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GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**FATE OF EMERGING POLLUTANTS IN THE ENVIRONMENT:
EFFECT OF CLIMATE CHANGE**



LAMA RAMADAN

A THESIS OF DOCTORATE
DEPARTMENT OF ENVIRONMENTAL ENGINEERING

ADVISOR: ASSOC. PROF. DR. EMEL TOPUZ

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*To the snowy heart of
Bloudan*

ABSTRACT

Emerging contaminants (ECs) have become a critical environmental concern due to their widespread presence and ecological risks. This thesis investigates the fate of ECs mixtures under climate change variables and co-contaminants, as well as their effects on soil microbial communities and plants. Using photolysis and adsorption experiments, we examined the degradation and transport of ECs in aquatic and terrestrial systems under varying temperatures and organic matter levels. The influence of co-contaminants such as polypropylene microplastics (PP-MPs) and silver sulphide nanoparticles (Ag₂SNPs) on ECs behavior was also assessed.

A rapid and sensitive analytical method was developed for the simultaneous detection of five ECs in aqueous solution using solid-phase extraction (SPE) followed by liquid chromatography-mass spectrometry (LC-MS/MS). High recovery rates (72–114%) were achieved. Limits of detection and quantification ranged from 10 ng/L to 50 ng/L and from 5 µg/L to 25 µg/L, respectively. Quality control confirmed the suitability of the method for accurate extraction and analysis of multiclass ECs.

Photolysis experiments showed that compounds with high molar absorption coefficients (e.g., diclofenac, ciprofloxacin) degraded rapidly in distilled water (DW), while dissolved organic matter (DOM) in synthetic surface water (SSW) acted as both photosensitizer and inhibitor. ECs mixtures degraded more slowly than single compounds. Elevated temperatures accelerated photolysis in DW but reduced it in SSW. Co-contaminants such as PP-MPs and Ag₂SNPs modulated photolysis, either inhibiting or enhancing degradation depending on compound chemistry.

Adsorption studies revealed that most ECs followed a pseudo-second-order kinetic model. Hydrophobic compounds (diclofenac, terbutryn) showed stronger sorption to soil organic matter than polar ones (ciprofloxacin). The presence of multiple ECs or co-contaminants altered adsorption kinetics. For instance, PP-MPs reduced ciprofloxacin adsorption from 0.244 min⁻¹ to 0.064 min⁻¹, likely due to hydrophobic interactions that promote desorption. Diuron and terbutryn showed smaller decreases, suggesting structure-dependent interactions.

Biodegradation experiment in soil indicated that ECs+PP-MPs increased microbial activity and altered microbial community composition. All ECs degraded by 50–90% in ECs-alone treatment. PP-MPs reduced degradation efficiency of terbutryn and diuron, suggesting higher stability and altered microbial exposure via modified adsorption dynamics. Soil microbial analyses showed that ECs or PP-MPs alone caused limited effects, but their combination induced significant shifts in bacterial community composition and transiently elevated respiration rates. These changes persisted over 15 days, while fungal communities remained relatively stable. Combined ECs+PP-MPs exposure also altered rhizosphere volatile emissions, suppressing beneficial volatiles (e.g., heneicosane) and enhancing phytotoxic compounds (e.g., 2-methoxyphenol, 2,4-DTBP), resulting in reduced maize biomass. Overall, this work highlights the complex interplay between climate factors, co-contaminants, and compound chemistry in controlling the fate and ecological impacts of ECs. Integrating photolysis, adsorption, biodegradation, and plant responses, the study demonstrates that climate change and co-contaminants jointly influence ECs persistence, mobility, and toxicity. These findings underscore the need to incorporate co-contaminant interactions and climate factors into risk assessment frameworks and predictive models to better manage ECs related ecological risks.

Keywords: Emerging Contaminants, Photodegradation, Adsorption, Liquid Chromatography-Mass Spectrometry, Microorganisms, Maize Plants.

ÖZET

Yeni ortaya çıkan kirleticiler (ECs), yaygın bulunurlukları ve potansiyel ekolojik etkileri nedeniyle kritik bir çevresel sorun haline gelmiştir. Bu tez, bir ECs karışımının iklim değişkenleri ve eş kirleticiler etkisi altındaki kaderini ve ayrıca toprak mikrobiyal toplulukları ile bitkiler üzerindeki ekolojik etkilerini incelemektedir. Fotoliz ve adsorpsiyon deneylerinin kombinasyonu kullanılarak, farklı çevresel koşullar (sıcaklık ve organik madde dahil) altında sucul ve karasal sistemlerde ECs'nin bozunması ve taşınımı araştırılmıştır. Ayrıca, mikroplastikler (PP-MPs) ve gümüş nanoparçacıkların (AgNPs) ECs davranışını nasıl değiştirdiği değerlendirilmiştir.

Bu çalışmada, beş farklı EC'nin sulu çözeltilerde çok düşük derişimlerde eşzamanlı tespiti için katı faz ekstraksiyonu (SPE) ve ardından sıvı kromatografi-kütle spektrometrisi (LC-MS/MS) tabanlı hızlı ve hassas bir ölçüm yöntemi geliştirilmiştir. Tüm hedeflenen bileşikler için yüksek geri kazanım oranları (%72–114) elde edilmiştir. Siproflaksasin (CIP), diuron (DIU), terbutrin (TER) ve diklofenak (DCF) için tespit limiti (LOD) 10 ng/L, tayin limiti (LOQ) ise 5 µg/L olarak belirlenmiştir. EE2 için ise LOD 50 ng/L ve LOQ 25 µg/L'dir. Hedef kirleticilerin fotodegradasyonu, farklı su matrislerinde (saf su (DW) ve sentetik yüzey suyu (SSW)) hem tekil bileşikler hem de karışım halinde incelenmiştir. Geliştirilen yöntemlerin kalite kontrol testleri, çok sınıflı ECs'nin çevrede doğru şekilde ekstraksiyonu ve analizi için uygunluğunu doğrulamıştır.

Fotoliz deneyleri, yüksek molar absorpsiyon katsayılarına sahip kirleticilerin (örn. diklofenak ve siproflaksasin) saf suda hızlı bir şekilde bozunduğunu, ancak sentetik yüzey suyundaki çözünmüş organik maddenin (DOM) hem fotosensitizer hem de inhibitör rolü oynadığını göstermiştir. ECs karışımları, foton absorpsiyumu için rekabet nedeniyle tekil bileşiklere kıyasla daha yavaş fotodegradasyona uğramıştır. ECs karışımının fotodegradasyonu ayrıca farklı sıcaklıklarda (25 °C ve 35 °C) incelenmiştir. Artan sıcaklık, çoğu EC için DW'de fotoliz hızını artırırken, SSW'de doğal bileşenlerin (örneğin organik madde) varlığı tüm ECs için fotodegradasyonu azaltmıştır. PP-MPs ve AgNPs gibi eş kirleticiler fotolizi ayrıca etkilemiş, kirleticinin kimyasal özelliklerine bağlı olarak bozunmayı ya inhibe etmiş ya da hızlandırmıştır.

Adsorpsiyon çalışmaları, çoğu EC'nin sözde ikinci dereceden doğrusal olmayan kinetik modele uyduğunu göstermiştir. Hidrofobik bileşikler (örn. diklofenak, terbutrin) toprak organik maddesine (SOM) daha güçlü bağlanma eğilimi gösterirken, polar bileşikler (örn. siproflaksasin) daha değişken adsorpsiyon kinetiği sergilemiştir. Toprak çözeltilerinde birden fazla EC'nin bulunması, tekil bileşiklerin adsorpsiyon verimliliğini azaltmıştır. PP-MPs ve AgNPs'nin varlığı, her kirleticinin kendine özgü fiziko-kimyasal özelliklerine bağlı olarak adsorpsiyon kinetiğini farklı şekillerde etkilemiştir. Örneğin, PP-MPs varlığı siproflaksasin'in adsorpsiyonunu belirgin şekilde azaltarak hızını 0.244 dk⁻¹'den 0.064 dk⁻¹'e düşürmüştür. PP-MPs'nin hidrofobik doğası, hidrofobik ECs ile güçlü etkileşim kurarak toprak yüzeyinden desorpsiyona neden olabilmekte ve toprakta tutulmayı azaltabilmektedir. Buna karşılık, diuron ve terbutryn adsorpsiyon hızında yalnızca küçük düşüşler göstermiştir.

Toprak biyodegradasyon deneyleri, ECs'nin dönüşümünde mikrobiyal aktivitenin ana etken olduğunu ortaya koymuştur. Steril olmayan topraklarda siproflaksasin, diklofenak, diuron ve EE2 önemli ölçüde parçalanırken (%50–90 azalma), terbutrin düşük biyobozunurluğu ve kararlı adsorpsiyonu nedeniyle kalıcı bulunmuştur. Ancak PP-MPs varlığı, EE2 dışında çoğu EC'nin bozunma verimliliğini azaltmıştır. Bu

durum, mikroplastiklerin adsorpsiyon-desorpsiyon dinamiklerini deęiřtirerek kirleticilere mikrobiyal maruziyeti modüle ettięini dūřündürmektedir.

Toprak mikrobiyal topluluk analizleri, yalnızca ECs veya yalnızca PP-MPs uygulamalarının çevresel olarak anlamlı deřiřimlerde sınırlı etkilere yol ađtıęını, ancak kombine uygulamanın (ECs+PP-MPs) bakteri topluluęu bileřiminde belirgin bir kaymaya ve inkübasyonun ilk ařamasında solunum hızında anlamlı bir artıřa neden olduęunu göstermiřtir. Solunum stabilize olduktan sonra bile topluluk yapısındaki bu deęiřiklikler 15 gūn boyunca devam etmiř ve deęiřmiř iřlevsel potansiyel miras bırakmıřtır. Buna karřılık, mantar toplulukları gōrece dirençli bulunmuřtur. Ayrıca, Mix+PP-MPs uygulaması rizosfer VOC salınımlarını deęiřtirerek heneicosane gibi faydalı uçucu bileřikleri baskılamıř ve 2-metoksifenol ile 2,4-DTBP gibi fitotoksik bileřikleri artırmıřtır. Bu deęiřimler, mısır biyokūtlesinde anlamlı bir azalma ile iliřkilendirilmiř ve kirletici etkileřimlerini, mikrobiyal dinamikleri ve bitki saęlıęı sonuçlarını birbirine baęlamıřtır.

Genel olarak, bu tez, ECs'nin çevresel kaderini ve ekolojik etkilerini belirlemede iklim faktōrleri, eř kirleticiler ve bileřik kimyası arasındaki karmařık etkileřimleri vurgulamaktadır. Fotoliz, adsorpsiyon, mikrobiyal biyodegradasyon, mikrobiyal topluluk dinamikleri ve bitki tepkilerini birleřtirerek, iklim deęiřiklięinin ECs'nin kalıcılıęını ve dōnūřūmūnū önemli ölçūde etkileyebileceęini ortaya koymaktadır. Aynı zamanda, eř kirleticiler yalnızca ECs'nin tutulmasını ve hareketlilięini deęiřtirmekle kalmayıp, mikrobiyal metabolizmayı yeniden řekillendirerek, rizosfer kimyasını bozarak ve bitki būyūmesini baskılayarak ekolojik riskleri artırmaktadır. Bu bulgular, ECs risklerini deęerlendirirken ve çevresel azaltım stratejileri tasarlarken hem eř kirletici etkileřimlerini hem de iklim deęiřimini dikkate almanın aciliyetini vurgulamaktadır. Bu çalıřma, iklim deęiřkenlerini ve toprak veya su özelliklerini bütūnleřtiren öngörücü modeller ve erken uyarı sistemleri geliřtirilmesi için bir temel saęlamaktadır.

Anahtar Kelimeler: Yeni Ortaya Çıkan Kirleticiler, Fotodegradasyon; Adsorpsiyon, Sıvı Kromatografi-Kūtle Spektrometrisi, Mikroorganizmalar, Mısır Bitkisi.

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LIST OF SYMBOLS AND ABBREVIATIONS

λ	: Light wavelength
ROO•	: Peroxyl radicals
OH•	: Hydroxyl radicals
k	: Rate constant
E λ	: Energy emission rate
$\epsilon\lambda$	: Molar absorption coefficient at specific wavelength
HCO ₃ ²⁻	: Bicarbonate
CO ₃ ²⁻	: Carbonate
q _e	: Adsorption capacity at equilibrium
q _t	: Adsorption capacity at time t
q _m	: Maximum capacity
C _e	: Equilibrium constant
b	: Langmuir constant
C _o	: Adsorbate initial concentration
2,4-DTBP	: 2,4-Di-tert-butylphenol
Ag ₂ S-NP	: Silver sulfate nanoparticles
AgNPs	: Silver nanoparticles
APCI	: Atmospheric Pressure Ionization
BMP	: Biodegradable microplastics
CAS	: Chemical Abstracts Service
CEC	: Cation exchange capacity
CECs	: Contaminants of emerging concern
CIP	: Ciprofloxacin
COOH	: Carboxylic acid functional group
DCF	: Diclofenac
DIU	: Diuron
DOC	: Dissolved organic carbon
DOM	: Dissolved organic matter
DS	: Diclofenac sodium
DW	: Distilled water
EOM	: Extracellular organic matter
ECs	: Emerging contaminants
EE2	: 17 α -Ethinylestradiol
EU	: European Union
FA	: Fulvic acid
GC-MS/MS	: Gas chromatography-mass spectrometry
HA	: Humic acid
IOM	: Intracellular organic matter
JCR	: European Commission Joint Research Center
KF	: Freundlich constant
KL	: Langmuir constant
K _{oc}	: Organic-carbon coefficient
K _{ow}	: Octanol-water partition coefficient
LC-MS/MS	: Liquid chromatography-mass spectrometry
LNG	: Levonorgestrel
LOD	: Limit of detection
LOQ	: Limit of quantification

LRI	: Linear retention indexes
MAC	: Molar absorption coefficient
MPs	: Microplastics
MTBE	: Methyl tert-butyl ether
NaNO ₃	: Sodium nitrate
NIST	: National Institute of Standards and Technology
NPX	: Naproxen
NSAIDs	: Non-steroidal anti-inflammatory drug
OM	: Organic matter
PA	: Polyamide
PAHs	: Polycyclic aromatic hydrocarbons
PCBs	: Polychlorinated Biphenyls
PCPs	: Personal care products
PE	: Polyethylene
PFAS	: Polyfluoroalkyl substances
PP	: Polypropylene
PP-MPs	: Polypropylene microplastics
PS	: Polystyrene
PW	: Pond water
PVC	: Polyvinyl chloride
RSD	: Relative standard deviation
ROS	: Reactive oxygen species
S/N	: Signal-to-noise ratio
SPE	: Solid phase extraction
SW	: Surface water
TER	: Terbutryn
TOC	: Total organic carbon
TP	: Tap water
TRAT	: Tartrazine
TSS	: Total suspended solid
TWW	: Treated wastewater
UV	: Ultraviolet
UPLA	: Ultra Pressure Liquid Chromatograph
UWW	: Untreated wastewater
VOCs	: Volatile organic compounds
WW	: Wastewater
WWTPs	: Wastewater treatment plants

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1. INTRODUCTION

Water is one of the most crucial natural resources for the sustainable life on earth. However, due to the ever-growing anthropogenic impact by various activities such as manufacturing, agriculture applications, construction, pharmaceutical production and textile industries, maintaining the water quality has become a major concern for the scientific society as a consequence of the numerous pollutants that are globally and daily emitted from human activities. These pollutants are still not adequately measured, identified nor regulated in the natural environment. Emerging contaminants (ECs) are released substances in the environment for which no regulations are currently established for their vast majority. The fate and transport of ECs in environment is still a developing area of research due to the limited studies and information about their environmental behavior, mainly due to their huge number and restricted methods of analysis. The European Commission Joint Research Center (JRC) had recently specified more than 2700 ECs in the marine ecosystem as priority substances. Moreover, according to NORMAN association, the most frequently identified emerging pollutants are more than 4000 compounds which are categorized in 20 classes including pharmaceuticals, polycyclic aromatic hydrocarbons (PAHs), personal care products, steroid hormones, estrogens, pesticides, plasticizers, surfactants etc [1]. Moreover, the European Union (EU) is periodically issuing watch lists of priority substances that should be monitored for establishing environmental quality standards. Starting from Directive 2013/39/EU that published the water quality limit for the first revised list of priority substances. Until now, there are three EU watch lists that have been established for emerging contaminants including Decision (EU) 2015/495, Decision (EU) 2018/840 and Decision (EU) 2020/1161. Nonetheless, due to their daily applications, the list of ECs is expected to constantly expand over time, while there are more than 500 thousand chemical substances currently identified in the Chemical Abstracts Service (CAS). Moreover, plastics are widely used in daily life for numerous activities such as construction, agriculture, fishery and packaging [2]. The production of plastics is anticipated to double in 20 years, that would exceed the current capabilities for plastic management, making it one of the major environmental challenges [3]. Due to the extensive production, a great amount of plastic wastes is

reaching the natural environment which are fragmented into finer particles with various shapes and sizes distributions. The plastics with 1 μm –5 mm particles size are termed as microplastics (MPs) [4].

