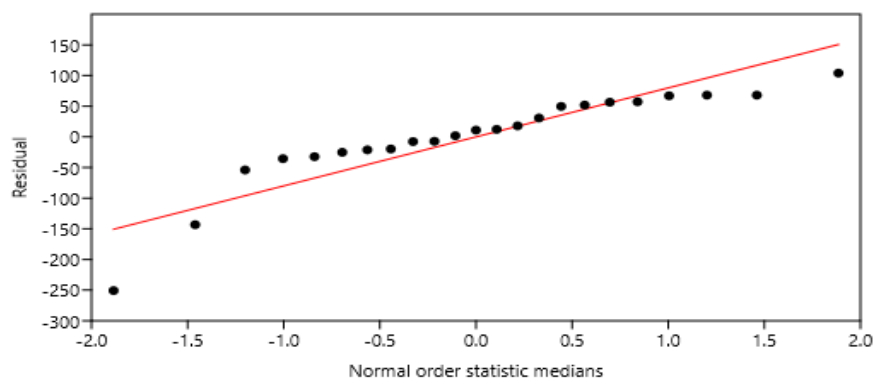
5. Kruskal-Wallis
Kruskal-Wallis test for equal medians

H (chi2): 3.805

Hc (tie corrected): 3.813

p (same): 0.2824

There is no significant difference between sample medians

6. **Mann-Whitney Pairwise**

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
WWTP-I		0.8089	0.6481	0.04533
WWTP-II	0.8089		0.7837	0.2971
WWTP-III	0.6481	0.7837		0.3153
WWTP-IV	0.04533	0.2971	0.3153	

7. **Dunn's Post hoc**

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
WWTP-I		0.6393	0.495	0.06085
WWTP-II	0.6393		0.8137	0.1597
WWTP-III	0.495	0.8137		0.2692
WWTP-IV	0.06085	0.1597	0.2692	

8. **Test for Normal Distribution**

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
N	6	6	5	6
Shapiro-Wilk W	0.9627	0.8461	0.9646	0.7669
p(normal)	0.8399	0.1464	0.8398	0.02898
Anderson-Darling A	0.2018	0.4584	0.2043	0.7062
p(normal)	0.7779	0.162	0.7336	0.03078
p(Monte Carlo)	0.8451	0.1754	0.8339	0.0294
Lilliefors L	0.1725	0.2368	0.1992	0.3093
p(normal)	0.833	0.3641	0.7423	0.07055
p(Monte Carlo)	0.8586	0.3831	0.7751	0.0738
Jarque-Bera JB	0.4201	0.8237	0.334	2.238
p(normal)	0.8105	0.6624	0.8462	0.3266
p(Monte Carlo)	0.7183	0.2059	0.8111	0.0154

9. **Normal Probability Test**

NOSM	WWTP-I	NOSM	WWTP-II	NOSM	WWTP-III	NOSM	WWTP-IV
-1.23132	14.8439	-1.23132	-111.216	-1.129	-13.7992	-1.23132	-293.458
-0.630034	29.1213	-0.63003	6.85292	-0.48565	7.90572	-0.630034	-50.5011
-0.198197	43.1051	-0.1982	12.2668	-1.09E-09	51.1871	-0.198197	-11.8997
0.198197	52.1994	0.198197	83.7868	0.485653	58.1501	0.198197	13.755
0.630034	62.5845	0.630034	100	1.129	97.4561	0.630034	24.2003
1.23132	100	1.23132	100			1.23132	61.2795
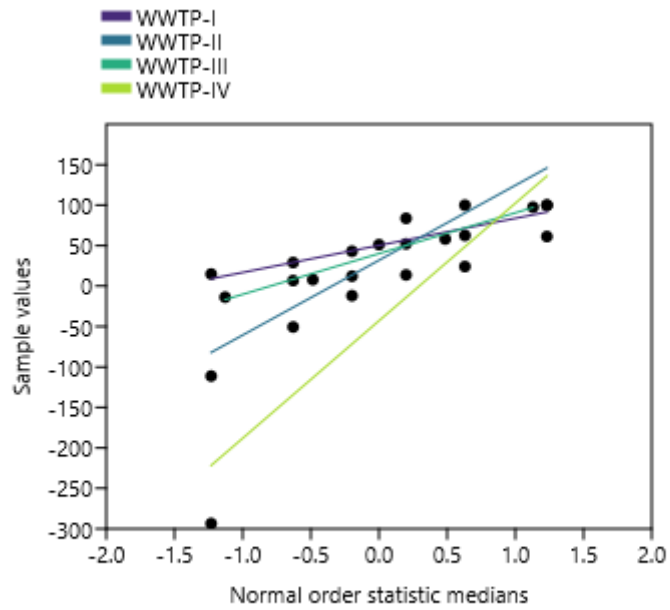
10. **Univariate Statistics**