Emerging contaminants enter the environment from multiple sources e.g. agricultural runoff, hospital wastewater, domestic and industrial effluent discharges, etc [5], thus, it is ubiquitous and most frequently detected in various environmental compartments such as surface water, soil, sediments and biofilms, usually at trace concentration ranges of ng/g to $\mu\text{g/g}$ for solid matrices and ng/L to $\mu\text{g/L}$ in the aquatic environment. Although ECs are detected at trace concentrations, however, due to the persistent nature in the environment, toxicity and bioaccumulation potential of a wide array of ECs, it could pose detrimental effects on the living organisms that are exposed to them for a prolonged duration [6]. The long exposure to ECs have the potential to change the hormonal functions and metabolic of living organisms [7]. Moreover, recent studies have shown that detected environmental concentrations of ECs can influence the reproduction, growth and behavior of various living organisms, and even a dose of 1 ng/L of some ECs induced immunological toxicity, carcinogenicity, and genotoxicity in lab animals [8], [9], which made the presence of ECs in the natural environment a major concern for the scientific community as the potential risk they could pose to ecosystem is still not fully understood.

ECs for this study were chosen based on their distinct physicochemical properties such as different solubilities in water and organic solvents, and the chemical structures including phenylacetic acid (Diclofenac), carbonyl diamide (Diuron), heterocyclic N,S triazines (Terbutryn), quinoline carboxylic acid (Ciprofloxacin) and steroids (EE2), in addition to their diverse sources and applications (anti-inflammatory drugs, pesticides, herbicides, antibiotics and estrogens). Moreover, these contaminants are included in the EU watch list of substances that should be monitored,[10], [11] and are among the most frequently worldwide used and detected ECs in the natural environment. Multiple studies have appraised the fate of ECs in the aquatic and terrestrial environment. However, the majority of these studies were based on the experiments with a single contaminant. Furthermore, some studies and reviews have highlighted the need for understanding the mixture effect of different pollutants species on the fate of ECs in the natural environment such as [12], [13].

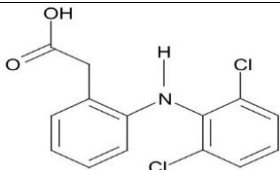
1.1. Literature Review

Emerging contaminants (ECs), also identified as contaminants of emerging concern (CECs), are substances whose occurrence in the natural environment is not new but it has been examined in the last 20 years, primarily due to the absence of a sensitive analytical method for their detection at trace concentration levels in the environmental matrices. ECs contain naturally occurring and anthropogenic chemicals that are categorized in various classes, including pharmaceuticals (prescribed drugs and illicit), personal care products (PCPs) (surfactants, disinfectants, cosmetics, food additives and domestic biocides), engineered nanomaterials, flame retardants, microplastics, surfactants, per- and polyfluoroalkyl substances (PFAS), disinfection by-products originated from water treatment plants (e.g. haloacetonitriles, trihalomethanes, halonitromethanes Nitrosamine, halo acetic acids), pesticides, algal toxins (the toxic chemicals released from algae such as microcystin and cyanotoxins) [14].

Diclofenac (2-(2-(2,6-DCFhlorophenylamino)phenyl)acetic acid) (DCF) is a phenylacetic acid available in oral formulations in potassium, sodium, or misoprostol forms. Diclofenac sodium (DS) is a non-steroidal anti-inflammatory drug (NSAIDs) mainly used as a medicine to relieve pain and swelling. DCF is the most detected pharmaceutical in the environment with an annual global consumption of 940 tons and an average of global concentration ranging from 0.032 to 0.922 $\mu\text{g/L}$ [69]. It is included in the Watch List of EU Decision 2015/495 and it has been classified among the contaminants of emerging environmental concern. The main sources that release DCF into the environment are hospitals, household drainage and pharmaceutical industries which impose environmental pollution from DCF or its metabolites. Up to 75% of the consumed Diclofenac enter the water cycle due to the insufficient removal of Diclofenac by conventional wastewater treatment plants WWTPs, ranges from 21 to 41%. Although Diclofenac is detected at low concentrations but it is considered potentially hazardous for the environment with various harmful impacts for many environmental species at concentrations of $\leq 1 \mu\text{g/L}$ [70]. To date, many studies have reported on the environmental risks of DCF. It is observed to cause many toxic effects such as oxidative stress, inhibition of growth for different species like fish, daphnia magna and three types of gyps vulture species at environmentally relevant concentrations 0.5 $\mu\text{g/L}$ - 50 $\mu\text{g/L}$ [69], [71]–[73]. Diclofenac tends to be

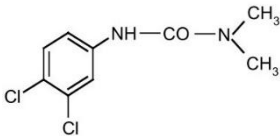
bioaccumulated and easily absorbed by wastewater sludge due to its low water solubility (2.37 mg/L), high octanol-water partition coefficient (log Kow: 4.51) and slightly acidic nature (acid dissociation constant pKa: 4.15) (**Table 1.1**), which facilitate the crossing of cell membranes, accumulation in living cells and absorption into the organic matter. Moreover, previous researches have shown that DCF have high potential to be taken-up by the aquatic organisms exposed to environmentally relevant concentrations (1 µg/L) [74].

Table 1.1: The physicochemical properties of Diclofenac.

Physicochemical properties	Value	Reference
Chemical structure		[75]
Molecular weight (g/mol)	296.15	[76]
Water solubility (mg/L)	2.37	[77]
Vapor pressure mmHg	6.14×10^{-8a}	[77]
Henry's law constant (atm m ³ /mol)	4.73×10^{-12}	[78]
Log Kow	4.51	[79]
pKa	4.15	[79]

Ciprofloxacin (CIP) (1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid) is a broad-spectrum and the most used chemotherapeutic antibiotic worldwide due to its vast use in both veterinary and human health care. Thus, the main source of ciprofloxacin discharge into the environment is the hospital effluent. The fate of CIP in the environment is dominated by photodegradation and adsorption to particulate organic matter. Ciprofloxacin's half-life is expected to be short (~ 2 hours) in the surface water because of the rapid photodegradation [80]. CIP physiochemical properties are shown in **Table 1.2** The high-water solubility (> 2 g/L) and low Log Kow (1.24) indicate its tendency to spread in the aquatic environment and leach from the soil to the ground water matrix. Similar to other antibiotics, ciprofloxacin could accumulate in the aquatic organism's bodies, thus it poses a serious threat to the environment and human health. Many studies have reported the environmental toxicological effects of ciprofloxacin even for its detected concentration levels in the natural environment such as [81], [82].

Table 1.2: The physiochemical properties of Ciprofloxacin.

Physicochemical properties	Value	Reference
Chemical structure		[83]
Molecular formula	C ₁₇ H ₁₈ FN ₃ O ₃	[84]
Water solubility (mg/L)	> 2 g/L	[85]
Vapor pressure mmHg	1.4×10^{-5} - 1.3×10^{-4}	[86]
Henry's law constant (atm m ³ /mol)	5.09×10^{-19}	[87]
Log Kow	1.24 ± 0.86	[88]
pKa	pKa1 5.89 and pKa2 8.61	[89]

17 alpha-ethinylestradiol (EE2) is one of the endocrine disrupting chemicals (EDCs) with highly elevated estrogenic activity, and the main constituent of contraceptive medicines. Therefore, the main source of EE2 in the natural environment is the excretion via feces or urine, industrial and hospitals wastewaters and sewage sludge which could be utilized agriculturally. EE2 has become a matter of concern in the natural environment mainly due to its high tendency to accumulate in the sediments, absorb to the natural organic matter and concentrate in the biota, in addition to its high resistance to multiple degradation processes in the natural environment [90]. The physiochemical properties of EE2 are shown in **Table 1.3**. Previous studies have indicated multiple effects of EE2 on the endocrine system of biota including sexual maturity delay, modifying sex determination, population declines, immune system disturbance and increasing the endocrine-related disorders [91], [92].

Diuron, [N-(3,4-DCFhlorophenyl)-N,N-dimethylurea] is a herbicide that belongs to the phenyl amide group used extensively for weed control. The physicochemical properties of diuron (**Table 1.4**) suggest that it is not volatile from soil or water medias with a low value for Henry's law constant and vapor pressure, and it predicts the strong adsorption affinity to the soil organic matter with a soil-organic fraction partition coefficient (Koc) of 485, low water solubility (42 mg/L) and high persistency for hydrolysis at pH range of 5-9. Therefore, diuron is expected to have long half-life (more than 300 days) in the terrestrial and aquatic environment with a relatively fixed

phenyl urea properties. Thus, it has the potential to reach the water bodies through surface runoff or leaching from soil. Compared to the conventional contaminants, diuron is classified as a chlorinated organic chemical that is resistant to biochemical degradation and has intensive toxicity due to the presence of a chlorinated functional group in its structure which could be extremely harmful to the ecosystem and human health [99]. Diuron was found to cause genotoxicity and growth inhibition to different living organisms such as plants, mammals, oyster and algae [100]–[102].

Table 1.3: The physicochemical properties of EE2.

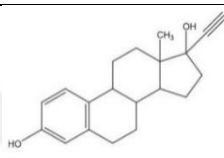
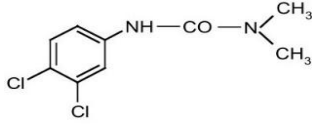
Physicochemical properties	Value	Reference
Chemical structure		[93]
Molecular formula	C ₂₀ H ₂₄ O ₂	[90]
Molecular weight	296.4	
Water solubility (mg/L)	9.5	[94]
Vapor pressure (mm Hg)	4.5 × 10 ⁻¹¹	[95]
Henry's law constant	3.3 × 10 ⁻¹⁰ μg/m ³ air/ μg/m ³ wastewater	[96]
Log K _{ow}	3.67	[97]
Log K _{oc}	3.45	[98]
pK _a	10.5	[95]

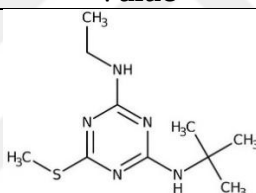
Table 1.4: The physicochemical properties of diuron.

Physicochemical properties	Value	Reference
Chemical structure		[103]
Molecular formula	C ₉ H ₁₀ Cl ₂ N ₂ O	[104]
Water solubility (mg/L)	42	[105]
Vapor pressure (mm Hg)	6.90 × 10 ⁻⁸	[106]
Henry's law constant (atm m ³ /mol)	7.04 × 10 ⁻⁶	[107]
Log K _{ow}	2.68	[105]
Log K _{oc}	2.68	[103]
pK _a	3.7	[108]

Terbutryn is an excessively used postemergence and preemergence s-triazine herbicide. It belongs to the methyl Thio-triazine group of triazine herbicides class, and

one of the most widely applied biocides in the industrial and urban facilities for film preservation of construction materials [109]. Terbutryn has a wide usage area, it is utilized to control the growth of multiple crops and broadleaf weeds. It is also used to control algae, free- floating and submerged weeds in water courses, fish ponds and reservoirs [110]. The low-moderate water solubility and the relatively high log Koc and log Kow values of terbutryn (**Table 1.5**) indicates its affinity to be adsorbed by the soil and bioaccumulate in the living organisms, which inhibits its mobility in the agriculture soil and decrease its tendency to leach to the groundwater, and subsequently, it is more likely to be detected in sediments in the aquatic environment. Moreover, terbutryn was found to be highly toxic to multiple environmental species mainly causing lethality and growth inhibition for daphnia magna, freshwater algae, soil bacteria and fungi [111]–[113].

Table 1.5: The physicochemical properties of terbutryn.

Physicochemical properties	Value	Reference
Chemical structure		[114]
Molecular formula	C ₁₀ H ₁₉ N ₅ S	[114]
Molecular weight (g/mol)	241.4	
Water solubility (mg/L)	22	[114]
Half-life	Stable in water. Soil: 15.4–84 days	[114]
Henry's law constant (atm m ³ /mol)	1.5 × 10 ⁻³	[107]
Log Kow	3.66	[114]
Log Koc	3.39	[114]
pKa	4.4	[115]

Microplastics (MPs) are debris of polymers with particle sizes less than 5 mm. The compositions of MPs in the aquatic environment are primarily including Polyethylene (PE), Polystyrene (PS), Polypropylene (PP), Polyamide (PA) and Polyvinyl chloride (PVC). As seen from **Table 1.6**, PP and PE are the most common detected types of MPs in the aquatic environment with a concentration range of 0.4 p/L - 6233 p/L. PE and PP are thermoplastic resins and the most commonly used polymers in daily life due to their convenient processing and low-cost production [116]. However, PP is

considered more preferable than PE as it has the lowest density among the commercial plastics, in addition to the high chemical and temperature resistance which make PP suitable for several versatile items including bottles, funnels, trays and particularly the jars that need to be frequently sterilized for the clinical use [117]. Moreover, the low density of PP MPs (lower than water) promotes its buoyancy in the surface waters which enhance its transportation and exposure to sunlight, which favors its role as a main vector for the long-range transport of organic contaminants in the aquatic environment compared to the higher densities MPs (e.g. PVC and PS) [66].

Table 1.6: The recorded concentrations of microplastics in the aquatic environment.

Country/Region	Source	Type	Concentration		Ref.
South China	Sea fish	-	6.6 items/fish		[118]
Australia	River sediments	Mostly PE and PA	0.2 – 60 mg/kg		[119]
China	Seawater	Mainly PS and PET	448.9 p/m ³		[120]
South Korea	River and riverine fish	PE, silicone, in river and PFTE, polyethylene (PE), and rayon in fish	0 – 42.9 p/m ³ in surface waters (0 m). 20.0–180.0 p/m ³ at a depth of 2 m.		[121]
Cadiz, Spain	IWWTPs	Mostly HDPE and PS	Influent	16 – 87 p/L	[122]
			Effluent	24 – 119 p/L	
	MWWTPs	Mostly PVC, PS and PE	Influent	275 – 586 p/L	
			Effluent	7 – 1567 p/L	
Turkey	Sea fish	26% PP, 21.9% PE, 8.2% PET and 7.5% cellulose	0.4 - 4.3 p/fish		[123]
China	River	50% PET	28.3 p/L		[124]
	River sediments	PET (40%), PP (27%),	6233 p/L		
China	Farmland WW	PE and PP	0.4 p/L		[125]
Denmark	WW	-	UWW	250 ng/L	[126]

PP-MPs are one of the most detected micropalstics in the terrestrial environment with a concentration range of 17 p/g to 1.0 p/kg (**Table 1.7**) There are two main categories

for the origin source of MPs. The primary source in which the particles are directly released from manufacturing and used products such as personal care products, plastic powder for molding, biomedical products, drugs and clothes (polyester or nylon) which are responsible for the direct release of MPs [127]. The secondary source is from where the particles are indirectly emitted by the fragmentation of macro-plastics. Macro-plastics can disseminate MPs via abiotic and biotic transformation process such as sand friction, biodegradation, thermal degradation, photodegradation, hydrolysis and thermo-oxidative degradation [128], [129]. It has been estimated that the primary source of MPs and NPs accounts only for 15–30% of the released plastics while the secondary source contribute for 70%-80% of the total plastics in the environment [130].

Table 1.7: The recorded concentrations of microplastics in the terrestrial environment.

Country	Source	Type	Concentration	Color	Ref.
UK	Landfill and urban soils	PE, PP, PS and PET	12.3 p/g in landfill and 15-17 p/g in urban soils	-	[131]
Southwest China	Cultivated soil	75% PE and 25% PVC	50 – 1158 p/kg	60% transparent and 39% black	[132]
Iran	Urban and industrial soils	PET and nylon	100 to 3135 p/kg in urban soils and 80 to 1220 p/kg in industrial soils	White and transparent	[133]
Northwest China	Sand Land soils	53% PP, 24.85% PE, 15.88% PS	1360 to 4960 p/kg	93% black and 4% transparent	[134]
Korea	Agricultural soils	PE > PP	10–7630 items/kg	-	[135]
China	Farmland and grassland	PE and PP	53.2 items/kg in shallow soil and 43.9 items/kg in and deep soil	Mostly transparent. Black, White and blue.	[136]

Due to their small particles sizes, MPs have high potential to be absorbed by various aquatic species, including fish, clams, shrimp, and mussels, which can be hazardous to the aquatic life and human health that is exposed to MPs through the

bioaccumulation in the food chain [137]. Furthermore, due to the hydrophobic properties of MPs, it have high ability to adsorb and concentrate numerous organic contaminants presence in surface waters which increase its toxic effect and serve as transportation vectors of these contaminants by releasing it in various environments [138]. Thus, altering the monitored environmental behavior of these contaminants and complicating their fate studies in the natural surface waters. The sorption on the surface of MPs could play a major role in the distribution of organic contaminants in diverse environmental compartments as indicated by previous studies. For instance, [139] have recorded an amplification in the concentration of Polychlorinated Biphenyls (PCBs) by 10^5 – 10^6 times in the MPs compared to the surrounding water in a coastal region, which indicates that PCBs have migrated from other areas through the adsorption and transportation with MPs. Due to the intense interaction between MPs and organic compounds, the elevated toxicity effect of organic contaminants that are accumulated by MPs is frequently observed in multiple species. MPs have considerably aggravated the genotoxicity, neurotoxicity and oxidative stress of organic pollutants in various aquatic organisms such as microalgae, zebrafish, mussels, copepods. [140], [141].

Silver nanoparticles (AgNPs), is one of the most utilized nanomaterials for numerous products all over the world, including toothpaste, clothes, medical masks, shirts, detergents, towels and teddy bear that are found to release AgNPs up to 45 μg Ag per gram product in the washing water [142]. Ag₂SNPs was selected for this study in order to investigate the potential of metal nanoparticles that exist in the surface water to influence the photodegradation and adsorption kinetics of targeted ECs, and due to the nearly entire conversion of AgNPs to Ag₂SNPs in the wastewater treatment facilities [143]. Thus, Ag₂SNPs were detected in the effluents of wastewater treatment plants at a range of 0.1 ng/L to 8.6 ng/L [144], [145].

The selected ECs were detected in all aquatic environment compartments including river and lake water, sediments, WWTPs effluents and influents, urban aquatic systems, and stormwater runoff (**Table 1.8**). The highest concentrations for terbutryn, EE2, Diclofenac and ciprofloxacin were found in wastewater influent with the most elevated concentration for ciprofloxacin (4.40 mg/L), while diuron had recorded the highest concentration in freshwater at 90 μg /L in Brazil. These data confirm the importance of aquatic fate studies of these contaminants for the risk mitigation

measures. Furthermore, as seen in Section 1.2.6, different types of microplastics were widely detected in the aquatic environment in a concentration range of 7 p/L to 6233 p/L, which indicates the importance of considering these particles in the risk assessment and fate studies of ECs in the aquatic environment.

Table 1.8: The recorded concentrations of targeted ECs in the aquatic environment.

Diclofenac				
Country/ Region	Source	Concentration		Reference
France	Raw WW	1115 ng/L - 3082 ng/L		[146]
	Treated WW	785 ng/L - 2786 ng/L		
France	Surface water	0.20 µg/L		[73]
Nigerian	WWTP	Influent	166 µg/L	[72]
Pakistan	Wastewater	8 – 127 µg/L		[147]
	Surface water	14 – 62 µg/L		
Cameroon	Surface water	419 ng/L		[148]
Latin America	Surface water	0.04 – 9600 ng/L		[149]
Europe	Surface water	18,740 ng/L		[150]
Malaysia, Johor	Surface water	0.47-79.89 ng/L		[151]
Ciprofloxacin				
Country/ Region	Source	Concentration		Reference
China	River	1.99 – 2.21 mg/L		[152]
	WWTP effluent	3.30 – 4.40 mg/L		
Brazil	River	0.07 µg/L		[153]
Pakistan	Groundwater	18.2 ng/L		[154]
Brazil	River	344 ng/L		[155]
Poland	WWTP 1	Influent	1260 ng/L	[156]
		Effluent	184 ng/L	
	WWTP 2	Influent	4300 ng/L	
		Effluent	312 ng/L	
	River 1	Upstream	108 ng/L	
		Downstream	95 ng/L	
	River 2	Upstream	12 ng/L	
		Downstream	182 ng/L	
Argentina	Farm WW	0.74–7.7 µg/L		[157]
Latin America	Surface water	0.41–740 ng/L		[149]
Europe	Surface water	13,567 ng/L		[150]
Malaysia	3 Rivers	24 – 299 ng/L		[158]
EE2				
Country/ Region	Source	Concentration		Reference
China	River	20.1 ng L		[93]
China	Sea	0.6 ng L		[159]
Malaysia	River	4.25 ng/L - 68.8 ng/L		[160]

Table 1.8: Continued.

Monterrey, Mexico	WWTP	1.3 ng/L - 407.5 ng/L		[161]
Asia	Lake water	n.d.-630 ng/L		[162]
South Africa	WWTPs	Effluent	0.448–4.608 µg/L	[163]
		Influent	2.654 -9.833 µg/L	
China	River	5.98 ng/L - 9.22 ng/L		[164]
Malaysia, Johor	Surface water	0.30-7.67 ng/L		[151]
Latin America	Surface water	0.16 – 5900 ng/L		[149]
Europe	Surface water	6- 57 ng/L		[150]
Northeast China	River	17,11 µg/L		[165]
Malaysia	WWTP	Influent	4.9 ng/L	[166]
		Effluent	0.4 ng/L	
Diuron				
Country/ Region	Source	Concentration		Reference
Brazil	Freshwater	0.005 – 90 µg/L		[167]
China	River water	5.45 to 157.66 ng/L		[168]
France	Raw WW	19 ng/L – 143 ng/L		[146]
	Treated WW	27 ng/L - 1143 ng/L		
Brazil	River water	4 to 279 ng/L		[169]
Northeast China	Seawater	19 - 3056 ng/L		[170]
Germany	Urban aquatic systems	0.17 µg/L		[112]
India	Wastewater	68 ng/L		[171]
China	River	ND - 13.5 ng/L		[172]
Catalonia, Spain	Llobregat River	170 ng/L		[173]
	Ter River	1.3 ng/L		
Europe	WWTPs	Influent	0.03-1.96 µg/L	[174]
		Effluent	0.002-2.53 µg/L	
Terbutryn				
Country/ Region	Source	Concentration		Reference
Guadiana Basin, Southern of Portugal	Surface water	4.8 ng/L		[175]
Freiburg city (South-western Germany)	Urban aquatic systems	0.04 µg/L		[112]
Northeast China	Seawater	Ranged from 9.33 to 745 ng/L		[170]
South-eastern Poland	Surface water	12.02 ng/L		[176]
Catalonia, Spain	Llobregat River	67 ng/L		[173]
Germany	WWTP 1	Influent	34 – 75 ng/L	[177]
		Effluent	55 – 74 ng/L	
	WWTP 2	Influent	69 – 204 ng/L	
		Effluent	54 – 142 ng/L	

As shown in **Table 1.9**, the targeted ECs were widely detected in the terrestrial environment in multiple matrices such as natural and agriculture soils and crops, wastewater sludge, and sewage sludge. Diclofenac has recorded the highest concentrations 7020 µg/kg in pharmaceutical units sludge and WWTP primary sludge in Germany and Pakistan respectively. Moreover, many studies have recorded the presence of MPs in the natural soil while the detection of AgNPs is still lacking due to difficulties in the extraction process of AgNPs from soil, and particularly from the organic-rich soils [178]. Therefore, the occurrence of AgNPs in natural soil is not reported yet in the literature. As indicated in Section 1.2.6, microplastics were excessively measured in many compartments of terrestrial environment including landfills, natural soils, industrial soils, farmlands and grasslands with the highest concentration of 17 p/g in UK urban soils. In addition, PP and PE accounted for the majority of the recorded MPs in different natural soils with less contribution for PVC, and PS.

Table 1.9: The recorded concentrations of studied ECs in the terrestrial environment.

Diclofenac			
Country	Type	Concentration	Reference
Australia	WW sludge	100 ng/g	[179]
Cyprus	Tomato crop field	0.35 µg/kg	[180]
Pakistan	Soil	257 µg/kg	[181]
Australia	Irrigated field (Radish crop)	0.07 µg/g	[182]
	Irrigated field (Ryegrass crop)	0.05 µg/g	
China	Irrigated field	1.16 µg/kg	[183]
Israel	Soil	0.2 ng/g	[184]
Spain	River surface soil	0.3 µg/kg	[185]
Brazil	River sediments	3.95 ng/g	[186]
Malaysia	River sediments	13.88 ng/g	[187]
South Africa	River sediments	309 ng/g	[188]
Spain	River sediments	100 ng/g	[189]
China	WWTP sludge	1 ng/g	[190]
Germany	Primary sludge	7020 µg/kg	[191]
	Secondary sludge	310 µg/kg	
Turkey	WWTP sludge	5 ng/g	[192]
Diuron			
Country	Type	Concentration	Reference
Australia	WW sludge	60 ng/g	[179]
Japan	Sea sediments	0.01 – 0.09 µg/g	[193]
France	Sewage sludge	6.6 - 84.0 µg/kg	[194]
Costa Rica	River sediments	11.75 µg/kg	[195]
USA	Agriculture soil	0.38 mg/kg - 0.53 mg/kg	[196]

Table 1.9: Continued.

Terbutryn			
Country	Type	Concentration	Reference
Costa Rica	River sediments	38.7 µg/kg	[195]
Spain	Sewage sludge	0.91 – 60.35 ng/g	[197]
EE2			
Country	Type	Concentration	Reference
China	Sewage sludge	1.2 - 139 ng/g	[198]
Germany	Sewage sludge	1.5 – 3 ng/g	[199]
Tunisia	Sewage sludge	50.5 – 179 ng/g	[200]
Iran	Sewage sludge	10 - 20 ng/g	[201]
Australia	Sewage sludge	0.42 ng/g	[202]
China	River sediments	0.06 – 120 ng/g	[203]
USA	Sewage sludge	12 - 232.8 ng/g	[204]
Ciprofloxacin			
Country	Type	Concentration	Ref
China	Municipal sewage sludge	153 – 608 µg/kg	[205]
Spain	WWTP Sludge	49 - 1573 ng/g	[206]
Brazil	WWTP Sludge	2.217 mg/kg	[207]
India	Dumpsite soil	11.32 - 126.29 µg/kg	[208]
France	Sludge-amended soil	8.7 ng/g	[209]

Photolysis is the transformation of photodegradable compounds induced by the absorption of light photons, particularly at the wavelength ranges found in sunlight (e.g. visible light, infrared radiation, and ultraviolet light) causing chemical bonds breaking of the parent molecule [210]. There are two main photochemical transformation processes for ECs that could take place in the natural environment, the direct photodegradation that occurs when the contaminants absorb the light directly from the sun ($\lambda > 290$ nm), and indirect photodegradation that involves the absorption of sunlight by various types of photosensitizers present in the surface water such as nitrate/nitrite and organic matter (OM), followed by the production of various reactive species (e.g. peroxy radicals $\text{ROO}^{\bullet}$, hydroxyl radicals $\text{OH}^{\bullet}$, triplet excited states of DOM ($^3\text{DOM}^*$) and singlet oxygen radicals ($\text{O}_2^{\bullet}$)), these radicals react with ECs in the water matrix causing their photooxidation [211]. The indirect photolysis by photosensitizers play a dominant role in the photodegradation of ECs in the aquatic environment [50].

There are several parameters that control the extent to which the compound can exhibit photodegradation. The main feature is its ability to absorb the photons from the incident's sunlight. The molar absorption coefficient (MAC) measures the capability

of a certain molecule to absorb UV light at a certain wavelength, which is usually determined by measuring the absorbance of the solution that contains the targeted compound within a vast wavelength range (200 to 400 nm). Afterwards, the MAC can be calculated using Beer-Lambert Law equation as follows: $A = \epsilon \cdot b \cdot C$. Where A is the absorbance (unitless), ϵ is the molar absorption coefficient ($M^{-1} \cdot cm^{-1}$), and C is the molar concentration of the compound [212]. Although MAC is an important parameter for direct photolysis, that measure the tendency of a molecule to absorb light, however, only because the compound is able to absorb the light photons at certain wavelength, it does not mean that it must undergo photo transformation. Therefore, the quantum yield is another significant parameter to assess the direct photolysis of ECs as it measures the exact number of molecules that are transformed by exposure to light. The quantum yield can be estimated using the following equation:

$$k_{\lambda} = 2.303 \cdot E_{\lambda} \cdot \epsilon_{\lambda} \cdot \Phi_{\lambda} \quad (1.1)$$

Where k_{λ} is the photolysis rate constant (min^{-1}), E_{λ} , the energy emission rate, which corresponds to the flow of photons emitted from the lamp ($Einstein \ s^{-1} \ m^{-2}$), ϵ_{λ} is the MAC at the considered wavelength ($m^2 \ mol^{-1}$), and Φ_{λ} is the quantum yield ($mol. \ Einstein^{-1}$). The rate of energy emitted by the lamp.

The degradation kinetic (number of degraded molecules per time unit) and half-life (the time required for a number of molecules to degrade to half of its initial number), estimate the velocity at which the photodegradation process occurs. The pseudo-first-order has been found to be the dominant kinetic model for the photodegradation reaction of most chemical compounds in the environment. Therefore, the half-life parameter of the ECs is expected to be significantly influenced by the temperature and initial concentration.

There are some environmental conditions that could influence the photochemical transformation of ECs. For instance, the natural organic matter that is present in the aquatic environment is considered the strongest light absorbing constituent in the surface water [213] that can have a fundamental impact on the indirect photodegradation of ECs by the generation of some reactive species as mentioned previously. The presence of organic matter had recorded various effects on the degradation of organic micropollutants ranging from promoting, declining or no

recorded significant effect. Moreover, temperature is another factor that could control the photochemical behavior of ECs. Rising temperature has either recorded a gradual increase in the direct photolysis rate of most of the ECs in the distilled water matrix, or there was no significant effect observed [214], [215].

The photodegradation of diclofenac has been widely studied by the use of ultraviolet radiation in different water matrices. Few studies have investigated DCF photolysis using environmentally relevant concentrations (1 ng/L to 1 µg/L) such as [20], [216]. While most of the studies have used higher concentration range up to 120 mg/L. This was mainly due to the rapid photodegradation of DCF. When experimental conditions were relatively similar, photodegradation was more rapid at the lower initial concentrations and the complete degradation was achieved in the low initial concentration range of 5 mg/L to 30 mg/L with a corresponding half-life of 3 min to 15 min. Whereas for higher studied concentration ranges from 50 mg/L to 100 mg/L, the photodegradation was slower and around 90% of DCF were degraded with half-life of 30 min to 2 hours.