	WWTP-I	WWTP-II	WWTP-III	WWTP-IV
N	6	6	5	6
Min	14.84393	-111.216	-13.7992	-293.459
Max	100	100	97.45609	61.27954
Sum	301.8543	191.69	200.8998	-256.625
Mean	50.30905	31.94834	40.17996	-42.7708
Std. error	12.08587	33.39789	19.59594	52.39716
Variance	876.409	6692.516	1920.004	16472.77
Stand. dev	29.60421	81.8078	43.81785	128.3463
Median	47.65227	48.02677	51.18714	0.927606
25 prcntil	25.55194	-22.6644	-2.94674	-111.24
75 prcntil	71.9384	100	77.80308	33.47012
Mode	NA	100	NA	NA
Skewness	0.81009	-1.19899	0.020477	-2.00327
Kurtosis	0.954978	1.107196	-1.06374	4.321141
Geom. mean	42.73038	0	0	0
Coeff. var	58.8447	256.0628	109.054	-300.08

LIST OF PUBLICATIONS FROM THE CURRENT WORK

1. **Silori, R.**, & Tauseef, S. M. (2022). A Review of the Occurrence of Pharmaceutical Compounds as Emerging Contaminants in Treated Wastewater and Aquatic Environments. *Current Pharmaceutical Analysis*, *18*(4), 345–379. https://doi.org/10.2174/1573412918666211119142030

2. **Silori, R.**, Shrivastava, V., Singh, A., Sharma, P., Aouad, M., Mahlknecht, J., & Kumar, M. (2022). Global groundwater vulnerability for Pharmaceutical and Personal care products (PPCPs): The scenario of second decade of 21st century. *Journal of Environmental Management*, *320*, 115703. https://doi.org/10.1016/J.JENVMAN.2022.115703

3. Kumar, M.[#], **Silori, R.**[#], Mazumder, P., & Tauseef, S. M. (2023). Screening of Pharmaceutical and Personal Care Products (PPCPs) along wastewater treatment system equipped with Root Zone Treatment: A potential model for domestic waste leachate management. *Journal of Environmental Management, 335,* 117494. https://doi.org/10.1016/j.jenvman.2023.117494. [#]**Joint first author**.

4. **Silori, R.,** Kumar, M., Madhab Mahapatra, D., Biswas, P., Prakash Vellanki, B., Mahlknecht, J., Tauseef, S. M, & Barcelo, D. (2023). Prevalence of Endocrine Disrupting Chemicals in the urban wastewater treatment systems of Dehradun, India: Daunting presence of Estrone. *Environmental Research*, *235*, 116673. https://doi.org/10.1016/j.envres.2023.116673

5. **Silori, R.**, Zang, J., Raval, N. P., Giri, B. S., Mahlknecht, J., Mora, A., Dueñas-Moreno, J., Tauseef, S. M, & Kumar, M. (2023). Adsorptive removal of ciprofloxacin and sulfamethoxazole from aqueous matrices using sawdust and plastic waste-derived biochar: A sustainable fight against antibiotic resistance. *Bioresource Technology,* 129537. https://doi.org/10.1016/j.biortech.2023.129537

6. **Silori, R.**, Kumar, M., Mahapatra, D. M., Biswas, P., Vellanki, B. P., & Tauseef, S. M. Occurrence, seasonal variation, and fate of pharmaceutical and personal care compounds (PPCPs) in wastewater treatment plants in the major metropolitan city of Uttarakhand, India. Submitted in *Environment International*.

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