The comparison of DCF photodegradation with different water matrices including river and lake water (SW), tap water (TW), distilled water (DW) and wastewater (WW) was done by [20], [216], [217] with no or a negligible difference in DCF degradation rate constant and half-life in all of the tested water matrices. For instance, [20] have investigated DCF photolysis under natural sunlight between June and July with DW, TW and SW. The values for diclofenac photodegradation rate constant ranged from 2.6 to 3.7 h⁻¹ with corresponding half-lives of 0.19 to 0.27 h in all the tested water samples. However, [24] have reported a slight difference in DCF photolysis (30 mg/L) with distilled water, drinking water and river water. The highest photodegradation rate constant was 0.0092 min⁻¹ in distilled water and decreased to 0.0072 min⁻¹ and 0.0068 min⁻¹ for drinking water and river water respectively. This can be explained by the presence of some components in surface water such as bicarbonate that might compete with DCF for photon absorption.

[24] have investigated the photolysis of DCF as an individual compound and in a mixture with naproxen (NPX) in distilled water, drinking water and river water. The photodegradation levels of DCF alone by solar photolysis were slightly lower (0.0089 min⁻¹) than those observed in the presence of NPX (0.0095 min⁻¹) whereas when NPX alone was irradiated, a higher degradation rate (0.0302 min⁻¹) was obtained compared

to that in the presence of DCF (0.0092 min^{-1}). This indicates that the photodegradation of DCF was not significantly affected by the presence of NPX while the photolysis of NPX exhibited higher inhibition in the presence of DCF. This could be explained by the difference in the maximum UV light absorption spectra which is higher for DCF (276 nm) than NPX (230 nm), and as the study was conducted in wavelength ranges $\leq 290 \text{ nm}$. Therefore, DCF will probably absorb more light depending on its absorption spectra which will enhance its photodegradation over NPX.

Photodegradation of diuron was examined with relatively low concentration range which are environmentally relevant ($5 \text{ }\mu\text{g/L}$ to $150 \text{ }\mu\text{g/L}$) by only few studies such as [218], [219]. Whereas diuron photolysis was mostly investigated in a higher concentration range of 1 mg/L to 40 mg/L in order to conduct a clear comparison between different photolysis rate constants [27], [220]. However, [221] conducted diuron photolysis experiment under UV light using two different initial concentrations ($100 \text{ }\mu\text{g/L}$ and 11 mg/L). At the low concentration ($100 \text{ }\mu\text{g/L}$), the photodegradation rate was not affected by diuron photoproducts absorption of UV light. While at higher initial concentration (11 mg/L) there was an overestimation for photolysis rate when the kinetic model did not incorporate diuron photoproducts that absorb the UV light at the same wavelength used in the experiment (253.7 nm). Therefore, this study suggested that the diuron photolysis kinetic model has to be modified when studying with high concentrations to include all the possible diuron photoproducts that might occur during the photolysis process and at the same time, have the tendency to be further photolysis at the same used experimental wavelength.

The photodegradation of diuron under UV light in the presence of natural aquatic organic matter represented by fulvic acid (FA). In addition to the algae organic matter including intracellular organic matter (IOM) and extracellular organic matter (EOM) that are corresponding to a dissolved organic carbon (DOC) concentration of 6 mg/L were studied by [222]. Diuron removal and photolysis rate constant (k) in the control sample were 99.53% and $0.18/\text{s}$ respectively while it declined to a removal rate of 98.70% and a k value of $0.148/\text{s}$ after adding EOM. The values exhibited higher decreasing with FA (94% removal and $0.093/\text{s}$ photolysis rate constant) which indicated the inhibitory effect of natural organic matter on diuron photodegradation. These results could be illustrated by the tendency of some components existing in the algae organic matter (e.g. polysaccharides and proteins) to scavenge the reactive

oxygen species (ROSs) including hydroxyl radical and singlet oxygen that play a major role in enhancing the photodegradation process or by screening out the diuron reactive light wavelengths.

The photolysis of diuron was investigated in different water matrices. [223], [224] and [225] have studied diuron photodegradation under simulated sunlight and UV radiation with ultrapure water, tap water and wastewater matrices. The results demonstrated that the highest photodegradation rate constant of 0.220/min was with ultrapure water followed by tap water (0.194/min) and wastewater (0.114/min). These results can be explained primarily by the absence of organic and inorganic compounds in the ultrapure water which can compete with diuron for UV light radiation [218].

[226] have examined diuron photodegradation in surface water with and without a mixture containing other pesticides including atrazine, isoproturon, alachlor, pentachlorophenol and chlorfenvinphos. The result demonstrated a slight decrease in the photodegradation rate constant from $14.04 \times 10^4 \text{ cm}^2/\text{mJ}$ for diuron as a single compound to $12.15 \times 10^4 \text{ cm}^2/\text{mJ}$ in the mixture. This decline can be illustrated primarily by the competition on UV irradiation and OH radicals that might occur between the different pesticides in the mixture.

Photodegradation of EE2 was investigated in the previous studies with various water matrices and experimental conditions. Low initial concentrations (1 $\mu\text{g/L}$ to 20 $\mu\text{g/L}$) were used to examine EE2 photodegradation behavior in a concentration range that exist in the natural aquatic environment [227]–[229]. While some studies tested the EE2 photolysis process in higher concentration range (up to 5 mg/L) mainly due to the rapid photodegradation of EE2 reported in some studies using low concentrations. For example, [230] and [31] studied EE2 photolysis in distilled water under UV light with different initial concentrations. A degradation in the removal rate (91.6% to 64.1%) and photodegradation rate constant (0.091/min to 0.037/min) was observed with rising EE2 initial concentration (0.6 mg/L to 2 mg/L). Therefore, increasing the concentration will allow the conduction of more accurate comparisons between different experimental parameters especially in the optimized conditions.

The influence of different water matrices on the photodegradation of EE2 was investigated by many studies. For instance, [231] tested the photodegradation of EE2 under UV light in two different water matrices (distilled water DA and wastewater

water WW). EE2 removal efficiency declined from 60% with DA to 21% with WW. This could be due to some unidentified compounds that contribute to light absorption resulting in less amount of available light for EE2 photodegradation leading to decrease in EE2 photolysis rate in wastewater. Moreover, [232] examined EE2 photodegradation under UV light in both drinking water (DW) and wastewater (WW). The two water matrices had no effect on the degradation rate and results did not show a significant difference in the photodegradation rate constant between DW ($0.12 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-2}$) and WW ($0.14 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-2}$). This could be demonstrated by the probable counterbalanced effect between the formation of reactive oxygen species by the organic molecules exist in wastewater which enhance the photolysis process and the low transmittance of WW that result to lower light amount available for EE2 photodegradation [233]. Furthermore, [31] investigated the influence of carbonate (CO_3^{2-}) and acid bicarbonate (HCO_3^{2-}) presence in natural water on the photodegradation of EE2 at a concentration of 12 mg/L. Carbonate ions did not had a significant influence on EE2 photolysis process and as suggested by the same study, this result could be due to the low concentration of EE2 in the solution. Thus, there would be a very limited formation of OH radical which will result in a negligible effect on the photodegradation process.

The study of the organic matter effect in the form of humic acid (HA) on the photodegradation of EE2 under UV light and by using different concentration of HA ranging from 0 to 20 mg/L was done by [234] and [31]. The results indicate that HA at low concentration could efficiently accelerate EE2 photodegradation rate which markedly increased from 0.005/min in the sample without HA to 0.013/min in the presence of 5.0 mg/L HA. However, it could also hinder the photodegradation of EE2 when HA concentration exceed 10 mg/L which can be a result of reactive species scavenging and competing for the light absorption with EE2. Therefore, HA have the tendency to play multiple roles as an inhibitor and a promoter depending mainly on its concentration in the solution.

Examining EE2 photodegradation in distilled water under UV light (254nm) as an individual component and in a mixture with other compounds including levonorgestrel (LNG) and tartrazine (TART) was done by [231]. The removal efficiency of EE2 was decreased from 60% as a single compound in the solution to 41% for the mixture. As stated above in the effect of UV light paragraph, EE2 has a low absorption of UV light

at 254nm wavelength which is unlike the other two compound (LNG and TRAT) that absorb UV light more efficiently on the wavelength range of 220nm to 275nm. Therefore, the available light amount for the photodegradation of EE2 is expected to hugely decline because of the competition and scattering effects between EE2 and the other compounds in the solution.

The photodegradation of terbutryn was studied under sunlight in different water matrices. The initial concentrations used in some studies which aimed to reflect terbutryn concentration in the aquatic environmental was in a low range starting from 8 ng/L to 100 ng/L [19], [29]. Compared to the studies which conducted the experiments in higher concentrations (up to 7000 mg/L) in order to simulate the concentration of terbutryn applied in the agricultural practices [22], [235].

Photolysis of terbutryn in different water matrices was investigated by [22]. They tested terbutryn photodegradation under UV light in distilled water (DW) and pond water (PW) containing two different amounts (19 mg/L and 6.4 mg/L) of total suspended solid (TSS). Longer exposure time (34 hours) was required with PW to obtain the similar degradation levels observed with DW (28 hours) with corresponding photolysis rate constants of $0.0257 \text{ m}^2 \text{ kJ}^{-1}$ and $0.0309 \text{ m}^2 \text{ kJ}^{-1}$ for PW and DW respectively. However, when the amount of loaded TSS in pond water decreased from 19 mg/L to 6.4 mg/L, photolysis rate constant also decreased from $0.0257 \text{ m}^2 \text{ kJ}^{-1}$ to $0.0169 \text{ m}^2 \text{ kJ}^{-1}$. This result contradicts with other studies which have reported the inhibitor effect of natural water matrices on photodegradation of terbutryn compared to the distilled water primarily due to the tendency of the particles existing in natural water to act as photon scavengers such as [224]. Therefore, water constituents might play a major role in the photodegradation of terbutryn. For instance, [29] examined the photolysis of terbutryn in distilled water with and without the addition of sodium nitrate (NaNO_3). The photodegradation rate constant in the presence of NaNO_3 was eight times higher ($0.5 \text{ M}^{-1}\text{S}^{-1}$) than the control sample ($0.06 \text{ M}^{-1}\text{S}^{-1}$). Thus, it is not compulsory that photodegradation would be more efficient in distilled water compared to other water matrices as some water constituents can act like photoreaction enhancers which could be mainly by the generation of more reactive radicals.

Studying the effect of the solution organic matter on terbutryn photodegradation was not widely investigated in the previous studies. However, [236] made a comparison for the effect of organic matter in the natural water on the photodegradation between

terbutryn and atrazine under natural sunlight. The results showed a shorter half-life range for terbutryn (181-644 days) compared to (no degradation – 430 days) for atrazine. This might be explained by tendency of C-Cl bond of atrazine to form stronger bonds with organic matter compared to terbutryn C-S bond. Therefore, adsorption to organic matter could inhibit the photodegradation of atrazine while it might not have a substantial influence on the photodegradation of terbutryn.

Ciprofloxacin photolysis has been investigated using natural sunlight in various water matrices and experimental conditions. CIP low initial concentrations were used in the range of 1 µg/L to 10 mg/L by some studies such as [21]. Basically, to reflect the actual environmental concentrations of CIP in the natural environment. Whereas other studies have examined CIP photolysis with higher initial concentrations ranging from 20 mg/L to 2 g/L such as [18]. Studying higher concentration was primarily to compare the photochemical behavior of CIP in the aqueous solution with different experimental conditions and to avoid the complete photodegradation of the compound. For instance, [237] did not record any significant differences in photolysis rate values with various experimental conditions when studying with low concentration (100 µg/L), while the variations began to occur when the initial concentration increased to 10 mg/L.

Some studies have investigated the photolysis of ciprofloxacin in different water matrices including distilled water (DW), surface water (SW) and synthesized wastewater (WW) such as [21] and [237]. The results did not show significant differences between the examined water matrices, and both of the studies have concluded that variation in CIP photodegradation rates (k) and half-life ($t_{1/2}$) in the water matrices depend primarily on the water constituents (e.g. Chloride, humic acid, phosphate and nitrate). For instance, CIP photolysis in DW had a value of 0.6297 min^{-1} for k and a half-life of 1.10 min. These values were decreased to $k = 0.2118 \text{ min}^{-1}$ and $t_{1/2} = 3.27 \text{ min}$ when adding humic acid to the water. Similarly, the addition of NO_3^- resulted in decreasing the photolysis rate (0.3127 min^{-1}) and increasing in half-life (2.22 min). This can be primarily because these two water constituents absorb sunlight in the same UV region as ciprofloxacin. Therefore, a competitive relation will occur between CIP and those water components for the absorption of light photons which will inhibit CIP photodegradation. However, the presence of PO_3^- in water had significantly increased the photodegradation rate constant to 1.1440 min^{-1} with a half-life of 0.61 min. Thus, the overall effect of water matrix on CIP photolysis particularly

depends on the balance between the opposing water constituents contributions in various matrices.

The influence of the organic matter on ciprofloxacin photodegradation was examined by [238]. The presence of FPOM reduced the amount of the photodegraded ciprofloxacin under UV light from 42% to 2% within 16 h with a corresponding half-life of 12 h in the solution that contains FPOM compared to four times faster degradation half-life of 2.9 h without FPOM. These findings can be illustrated by the adsorption of CIP to the organic matter present in the solution which will decrease the amount of CIP particles available for photodegradation.

Ciprofloxacin photodegradation as an individual pollutant and in a mixture with norfloxacin and enrofloxacin in different types of water matrices was investigated by [237]. Only ciprofloxacin had a slightly slower photodegradation rate from 0.62 min^{-1} as a single component in water to 0.55 min^{-1} in the mixture. Whereas the other two antibiotics were not affected by the mixture in all of the tested water matrices. This might be illustrated by the occurrence of ciprofloxacin as a byproduct of enrofloxacin photolysis process thus contributing to the increase in measured CIP concentration in the final solution. Therefore, the influence of a mixture containing other antibiotics on ciprofloxacin photodegradation could be neglected.

Adsorption is a mass transfer process that is occurred by spontaneous accumulation of molecules from a liquid or gas phase on the surface of a solid phase [239]. There are diverse adsorption mechanisms including hydrophobic interactions and intermolecular forces such as Van der Waals forces which assembly the physical adsorption, in addition to chemical adsorption which occurs primarily by multiple valence forces that establish chemical bonds between the substrate and the surface of adsorbent such as covalent bonds or ionic bonds. The adsorption kinetic studies are utilized to demonstrate the adsorption mechanisms and characteristics. There are two steps in the kinetic adsorption process. The first step presumes the transfer of molecules from the liquid solution to the surface of solid adsorbent, while the second step assume the diffusion and rearrangement of adsorbate inside the pores of sorbent [106].

The chemical reaction, diffusion control or mass transfer coefficient are used to determine the adsorption kinetic models. The kinetics model of the adsorption of dyes onto the adsorbent material can be used for determining the time required for

adsorption process to reach equilibrium. Determining the rate of adsorption can be employed to develop predictive models and in understanding the related factors that influence the sorption of solutes [240]. The pseudo-first-order and pseudo-second-order are the most widely used reaction kinetic models to analyze the data obtained from the adsorption studies of ECs with natural soil.

The Pseudo-first order was presented kinetic equation was the first in describing the adsorption of liquid-solid system based on solid capacity. The pseudo-first order kinetic model was defined as:

$$\text{Log } (q_e - q_t) = \log q_e - k_1 t \quad (1.2)$$

Where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (hr), respectively. k_1 is the adsorption rate constant of first-order adsorption. The linear plot of $\ln (q_e - q_t)$ against t will give the value for k_1 (slope).

Pseudo-second-order Kinetic Model was originated by [241]. It is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (1.3)$$

Where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (hr), respectively, and k_2 (g/mg.hr) is the rate constant of second-order adsorption. The linear plot of t/q_t against t will determine the value of rate constant, k_2 .

The adsorption isotherm illustrates the pathway of the substrate interactions from the liquid solution to the surface of soil. It symbolizes the relation between the amount of adsorbed compound per unit of adsorbent mass, in addition to the concentration of substrate in the solution at fixed temperature. There are two main types of adsorption, the physical and chemical adsorption. The major differences between the two types are presented in **Table 1.10**.

Langmuir is the simplest adsorption isotherm for the modeling of adsorption process. It assumes that the adsorption process occurs in monolayer on an homogenous surface of adsorbent [242]. Equation for the Langmuir adsorption isotherm is used for the

estimation of maximum capacity (q_m). q_m is the maximum quantity of adsorbate adsorbed per grams of adsorbent. The linear equation is represented as: q_m

$$\frac{Ce}{qe} = \frac{1}{q_m \times b} + \frac{Ce}{qe} \quad (1.4)$$

Where q_m is the monolayer of adsorption capacity (mg/g), b is the Langmuir constant (L/mg), C_e is the equilibrium constant (mg/L) and q_e is the amount of adsorbed on adsorbent at equilibrium (mg/L).

Hereby, the essential characteristics of Langmuir isotherm can be expressed as separation factor (R_L) which defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (1.5)$$

Where K_L refers as Langmuir constant, C_0 is the adsorbate initial concentration (mg/L). R_L value represented the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Freundlich isotherm is an empirical equation suited for non-ideal, reversible, and multi-layer adsorption with highly heterogeneous surfaces. In this perspective, amount adsorbed is the summation of adsorption on all sites, with the stronger bonding sites are occupied first, until adsorption energy are exponentially decreased upon completion of adsorption process. The equation of Freundlich isotherm is represented as:

$$qe = K_F \times Ce^{1/n} \quad (1.6)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L) and q_e is the amount of adsorption per unit mass of adsorbent (mg/g). Both K_F and n represent Freundlich constants, where n indicates the favorability of the adsorption process and $K_F ((\text{mg/g}) \cdot (\text{l/mg})^{1/n})$ indicates the adsorption capacity of the adsorbent.

Table 1.10: The main differences between physical and chemical adsorption mechanisms.

Criteria	Chemical Adsorption	Physical Adsorption
Nature of adsorption.	Depend on nature of adsorbent.	Depend on nature of adsorbent
Specificity	Highly-specific	Non-specific
Reversibility	Mainly irreversible	Reversible process.
Activation energy	Require high activation energy.	Does not require high activation energy.
Enthalpy	Higher than physisorption (40-300 kJ/mol).	Low (20-40 kJ/mol).
Layer of adsorption of saturation region	Mono layer	Multi layers
Bonding	Strong covalent bonds or ionic bonds	Weak Van der Waals, dipole-dipole attraction and London forces

Soil adsorption for DCF have been investigated with different soil textures, mainly using natural soils under various experimental conditions. Some studies investigated the adsorption process using low concentrations of Diclofenac ranging from 5 to 500 µg/L such as [39], [243]. While other studies have reported the adsorption with higher concentrations up to 1000 mg/L such as [35], this was mostly to enable an accurate determination of the remaining DCF in the aqueous solution and to make a clear comparison between all the studied soils which might display various adsorption capacities.

The main factors that have been found to be most effective for Diclofenac adsorption are the soil organic matter content and the pH value. While the pH values of tested soils were constant (7 to 9), the soils with the highest organic matter content (5.45% to 22.2%) have reported the highest Diclofenac adsorption coefficients up to 53 L/g [39]. Moreover, the negligible adsorption amount and the low adsorption coefficient (1.2 L/kg) obtained by both [244] and [36] that have investigated the adsorption of DCF with low organic matter content soils (0.16%, 0.33% and 0.44%) indicates that organic soil matrix play a major role in Diclofenac adsorption process. These findings could be explained by the high hydrophobicity of DCF which can facilitate its interactions with soil organic matter.

Diclofenac adsorption efficiency was greatly affected by the pH value in the solution. All studies that investigated the adsorption of DCF in different pH values have

reported higher adsorption efficiency with the lowest pH, and the recorded adsorption capacities were higher in the acidic conditions. [245] have experiment the adsorption of Diclofenac on goethite in natural soil, the adsorbed amount increased from 2.39 $\mu\text{g/g}$ at pH 8.84 to 45.96 $\mu\text{g/g}$ at pH 5.23 which was close to pK_a (4.15) of DCF. Another study conducted by [182] have also investigated the soil adsorption of DCF with different pH values ranging from 2 to 12. The maximum adsorption capacity (100 mg/g) with all of the tested soils was obtained at acidic pH 2 compared with 15 mg/g at alkaline pH 12. These findings can be correlated to the electrostatic interactions which play an important role in the adsorption process. Diclofenac have the structure of an acidic pharmaceutical molecule which is similar to that of an anionic surfactant. Therefore, a cationic adsorbent surface can significantly increase the adsorption of Diclofenac which is majorly enhanced by the acidic conditions.

Some studies have made a comparison for soil adsorption of Diclofenac between solutions that contain DCF as a single contaminant and in a mixture with other contaminants. [44] have reported Diclofenac adsorption with concentration of 0.9 mg/L in a loam-textured soil as an individual compound and in a mixture with other non-steroidal, anti-inflammatory drugs (NSAIDs) including naproxen, ibuprofen and ketoprofen. The adsorption coefficient of DCF as individual was 10.9 L/kg compared to 11.8 L/kg in the mixture. This result indicates the negligible effect of the mixed compounds system in Diclofenac adsorption coefficient.

The adsorption of diuron herbicide onto soils was mainly reported in literature by the use of natural agricultural soils. Few studies have investigated the adsorption using relatively low concentrations for diuron ranging from 5 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$ [34], [246] in order to reflect the environmental relevant concentrations of diuron. While most of the studies have used higher concentration range (0.5 mg/L to 50 mg/L) either with no specific explanation or as suggested by [42] to choose the range of herbicide initial concentrations such that the equilibrium solution concentration did not exceed 50% of the herbicide aqueous solubility.

Soil texture have been distinguished as the main factor affecting the adsorption of diuron. Many studies have reported the positive effect of soil clay content on diuron adsorption. For instance, [34] studied the adsorption of diuron with different percentage of clay content in three agriculture soils. The adsorption capacity increased from 2.8 mg/kg to 4.2 mg/kg when the soil clay amount increased (11% to 92%) with

corresponding adsorption coefficient of 1.740 L/kg and 3.064 L/kg respectively. Furthermore, the soil highest maximum adsorption capacity (44.24 mg/g) for diuron was reported by [247] using organophilic clay as sorbent with adsorption coefficient of 0.158 L/mg, which indicates the fundamental role of soil clay content in enhancing the adsorption of diuron.

Soil organic matter can play an important role in diuron adsorption efficiency, [248] have studied the adsorption of diuron into different soils with various organic matter content. The results showed a positive correlation between adsorption coefficients and the soil organic matter. While other studies have reported a negligible or no effect of the organic matter on diuron adsorption such as [33], [43]. This can be explained by the heterogeneity and complexity of organic matter which contains a mixture of humic acids, lignin, polysaccharides, proteins and organic acids. Therefore, different types of interactions between sorbent and adsorbate leading to different adsorption efficiencies for a specific compound can be observed depending on the soil organic matter composition.

Temperature is an additional factor that can affect the adsorption efficiency of diuron into soil. [247] reported an increase in adsorption coefficient (0.075 L/mg to 0.158 L/mg) and capacity (44.24 to 56.49 mg/g) when the experimental temperature increased from 298 K to 305 K. While there was no significant influence for pH variation reported in the literature for diuron adsorption by soil.

[105] have studied diuron adsorption onto various types of natural soils as a single component and in a mixture with hexazinone. In all of the tested soils, diuron mixtures have shown, on average, twice the adsorption coefficients and capacities values compared to diuron individual solutions. This indicates that hexazinone enhanced diuron adsorption and it did not compete with it for soil adsorption sites which could be explained by the different adsorption mechanisms of diuron and hexazinone that might occur simultaneously due to their distinct properties. Furthermore, interactions between the adsorbed herbicides can occur which facilitate the adsorption process.

Ciprofloxacin adsorption onto soils have been investigated mainly with the natural soils using a wide range of CIP concentrations. [40] have studied the soil adsorption of CIP using low concentrations ranging from 30 µg/L to 500 µg/L which are near to reported environmental concentration of CIP. However, most of the studies have used

high concentrations up to 1000 mg/L such as [249], [250]. High concentrations were mainly used to facilitate the detection of CIP residue in the solution and to conduct more accurate comparisons between different experimental conditions and soil components. Moreover, [40] were not able to determine CIP isotherm in the concentration ranged from 50 µg/L to 750 µg/L due to the complete adsorption of the compound. Thus, they suggested increasing the concentration range that would improve the isotherm experimental determination.

Soil minerals, and pH values were the most investigated experimental elements for the adsorption of ciprofloxacin. [251] have investigated CIP adsorption with montmorillonite, rectorite, and illite clay minerals. The cation exchange capacity (CEC) was the dominant mechanism responsible for CIP adsorption to minerals. The maximum adsorption capacity (395 mg/g) was obtained by montmorillonite which had the highest CEC of 1.23 meq/g compared to 33 mg/g for illite with 0.11 meq/g CEC. This could mainly be due to the reactions of CIP cationic amine moiety ($=\text{NH}_2^+$) to the negatively charged clay minerals. However, changing in pH values will significantly affect the adsorption efficiency of CIP on soil minerals. For instance, [252] have reported highest adsorption capacity and coefficient for montmorillonite and kaolinite in the acidic to neutral pH conditions. Maximum adsorption obtained with kaolinite was at pH 5–8 range and as the solution pH value increased beyond 8, the adsorption decreased significantly and reached close to zero at pH 11. Moreover, the Adsorption capacity of 300 mg/g obtained with montmorillonite in pH range of 2.8–8.8 had decreased to 247 mg/g as pH reached 11. This can be correlated to the CIP carboxylic group that lose a proton when pH is above 8.7. Subsequently, CIP will exist as an anionic form causing a strong repulsion between the negatively charged layers of soil minerals and ciprofloxacin.

Studying the adsorption of ciprofloxacin as an individual and in a mixture with tetracycline on montmorillonite clay mineral was done by [253]. The adsorption capacity of both CIP and DCF as a single compound were double of their adsorption capacity in the mixed solution with 1.04 mmol/g for CIP as individual and 0.54 mmol/g in the mixture. This result reveals a competitive adsorption relationship between ciprofloxacin and tetracycline on montmorillonite with no preferential adsorption.

EE2 adsorption to soils have been investigated by some studies at environmentally relevant concentrations to simulate EE2 in soil environment (0.3 ng/L to 10 µg/L) by

various studies such as [150], [151], [159], [162], [163]. While other studies have worked with higher concentrations to facilitate the results comparison and EE2 detection in the solution such as [41]. Soil organic carbon content plays a major role in changing EE2 adsorption efficiency. Studies have reported higher adsorption coefficients and capacities with the highest organic carbon content soils. For instance, [254] have investigated EE2 adsorption onto three different natural soils and goethite. The soil with the highest organic carbon content (14.6%) have reported the maximum adsorption capacity of 83.6 g/g and the highest adsorption coefficient (2.14×10^{-3} L/ μ g) compared to the lowest organic carbon content soil (0.25 %) which reported 10 g/g adsorption capacity and 0.97×10^{-3} L/ μ g adsorption coefficient which is near the value reported for goethite (0.28×10^{-3} L/ μ g). These findings can be demonstrated by the dominant hydrophobic interaction in the adsorption processes onto soils and sediments [255]. Therefore, the high hydrophobicity for EE2 will facilitate its adsorption by the soil organic matter.

Moreover, studies have reported the importance of soil clay fraction on the adsorption of EE2. [45] have studied EE2 adsorption onto two soils having different textures. The adsorption coefficient decreased from 15.0 mL/g to 7.95 mL/g when the soil clay fraction decreased from 20% to 8.0 %. On the other hand, the soil with the higher adsorption coefficient had the lower organic carbon content 2.5% compared to 1.1% for the lower adsorption coefficient soil. Therefore, the adsorption of EE2 does not depend only on the soil organic carbon content but also on the soil clay fraction content that provides huge number of additional adsorption sites for EE2.

pH parameter has not been widely studied for the adsorption of EE2 onto soil. However, it might play a role in the adsorption process. For instance, [256] have reported the effect of pH value ranging from 2 to 12 with loamy sand soil and sewage sludge as adsorbents. Adsorption capacities and coefficients had a negligible change when the pH ranged from 2 to 6. However, when pH in the sludge solution was further increased above 6, the adsorption capacity significantly decreased from 2.5 mg/g to 0.5 mg/g. As the sludge has a predominantly negative surface charge over the pH range (3.0 to 10.0) and above pH of 10.0, EE2 will probably become a negatively charged ion because of its pKa (10.5). Therefore, increasing pH above 6 will result in the increasing of EE2 negatively charged ions which will result in the reduction of adsorbed amount of EE2 onto sludge.

Adsorption of terbutryn onto soils was investigated in the previous studies mainly by the use of natural soils with different components, textures and experimental conditions. The terbutryn concentration range used in some studies was low (0.25 ng/L to 25 ng/L) such as [38] to reflect terbutryn concentration in the environment which are in the range of 0.3 ng/L to 44 ng/L [112], [170], [173], [175], [176]. Whereas other studies have investigated the adsorption of terbutryn with higher concentration range (up to 10 mg/L) in order to conduct clear comparisons between the experimental conditions results [46]. pH value was the most effective parameter reported in the literature for terbutryn adsorption with soils. [46] have investigated the adsorption of terbutryn onto sandy loam and clay loam soils in pH range (5.0 to 8.0). The results showed a significant decrease in adsorption coefficient (15.62 L/kg to 1.70 L/kg) when pH of the solution increased from 5.0 to 8.0. This could be related to the soils adsorption behavior which generally have higher adsorption to the ionizable compounds like terbutryn in lower pH values and also to the terbutryn pKa value (4.3) that assume more adsorption efficiency in the acidic conditions.

Organic matter might participate in terbutryn adsorption to natural soils. [38] have investigated the natural soil adsorption to a mixed herbicides solution including terbutryn, ethofumesate, 2,4-D, atrazine and metribuzin with different amounts of soil organic matter content. The adsorption coefficient values were mainly dependent on hydrophobicity degree of the herbicide. The highest adsorption coefficient for terbutryn (80 mg/kg) was recorded with 10.0-14 % soil organic matter compared to 3.2 mg/g for 0.9-9 % OM indicating a positive relation between terbutryn adsorption and soil organic matter. However, these results exhibited a significant change when pH value were varied which indicate the strong correlation between terbutryn adsorption and pH value compared to the soil organic matter content.

1.2. Novelty of the Study

The ultimate fate of ECs in the natural environment depends mainly on the physicochemical properties of each compound, the releasing location and season and its partitioning to environmental solid matrices [14], in addition to the transformation processes that ECs might undergo in the environment which include photodegradation, hydrolysis and biodegradation. Photochemical by solar light is a fundamental process for the environmental risk assessment of ECs in the aquatic environment [15].

Therefore, understanding the photodegradation behavior of ECs is an essential requirement for the fate prediction, adverse impact attenuating and risk assessment of these compounds in the aquatic environment. Furthermore, the investigation of adsorption process of ECs to the natural soil is of major significance for the risk assessment of these contaminants, due to the strong association of the adsorption process with transportation, degradation, bioaccumulation and ecotoxicity of ECs in the terrestrial environment [16], [17].

Many studies have investigated the photolysis behavior of various types of ECs under simulated sunlight in distilled water [18], [19], different water matrices [20]–[22], in addition to various environmental conditions of pH, organic matter, nitrate and salts [23]–[31]. There are also multiple studies in the literature that examined the adsorption of different kind of ECs on the surface of natural soil including agriculture soil [32]–[38], sandy soils [39]–[41], clay, silt and loamy soils [40], [42]–[46], and sewage sludge from municipal WWTP [47], [48]. However, these studies have typically focused on the fate of ECs by examining the photo-transformation and adsorption of each of these compounds individually or limited to a binary or triple contaminants that belong to the similar group of ECs (e.g. pesticides, antibiotics). Whereas ECs in the natural environment belong to different classes and chemical groups such as pharmaceuticals, endocrine disruptors, steroid hormones, and plasticizers with distinct physicochemical properties that constantly exist as a mixture in the environment which could substantially alter their overall photochemical behavior, adsorption to natural soil, fate and persistency due to their interactions [49].

Furthermore, various types of microplastics and metallic nanoparticles have been recently introduced to the environment from different industrial and municipal sources. These contaminants are frequently detected in the wastewater treatment plants, terrestrial and aquatic environment. However, there are very limited studies investigating the effect of the presence of microplastics on the photolysis and adsorption behavior of some ECs as a single compound [50]–[53]. while there are no studies conducted for the influence of metallic nanoparticles. Therefore, the findings previously obtained for the photochemical transformation of ECs are not fully sufficient for estimating its actual fate and behavior in the natural environment which highlights the significance of considering the potential collective fate of ECs as a mixture of distinct compounds, in order to support the environmental risk management

with the data obtained from the studies that are conducted with environmental relevant conditions.

Moreover, some studies have estimated the variation of temperature and organic matter in the natural environment due to human activities and climate change. A model study for a natural lake that is conducted by [54], have anticipated a significant modification in the mixing regimes of 635 lakes around the world that could result from the increase in the temperature of the lake surface water (2.5 °C- 5.5 °C) and the diminish of water ice cover with being permanently ice-free by the year 2080–2100, and subsequently affecting the distribution and OM concentration in the lake due to the disturbance and less frequently of mixing areas. Similarly, [55] have estimated an increase of 2°C to 4°C in the temperature of surface water by the year 2080 due to climate change effect under the anthropogenic medium emissions scenarios. In addition, the chemical properties of organic matter including its preservation and degradation patterns are altered in the natural lakes and rivers depending on the location, water column and sediments. For instance, [56] observed a decline in the OM concentration in a river stream by 60% and 70% after 160 m and 600 m respectively away from an effluent discharge point of a wastewater treatment plant. Furthermore, the temperature of high-latitude soils was found to be warmer than the ambient air during winter (up to 25°C), and cooler in summer (up to 10°C) at 0 cm to 15 cm soil depths [57]. Due to the positive offset between air and soil temperatures in cold environments, a declining of 17% was observed in the annual soil mean temperature in most of the cold environments. In addition, the land-use alteration is continuously modifying the amount and velocity of natural organic matter in agriculture soils. For example, the forest soils contained three times more of soil organic carbon compared to crop fields, and the fraction of particulate organic matter varied widely between plowing tillage, conservation tillage and the forest soil that had recorded 8.24, 30.08 and 6.54 w/w per fraction, respectively [58] which indicates the significance of investigating various temperatures and organic matter concentrations on the fate of ECs in the terrestrial environment.

The previous studies have quantified the change in photolysis rate of ECs by examining the effect of one factor variation at a time (temperature or organic matter) [59]–[61], which could give a false estimation for their photodegradation rate in the natural environment. For instance, in a model study done by [62] for a number of ECs

that were supported by actual lab experiments for comparison, most of the recorded photodegradation rates by the simulation was either underestimated or overestimated mainly due to not taking into account many of the probable indirect photodegradation pathways that could occur in the experimental solution. Furthermore, temperature alteration could influence the process of indirect photolysis in the presence of organic matter. For example, the kinetic reactions in the aquatic environment are influenced by the ambient temperature, and the rate of DOM decomposition in addition to the production of reactive species due to sunlight absorption by photosensitizers in surface water were found to be temperature dependent processes [63]. Furthermore, many studies have recorded a substantial variation in the concentration of monitored ECs depending on seasonal variations and sampling location sites such as [64], [65], which could indicate the strong influence of the combined interplay effect of temperature and organic matter on the fate of ECs in the natural environment. Moreover, the variation in temperature and organic matter could influence the interactions between ECs and other environmental components (micro/nano particles) which may substantially alter their ultimate environmental fate. For instance, the hydrophobic partitioning between the organic contaminants and the surface of micro/nano materials would determine their attachment or detachment in the ambient water [66]. However, [67] implied that the presence of dissolved organic matter (DOM) in the aqueous solution could disturb the interaction between the contaminants and MPs, which could inhibit the long-range transport of ECs by microplastics in natural surface water. In contrary, the attachment of some types of ECs (e.g. hormonal steroid compounds) to MPs could be enhanced by the presence of DOM due to the probable established complexations between MPs and DOM in the solution as reported by [68]. Therefore, the influence of the variation in the key environmental conditions (organic matter and temperature) with the presence of micro and nanoparticles that were not covered collectively in the previous studies, must be evaluated for the photochemical transformations of ECs in the aquatic environment and their adsorption potential to the natural soil in the terrestrial environment, in order to support the environmental risk assessment studies with accurate data obtained in environmentally relevant conditions. Thus, the objective of this study is to reveal the complex combined interaction of mixture, temperature and organic matter conditions, along with the presence of MPs and Ag₂SNPs in the surface water and soil matrices on the photodegradation and adsorption rates of various types of ECs.

1.3. Aim and Scope of the Thesis

Considering the need for an accurate environmental risk assessment of ECs, the main objective of this PhD study is to investigate the fate of a mixture of ECs in the aquatic and terrestrial environment at various conditions and in the presence of micro and nanoparticles (**Figure 1.1**). The photodegradation by natural sunlight, and the adsorption to the surface of natural soil were investigated to estimate the fate of ECs in the natural environment. Two temperatures were chosen including 25 °C and 35 °C, in addition to two organic matter concentrations including 4.5 mg/L and 13 mg/L as total organic carbon (TOC) content. Microplastics and silver sulfide nanoparticles were chosen to investigate the effect of their presence on the fate on ECs. Furthermore, in order to highlight the risk posed by the presence of ECs and microplastics on the natural soil health, correlating with the adsorption data to include the toxicity potential factor of these contaminants in the terrestrial environment, the effect of ECs and microplastics on the soil microbial community and maize plants were investigated.

In the context of the thesis main goal, the following objectives were studied to provide additional data for the risk management strategies of ECs:

- 1) To develop a fast, simple and sensitive analytical technique for the simultaneous extraction and analysis of multiclass ECs at trace concentrations using solid phase extraction (SPE) coupled with liquid chromatography mass spectrometry (LC-MS/MS).
- 2) To test the photolysis behavior of selected ECs in a mixture under simulated sunlight and in a synthetic surface water matrix (SSW). This step involves the preparation of SSW as per the natural surface water components found in the aquatic environment and the establishment of an appropriate photoreactor with natural sunlight wavelength.
- 3) To investigate the adsorption kinetics of selected ECs as mixture in the natural soil.
- 4) To evaluate the potential effect of microplastics and sulfide silver nanoparticles on the aquatic photolysis behavior and adsorption to natural soil of the mixture of studied ECs.

- 5) To examine the influence of different natural organic matter concentrations and temperatures on the photodegradation of targeted ECs in surface water, and their adsorption to the surface of natural soil, by the addition of humic acid and temperature control systems.
- 6) To inspect the possible alteration in the composition and functional activity of soil microbial community posed by the presence of ECs, MPs, and their combination.
- 7) To determine the possible alteration in the maize plant's growth, biomass, and rhizosphere microbial community.

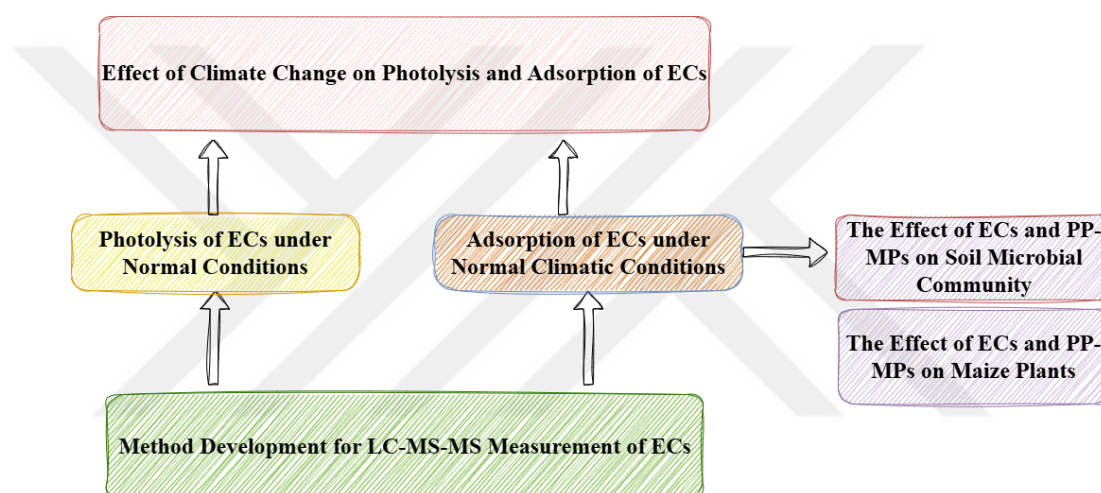


Figure 1.1: Flowchart of the thesis scope.

2. DEVELOPMENT OF ANALYTICAL METHOD FOR SIMULTANEOUS DETERMINATION OF THE FIVE TARGETED EMERGING CONTAMINANTS (ECs) IN AQUEOUS SOLUTION

2.1. Introduction

Emerging contaminants (ECs) are released substances in the environment for which no regulations are currently established for their vast majority [257]. According to NORMAN association, the most frequently identified emerging pollutants are more than 4000 compounds which are categorized in 20 classes including pharmaceuticals, personal care products, steroid hormones, pesticides, plasticizers, surfactants etc. [1]. Therefore, the occurrence of these substances in the natural environment has become a matter of concern globally, and there are continuous efforts to develop advanced analytical measurement techniques for the accurate monitoring and fate assessment of ECs in different environmental matrices which have become the main subject of many recent studies [258]–[264]. The detection of multiple ECs in the environmental samples are mostly performed by liquid chromatography-mass spectrometry (LC-MS/MS) and gas chromatography-mass spectrometry (GC-MS/MS) [265]–[271]. However, GC-MS/MS can only deal with the volatile and semi-volatile compounds, and a prolonged derivatization process are usually mandatory in order to ensure the volatility of the sample analytes [272]–[274]. Therefore, LC-MS/MS is the most preferred analytical technique for the measurement of the vast majority of ECs in the environmental matrices due to its versatility and sensitivity [259], [275]. Furthermore, sample preparation processes play a significant role in the monitoring of ECs. Most of the analytical instruments do not provide direct measurement of ECs within the original environmental matrix due to the interferences that could exist in the natural samples and the trace concentration of ECs. Therefore, a preliminary step of cleanup and/or sample enrichment is required before the detection of the contaminants.

LC-MS/MS is usually combined with selective extraction, clean-up and pre-concentration techniques for the accurate measurement of ECs at trace concentrations,

and for the elimination of possible interferences from the natural environmental matrices [276]. Solid phase extraction (SPE) is the most widely utilized technique for the pre-treatment of environmental samples because of its simplicity and enhanced selectivity [268], [277]–[285]. Although these measurement techniques have provided efficient monitoring for a wide range of ECs, however, most of the developed pre-treatment and measurement methods for the quantification of ECs have exclusively focused on one group of compounds (e.g. pesticides, pharmaceuticals) [286]–[289]. While there are numerous number of ECs that belong to various classes and chemical groups such as pharmaceuticals, endocrine disrupters, pesticides, steroid hormones, plasticizers and surfactants with distinct physicochemical properties that almost always coexist together as mixture in the environment. Therefore, there is an urgent need for the development of new methods for the simultaneous detection of ECs in the natural environmental samples that is considered the current challenge of monitoring these contaminants in the environment [290]. Thus, this study aimed to develop a fast and sensitive technique for the simultaneous detection of various class of ECs.

2.2. Chemicals and Instruments

Target compounds were obtained in powder form: Diclofenac sodium salt (15307-79-6), terbutryn (886-50-0), ciprofloxacin (85721-33-1), 17 α -ethynylestradiol (EE2) (57-63-6) (Sigma-Aldrich, China) and diuron (330-54-1) (Sigma-Aldrich, Germany). All chemicals were of high purity grade $\geq 97\%$. Methanol (99.9%), methyl tert-butyl ether (MTBE) (99.8%), acetonitrile (ACN, >95%), ethylacetate (99.8%), acetone (98%), isopropyl (98%), Dichloromethane (99.8%) and hexane (99.8%) were of gradient grade for liquid chromatography and purchased from Sigma Aldrich. Deuterium-labeled hydrogen isotopes, Diclofenac-d4 (CDN, purity 99.0%), Ciproflaxin-d8 (CDN, purity >98%), 17-alpha -ethynylestradiol-d4 (CDN, purity 99.0%), Diuron-d6 (LGC, purity >98%), Terbutrin-d5 (LGC, purity 99.0%) are used for LC-MS/MS internal standard solution preparation (stored at 4 °C) in order to digitize sensitive measurements with LC-MS/MS. Oasis HLB SPE cartridges (60 mg, 3 mL), Thermo Scientific SolEx C18 cartridges and HyperSep Retain PEP cartridges were purchased from Agilent Technologies. LC-MS/MS measurements were made with Thermo TSQ Fortis Model Tandem Mass Spectrometer (MS-MS) that connected with Thermo Ultimate 3000 Model Ultra Pressure Liquid Chromatograph (UPLC).

2.3. SPE Method Development

A SPE method was optimized for the synchronous extraction of selected ECs in 4 trials. The initial selection of extraction solvents was done by conducting a research review to determine the possible appropriate conditioning and elution solvent candidates of each contaminant as a single compound. The extractions were carried out in duplicates for each sample containing 1 µg/L of the targeted analytes mixture and 50 µL of 1000 mg/L internal standard. Oasis HLB (60 mg, 3 mL), Thermo Scientific SolEx C18 and HyperSep Retain PEP cartridges were used for SPE method optimization (**Figure 2.1**). Dichloromethane, hexane, methanol, ethyl acetate, acetone, acetonitrile, isopropil and MTBE were used for conditioning and eluting the SPE cartridges with a volume of 5 mL for each solvent. Conditioning was done in order to remove any impurity coming from the cartridges manufacturing in addition to activating the cartridge's surface by wetting the sorbent material [291]. Afterwards, 500 mL sample of contaminants mixture (1 µg/L) was percolated through the cartridges under vacuum to maintain a flowrate of 5 mL/min.

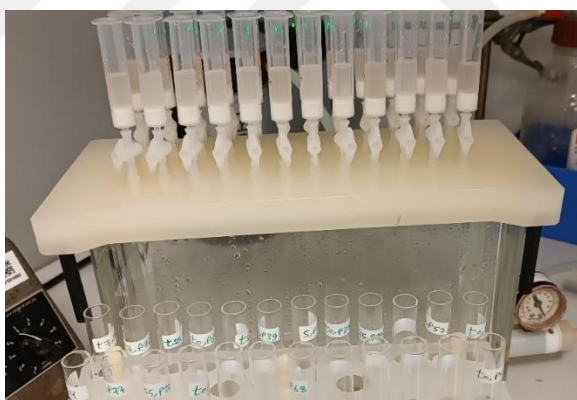


Figure 2.1: SPE setup for the extraction trials of targeted ECs.

Thereafter, the cartridges were rinsed with 5 mL ultrapure water (UPW) or a mixture of solvent/UPW in order to remove any undesired contaminants attached to the surface of sorbent. Then, they left to dry under vacuum for 30 min to decrease the probability of excluding the water-immiscible elution solvents by the remained water on the surface of cartridge that will negatively affect the analytes recovery rates. The analytes were eluted from the cartridges by successively adding the organic solvents and the final extract were put to dryness under a gentle stream of nitrogen overnight. After

complete dryness, the extracts were reconstituted to 1 mL by a mixture of UPW and organic solvent for LC-MS analysis.

2.4. Results and Discussion

2.4.1. SPE Trial 1

OASIS HLB (Hydrophilic-lipophilic balanced N-vinylpyrrolidone-co-divinylbenzene) SPE cartridges were used for the first trial. The pH values of the solution varied between 2, 7 and 9. As shown in **Table 2.1**, CIP and TER had the highest recovery percentages in the first method (87.8%, 114%, respectively), while the recovery rates of diuron, Diclofenac and EE2 were at unacceptable levels (0%-44%). At first attempt, an elution mixture of UPW, methanol, and acetonitrile (70:20:10) were used as elution solvents. In the second trial, replacing methanol and acetonitrile with acetone leads to decrease in recoveries for all ECs except for EE2. Conditioning with MTBE and acetonitrile and eluting with isopropil:UPW (15:85) resulted in low recoveries expect for TER. Changing the reconstitution solution with acetonitrile instead of UPW:isopropil mixture did not increase the recoveries. The recovery rates of targeted compounds except TER increased with decreasing pH value from 9 to 2 with using the same conditioning and elution solvents in method 6; however, they were still not in the acceptable range. The acidic pH could enhance the recovery rate of the targeted pollutants especially by avoiding the precipitation of DCF and improve the retention of EE2 compound on the SPE cartridge [292]–[294]. Therefore, methanol and acetonitrile were further examined with other types of SPE cartridges and different elution solvents at acidic pH in the second trail.

Table 2.1: The recovery rates of targeted compounds in the first trial using OASIS HLB cartridges.

Meth od	p H	Conditioning	Washi ng	Elution	Re-solution	Compou nd	Recove ry %
1	7	ethylacetate	10 mL UPW	%70 water +%20 methanol+ %10 acetonitrile	%70 acetonitrile+ %30 methanol	DCF	44
		%70 acetonitrile+				CIP	88
		%30 methanol+%0				EE2	16
		.1 formic acid				TER	114
						DIU	10

Table 2.1: Continued

2	7	%50 acetone % ethyl acetate	10 mL UPW	%70 water+%20 methanol+ %10 acetonitrile	%20 methanol+%8 0 acetonitrile	DCF	39
						CIP	5
		%50 acetone ethyl acetate				EE2	74
						TER	9
						DIU	0
						DCF	0
3	7	MTBE	10 mL UPW	%15 isopropil+% 85 UPW	%15 isopropil+%8 5 UPW	CIP	0
		acetonitrile				EE2	15
						TER	74
						DIU	15
						DCF	0
4	7	MTBE	10 mL UPW	%15 isopropil+% 85 UPW	acetonitrile	CIP	0
		methanol				EE2	9
						TER	61
						DIU	12
						DCF	27
5	2	MTBE	10 mL UPW	%70 UPW+%20 mehanol+% 10 acetonitrile	acetonitrile	CIP	60
		acetone				EE2	14
						TER	21
						DIU	21
						DCF	0
6	9	MTBE	10 mL UPW	%70 UPW+%20 mehanol+% 10 acetonitrile	acetonitrile	CIP	0
		acetone				EE2	22
						TER	80
						DIU	19
						DCf	30

2.4.2. SPE Trial 2

In addition to OASIS HLB cartridge, the Thermo Scientific SolEx C18 (Silica), which is a nonpolar cartridge and mainly chosen for its sufficient selectivity for the steroidal and nonpolar to moderately polar compounds, [283], [294]–[297] and HyperSep Retain PEP (HyperSep Urea-Modified Polystyrene DVB), which is also a frequently used cartridges for the extraction of ECs were examined. In this trial, all three cartridges had relatively similar recovery rates. However, C18 and HLB are known to retain a wider range of various compounds structures compared to PEP which could prohibit the adsorption of highly polar compounds on its surface due to its low polarity [298]. C18 and HLB cartridges have the tendency of increasing the retention of high polar substances by the special polar trapping groups that are generated in their sorbent

material by the polymerization of hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene monomers [299].

Thermo Scientific SolEx C18 and HLB cartridges were chosen for further examination in following trails. Adjusting the pH of solutions to 2 improved the recoveries for TER and DIU for all cartridges (**Table 2.2**), as these compounds are weakly acidic (pKa 4.4 and 3.7 respectively), their dissociation and solubility in water is expected to increase under acidic conditions, thus enhancing their adsorption to the sorbent material [300], [301]. Elution with acetonitrile and methanol increased the recovery of CIP while the recoveries of TER and DIU was still high. The high recovery rate of CIP with acetonitrile and methanol compared to other solvents was also observed in other studies such as [302]–[305]. This could be due to the higher capability of these solvents to disrupt the interactions between the functional groups of targeted analytes and the sorbent surface, which depend upon the analyte’s retention mechanism such as polarity.

Table 2.2: The recovery rates of the targeted substances in the second trail at 3.7 pH for elution solvents and 2 pH for conditioning solvents.

Meth od	Cartrid ge	Conditioni ng	Elution	Re-solution	Compou nd	Recovery %
1	OASIS HLB	methanol	3 mL methanol	%20 methanol+ %80 UPW	DCF	11
					CIP	19
		hexane	3 mL Dichloromethane		EE2	26
					TER	102
		UPW	3 mL ethyl acetate		DIU	90
2	OASIS HLB	methanol	5 mL acetonitrile	%20 methanol+ %80 UPW	DCF	24
					CIP	90
		ethyl acetate			EE2	20
			5 mL methanol		TER	88
					DIU	91
		UPW				
3	C18	methanol	3 mL methanol	%20 methanol+ %80 UPW	DCF	13
					CIP	44
		Hexane	3 mL Dichloromethane		EE2	0
					TER	94
		UPW	3 mL ethyl acetate		DIU	99

Table 2.2: Continued

4	C18	methanol	5 mL acetonitrile	%20 methanol+ %80 UPW	DCF	29
					CIP	78
		ethyl acetate	5 mL methanol		EE2	39
					TER	87
		UPW	DIU		90	
5	PEP	methanol	3 mL methanol	%20 methanol+ %80 UPW	DCF	35
					CIP	116
		hexane	3 mL Dichloromethane		EE2	35
					TER	93
		UPW	3 mL ethyl acetate		DIU	97
6	PEP	methanol	5 mL acetonitrile	%20 methanol+ %80 UPW	DCF	6
					CIP	105
		ethyl acetate (pH=2)	5 mL methanol (pH=3.7)		EE2	23
					TER	92
					DIU	95

2.4.3. SPE Trial 3

This trial was conducted to test the OASIS HLB and C18 cartridges and using new solvents combination as shown in **Table 2.3** to increase the recoveries of DCF and EE2. C18 cartridge has given the highest recovery rates for all the targeted compounds, especially for EE2 which ranged from 56% to 74.6% with C18 while it recorded 0% and unacceptable recovery for most of the tested trials with HLB cartridge.

Compared to Oasis HLB which is preferred for the extraction of high polarity compounds [306], silica C18 is a nonpolar cartridge and have sufficient selectivity for the steroidal and nonpolar to moderately polar compounds [307]. Thus, it would be more suitable for the retention of estrogens and aliphatic compounds such as EE2 by the strong interactions of electron lone pair [308].

The addition of ethyl acetate solvent for elution with C18 cartridge enhanced the recovery of DCF and EE2 from 16% to 32% and 66% to 98.6% respectively (methods 2 and 4). Removing methanol and acetone from the elution solvents and methanol and acetonitrile from the conditioning combination did not affect any compound's

recovery rate (methods 5, 6, 7 and 8). The presence of other solvents in the elution and conditioning steps such as MTBE could have a dominant influence on the recovery rates of analytes over other types of used solvents due to polarity differences.

Therefore, methanol and acetone had minor role in SPE and it were excluded from the next trials. However, the exclusion of ethyl acetate from conditioning and elution (5,6,7,8) decreased the recoveries of EE2 significantly. As estrogens are medium polarity compounds, and the elution step depends mainly on the resemblance of solvents and analytes polarity level, ethyl acetate might be matching or approaching the polarity of EE2 compound. As a result of this, elution with ethyl acetate can provide high recovery rate for EE2 that is similarly observed in other studies such as [295], [299], [309]–[311]. The combination of MTBE, acetonitrile and ethyl acetate solvents had further enhanced the recovery rates of all the targeted compounds without the need of solvents acidic pH. Therefore, these solvents with C18 cartridge were further examined in the next trial with different analytes concentration and re-solution mixtures.

Table 2.3: The recovery rates of the targeted analytes in the third trail.

Cartridge	Conditioning	Washing	Elution	Re-solution	Compound	Recovery%
HLB	methanol(pH=2)	UPW	5 mL acetonitrile (pH=3.7)	%30 methanol+ %70 UPW	DCF	2.8
					CIP	200
	ethyl acetate (pH=2)				EE2	0
			5 mL methanol (pH=3.7)		TER	90.6
	UPW (pH=2)				DIU	109
C18	methanol(pH=2)	DW	5 mL acetonitrile (pH=3.7)	%30 methanol+ %70 UPW	DCF	16.8
					CIP	70.6
	ethyl acetate (pH=2)				EE2	66.6
			5 mL methanol (pH=3.7)		TER	98
	UPW (pH=2)				DIU	106.2
HLB	methanol(pH=2)	UPW	5 mL acetonitrile (pH=3.7)	%30 methanol+ %70 UPW	DCF	22.4
					CIP	90.4
	ethyl acetate (pH=2)		4 mL methanol (pH=3.7)		EE2	43.8
					TER	96.6
	UPW (pH=2)		4 mL ethyl acetate(pH=3.7)		DIU	117.4

Table 2.3: Continued.

C18	Methanol (pH=2)	UPW	5 mL acetonitrile (pH=3.7)	%30 methanol+ %70 UPW	DCF	32
					CIP	83
	ethyl acetate (pH=2)		4 mL methanol (pH=3.7)		EE2	72.2
	UPW (pH=2)		4 mL ethyl acetate (pH=3.7)		TER	90.6
					DIU	110.4
HLB	MTBE	UPW	5 mL MTBE	%20 acetonitrile + %80 UPW	DCF	23.2
	acetone				CIP	144.2
	methanol		3 mL acetone		EE2	0
	acetonitrile		3 mL methanol		TER	94.6
	UPW		3 mL acetonitrile		DIU	93
C18	MTBE	UPW	5 mL MTBE	%20 acetonitrile + %80 UPW	DCF	24.2
	acetone				CIP	85.4
	methanol		3 mL acetone		EE2	56
	acetonitrile		3 mL methanol		TER	97
	UPW		3 mL acetonitrile		DIU	118.8
HLB	MTBE	%20 acetonitrile + %80 water	5 mL acetonitrile	%15 isopropil+ %85 UPW	DCF	0
	acetone				CIP	0
	UPW		5 mL MTBE		EE2	0
					TER	0
					DIU	0
C18	MTBE	%20 acetonitrile + %80 water	5 mL acetonitrile	%15 isopropil+ %85 UPW	DCF	17
	acetone				CIP	103.2
	UPW		5 mL MTBE		EE2	74.6
					TER	104.8
					DIU	111

2.4.4. SPE Trial 4

In this trial, modifications were made in Trial 3 to increase the recovery of DCF which was still at unacceptable levels. Combination of MTBE and ethyl acetate increased the recovery for DCF and EE2 as seen in **Table 2.4**. The Elution with the reverse order of conditioning solvent combination gave the best results for the recoveries of all ECs. The selected solvents from Trial 3 had been further examined with lower concentration (50 µg/L) and two different re-resolution mixtures.

Table 2.4: The recovery rates of the targeted compounds in the fourth trail.

Method	Conditioning	Washing	Elution	Re-solution	Compound	Recovery %
1	5 mL ethyl acetate	5 mL distilled water	5 mL acetonitrile (pH 3.7) 4 mL methanol (pH 3.7) 4 mL ethyl acetate (pH 3.7)	1 mL %70 water +%30 methanol	DCF	92
	5 mL methanol 5 mL UPW				CIP	107
					EE2	40
					TER	92
					DIU	97
2	5 mL MTBE	10 mL distilled water	5 mL Acetonitrile 5 mL MTBE	1 mL 85% UPW:15% IPA	DCF	107
	5 mL acetonitrile 5 mL UPW				CIP	92
					EE2	77
					TER	94
					DIU	90
3	5 mL MTBE	10 mL distilled water	5 mL Acetonitrile 5 mL ethyl acetate 5 mL MTBE	1 mL %15 isopropyl+%85 water	DCF	72
	5 mL acetonitrile 5 mL Ethyl acetate 5 mL UPW				CIP	98
					EE2	99
					TER	91
					DIU	94

As shown in **Table 2.4** and **Table 2.5**, all the extracted compounds had acceptable recovery rates at 50 µg/L and 500 µg/L. The reconstitution with the mixture of methanol: UPW (30:70 v/v %) had given higher redissolution for EE2 (65% to 90%) and the relatively similar redissolution rates for other analytes. Depending on the findings obtained in all of the four experimental trials conducted for the solid phase extraction of selected compounds, the method that was determined as the best possible method for the simultaneous recovery of all the targeted analytes from the aqueous phase by SPE is presented in **Table 2.6**.

Table 2.5: Recovery percentages at 50 µg/L using the selected solvents with different re-resolution mixtures.

Compound	15% isopropyl	30% MeOH
DCF	104%	97%
CIP	91%	114%
EE2	65%	90%
TER	112%	112%
DIU	106%	107%

Table 2.6: The final optimized SPE method for the extraction of targeted analytes with C18 cartridge.

Solution pH	Conditioning	Washing	Dryin g	Elution	Re-solution
2	MTBE	5 mL (%20 acetonitrile+ %80 UPW)	20 min	5 mL acetonitrile	%30 methanol + %70 UPW
	acetonitrile			5 mL ethyl acetate	
	ethyl acetate				
	UPW			5 mL MTBE	

2.4.5. LC-MS/MS Optimization

After SPE, 1 µL of reconstituted extracts are directly injected in the LC-MS/MS instrument. LC-MS/MS measurements were made with Thermo TSQ Fortis Model Tandem Mass Spectrometer (MS-MS) that connected with Thermo Ultimate 3000 Model Ultra Pressure Liquid Chromatograph (UPLC) (**Figure 2.2**). Atmospheric Pressure Ionization (APCI) is used as ionization source. First of all, the MS parameters were optimized to insure that the targeted contaminants are recognized by the detector, the conditions that give a sufficiently high signal are determined and the appropriate peak integration for qualitative analysis was made. Afterward, the LC parameters were optimized.

The auto sampler temperature in the developed method has been optimized to 10 °C. In order to reduce the measurement limit for EE2, the injection volume was kept high as 100 µL. For this reason, both different material structures and volumes have been tried in order to achieve the highest recovery efficiency from column.

The following columns are used in trials;

- Thermo Accucore C18 brand 2.6 µm pore diameter 100*2.1 mm size.

- Thermo Acclaim Polar Advantage 2.2 μm pore diameter 100*2.1 mm size.
- Terra C18 3.5 μm pore diameter 100*2.1 mm size.
- X-Bridge C18 3.5 μm pore diameter 50*4.6 mm size.
- Waters Symetry C18 3.5 μm pore diameter 50*4.6 mm size.

The columns showed the necessary selectivity for the separation of substances, and attention was paid to the tolerance of high sample volume, especially with their pore diameters. Thermo Accucore C18 brand column with a medium pore size of 100*2.1 mm with a pore diameter of 2.6 μm was selected.



Figure 2.2: Thermo TSQ Fortis Model LC-MS/MS with ESI.

Mobile phase solutions were selected in accordance with the polarities of the substances measured. The most used Methanol and UPW were preferred as mobile phase solutions due to their common usage in different methods. As multiple measurements are made in a single injection, an optimization has been made to obtain a polarity gradient that will allow the separation of the substances, considering the degree of polarity of the substances to be separated. Since the mobile phase solution also carries the substances to the MS where ionization takes place, a buffer solution is added to the mobile phase. The concentration for ammonium fluoride, which provides the most effective ionization during the optimization of MS parameters, was determined as 5 mM by trial and error, considering the pH levels in which the substance ionized. The carrier phase gradient, in which the measured substances are separated efficiently from each other, is shown in **Table 2.7**.

Accordingly, the mobile phase gradient starting with methanol containing 10% of 5 Mm ammonium fluoride is kept constant for 0.2 min, then increased to 70% within 2 min, increased to 90% between 2 and 5 min, and it remained stable at 90% for 2 min,

and then returned to its initial condition for 2 min. The other carrier phase was ultrapure water containing 1 mM ammonium fluoride. Therefore, the developed method takes 7 minutes. Then, chromatographic conditions such as injection volume, mobile phase velocity and column temperature were tested and optimized so that all the substances to be measured were efficiently separated and formed non-intermingled peaks (**Table 2.7**). The optimized injection volume was 100 μ L and the mobile phase velocity was 0.300 mL/min. While the column temperature was determined as 40 $^{\circ}$ C.

Table 2.7: Carrier load velocity and gradient conditions for LC in the optimized measurement method.

Time (min)	Flow Rate (ml/min)	% Methanol (5 Mm with ammonium fluoride)	%UPW (1 Mm ammonium fluoride)
0	0.300	10	90
0.2	0.300	10	90
2	0.300	70	30
5	0.300	90	10
7	0.300	90	10
7	0.300	10	90

2.4.6. Optimized MS Parameters

The optimized parameter values are summarized in **Table 2.8** In MS/MS scanning systems, attention has been paid to using at least two ionization products in order to make precise measurements. The higher signal ion is used for digitization, and the other is used to verify the substance [312].

Table 2.8: Mass Spectrometer (MS) Parameters.

Parameters	Value
Spray Voltage (V)	5
Volatile temperature ($^{\circ}$ C)	350
Carrier gas pressure (arb.)	45
Ion stripping gas pressure (arb.)	0
Additional gas pressure	15
Capillary tube temperature ($^{\circ}$ C)	300
Peak width	12
Scan width	5
Scan time	0.8
Number of micro scans	1

The ionization products detected in LC-MS/MS belonging to the selected contaminants for this study are shown in **Table 2.9**. After the ionization products are detected, the parameters of the peak width, scan width, scan time, micro scan number, which determine the quality of the peak, have been tested and optimized.

Table 2.9. The m/z values of the main substance and ionization products of the targeted analytes.

Substance Name	Main Substance Mass m/z	Degradation Product	Collision Energy	Ionization Mode	Arrival Time
Ciprofloxacin	332.141	245.083	24.18	Positive	4.25
Ciprofloxacin	332.141	288.137	17.58	Positive	4.25
Ciprofloxacin	332.141	314.053	20.08	Positive	4.25
Ciprofloxacin – d8	340.2	249.054	25.16	Positive	4.25
Ciprofloxacin – d8	340.2	296.137	17.92	Positive	4.25
Diuron	233.024	45.889	16.67	Positive	5.38
Diuron	233.024	72.014	18.44	Positive	5.38
Diuron	233.024	132.889	39.53	Positive	5.38
Diuron	233.024	159.942	26.79	Positive	5.38
Diuron-d6	239.17	52.071	17.76	Positive	5.38
Diuron-d6	239.17	78.042	19.49	Positive	5.38
EE2	295.4	158.962	34.28	Negative	5.6
EE2	295.4	183.083	39.04	Negative	5.6
EE2	295.4	199.03	40.72	Negative	5.6
EE2	299.4	187.179	35.08	Negative	5.6
EE2-d4	299.4	266.167	27.28	Negative	5.6
EE2 -d4	299.4	269.113	24.59	Negative	5.6
Diclofenac	296.024	215	19	Positive	5.62
Diclofenac	296.024	250	17	Positive	5.62
Diclofenac-d4	300	219.113	19.62	Positive	30.474
Diclofenac-d4	300	254.042	13.34	Positive	30.474
Terbutryn	242.143	91	27.5	Positive	6.07
Terbutryn	242.143	186.07	18.75	Positive	6.07
Terbutryn-d5	247.2	90.917	28.08	Positive	6.07
Terbutryn-d5	247.2	191.054	19.11	Positive	6.07

2.4.7. Method Validation

In order to ensure the suitability of the optimized method for applications in routine analysis, the analytical quality parameters were evaluated including selectivity, stability, robustness, linearity, sensitivity, accuracy and precision.

2.4.7.1. Selectivity

Selectivity is an essential qualitative assessment for the analytical method which test the capability of the extraction method and it represents to which extent the interferences were avoided, and the targeted analytes were distinguished among other organic compounds in the matrix. For this reason, the extraction of blank samples was performed using UPW, synthetic surface water and real water matrices. The results were compared to the aqueous solution that was spiked with the targeted analytes. The recovery rates obtained of the blank samples (0% - 0.05%) and the targeted analytes spiked samples were (90% - 114%) in an acceptable range. Moreover, there were no interference peaks in the chromatogram of blanks which indicates a good selectivity for the separation and extraction of the targeted analytes by the developed method.

2.4.7.2. Stability and Robustness

Stability and robustness parameters measure the capacity of the optimized method to remain uninfluenced by little but dynamic alterations in different factors or experimental conditions such as sample storage time and water matrix. The stability was evaluated by applying the optimized SPE method on 3 samples sets including the targeted analytes at 50 µg/L. The first set was extracted immediately, while the other two sets were stored in dark at 4 °C and extracted after 24 h, 48 h and 72 h. While the robustness, which test the effect of the optimized method in different matrix, was examined by extracting 3 different sets including distilled water and two synthetic surface water matrices with different organic matter concentration (4.5 mg/L and 13.6 mg/L) The recovery percentages of all the analytes in the stability and robustness experiments did not exhibit any significant variation and were in the acceptable range (85% - 115%) which confirm the robustness and stability of the optimized method.

2.4.7.3. Linearity

The linearity of the method tests the ability of the optimized method to provide directly proportional results to the real concentration of the analytes in samples. The linearity was examined by the extraction of four spiked samples in the range of 10 µg/L – 750 µg/L (10 µg/L, 50 µg/L, 100 µg/L, 200 µg/L, 500 µg/L and 750 µg/L). The correlation coefficients r^2 values for the targeted analytes ranged between 0.988–0.999, which is

evidence for a good linearity of the optimized analytical method.

2.4.7.4. Accuracy and Precision

The accuracy of the method was tested at four different concentrations representing low, medium and high levels (10 µg/L, 50 µg/L, 100 µg/L and 500 µg/L) within the dynamic linear range. The recovery rates of the various concentrations of targeted analytes were in the range of 71% - 117%, The precision was demonstrated by the replicate injection of the aqueous solution with a relative standard deviation of (RSD) less than 20%, which shows that the developed method has good repeatability and precision.

2.4.7.5. Sensitivity

Sensitivity parameter includes the determination of the limit of detection (LOD) taking the three times value of signal-to-noise ratio (S/N) for LOD and limit of quantification (LOQ) taking ten times S/N value after the application of SPE that provides the concentration factor for the calculations. SPE was applied for 500 mL of samples, and the final volume is 1 mL after complete evaporation; therefore, the concentration factor is 500. The LOQs values for the targeted analytes were 5 µg/L for ciprofloxacin, diuron, terbutryn and diclofenac, and 25 µg/L for EE2, while LODs values were 0.01 µg/L for ciprofloxacin, diuron, terbutryn and diclofenac and 0.05 µg/L for EE2.

3. THE PHOTOLYSIS BEHAVIOR OF SELECTED ECS AS INDIVIDUAL AND IN MIXTURE IN DISTILLED WATER AND SYNTHETIC SURFACE WATER MATRICIES.

3.1. Materials and Methods

3.1.1. Chemicals and Instruments

Diclofenac sodium salt (15307-79-6), diuron (330-54-1), terbutryn (886-50-0), EE2 (57-63-6) and ciprofloxacin (85721-33-1) with a high purity grade $\geq 98\%$ were obtained in powder form (Sigma-Aldrich). NaHCO_3 , CaSO_4 , MgSO_4 , KCl and humic acid were used for synthetic surface water media. A cylindrical photoreactor containing 6 Philips TL-D 15W lamps (**Figure 3.1**), emitting a single-band simulated solar UV light at 365 nm wavelength and 120 W/m^2 light intensity was used for the photolysis experiments. The photoreactor comprised heating and cooling system to adjust the temperature of the irradiated sample, in addition to a magnetic stirrer to keep the water sample homogenized during the experiment. PP-MPs were sieved from 2 mm pore size and added to the test matrix. Ag₂S-NPs were synthesized in a university laboratory and characterized with SEM image. Diameter of nanoparticles were 20 nm.

3.1.2. Preparation of Stock Solution and Sampling Time Points

The stock solution for a mixture of selected compounds was prepared in methanol at a concentration of 10 mg/L, while in order to prepare the sample for photolysis experiment, 1 liter of sample was spiked with the compounds stock solution in a concentration of 1 ppb for each, which reflect the recorded concentrations of these compounds in the aqueous environment [147], [157], [163], [170], [174], [181], [313]–[315]. The initial sampling time points were selected in accordance with the reported half-live values in the literature for the compounds as individual. For example, ciprofloxacin and Diclofenac were reported to have a short half -life under simulated sunlight, ranging from 3 min to 16 min for Diclofenac [20], [316], [317] and from 2 min to 70 min for ciprofloxacin [318], [319]. While terbutryn and diuron had a longer

half-life, ranging between 125 min to 202 min for terbutryn [28], [114], and 61 min to 1128 min for diuron [225], [320]. Therefore, the selected time points varied from short to moderate and relatively long time points (0, 2, 5, 10, 20, 60, 240 and 480 min) in order to cover the expected half-life ranges for each compound for the photolysis experiments. The samples were collected from the photoreactor at each sampling time point in brown bottles using a 50 mL pipette. Afterward, the bottles were preserved in dark at 4 °C until SPE and LC-MS/MS analysis.

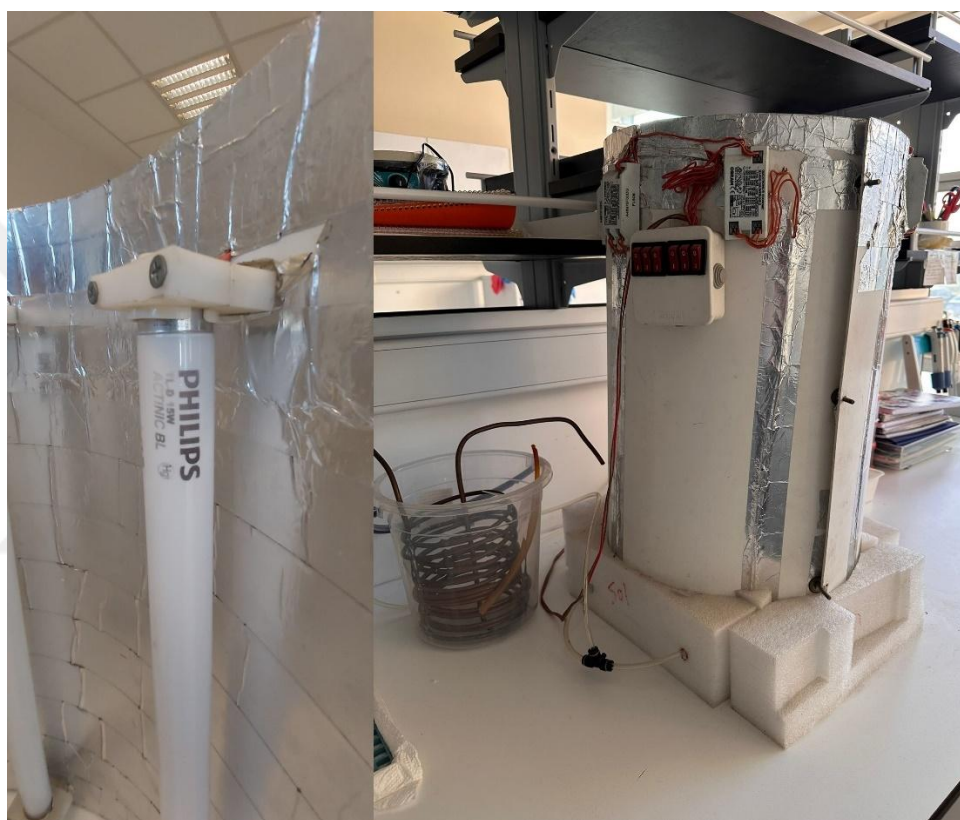


Figure 3.1: The photoreactor and Philips TL-D 15W lamps.

3.1.3. Surface Water Synthesis

To investigate the effect of mixture on the photodegradation of the selected compounds, the photolysis experiments for these compounds were conducted in mixture and as individual, and the obtained results were also compared to the reported photolysis rate in the literature for these compounds as individual. While the effect of water matrix on the photodegradation of the selected compounds in mixture was tested by using synthetic surface water (SSW) that is prepared according to an

environmentally relevant concentrations of salts and organic matter recorded in river water [321] as shown in **Table 3.1**.

Table 3.1: The concentrations of added elements for the synthetic surface water.

Element	Concentration (mg/L)
Na	20
Ca	70
Mg	30
SO ₄	287
K	3
Cl	2.73
HCO ₃	53
TOC	4.5

3.1.4. Addition of Microplastic and Silver Sulfide Nanoparticle

Polypropylene microplastics (PP-MPs) were added at a concentration of 1 mg/L in powder form, a level frequently detected in aquatic environments [123]–[125], [322], [323]. The PP-MPs were dispersed in SSW using a magnetic stirrer. Silver sulfide nanoparticles (Ag₂S-NPs) were prepared as a stock solution by dispersing the powder in distilled water followed by 10 min ultrasonication. Ag₂S-NPs were added to the SSW from its stock solution for a final concentration of 1 µg/L, consistent with levels reported in wastewater effluents and receiving waters [145], [324], [325].

3.1.5. Statistical Analysis

Statistical analyses were performed in R version 4.4.1 [326]. For each compound, the Pseudo–first-order degradation rate constant (k) obtained from kinetic fitting was used as the response variable. The effects of PP-MPs, Ag₂S-NPs, PP-MPs+Ag₂S-NPs, as well as their interactions, were evaluated using linear mixed-effects models (LMMs) implemented in the lme4 package. In these models, “Day” (independent experimental run) was included as a random effect to account for between-batch variability, while treatments were treated as fixed effects. The significance of fixed effects (main factors and interactions) was tested using ANOVA-type tables derived from the LMMs. Post-hoc comparisons of estimated marginal means (EMMs) were performed using the emmeans package, with Tukey’s adjustment applied for multiple testing. This approach allowed us to compare all treatment combinations (e.g., PP-MPs, Ag₂S-NPs,

PP-MPs+Ag₂S-NPs) and to determine which treatments differed significantly in their degradation rate constants. Statistical significance was defined at $p=0.05$.

3.2. Results and Discussion

In order to investigate the effect of mixture on the photodegradation of the selected compounds, a comparison was made between the photolysis rate of the mixture of these compounds and their reported photolysis rate in the literature as individual in the distilled water matrix. In addition, as the reported values for the photodegradation of these substances as individual in the surface water matrix varied widely in the previous studies depending on the surface water composition, and to investigate any possible variation for the effect of mixture between distilled water and surface water matrices, the photodegradation of the targeted compounds was tested as individual and in a mixture in the synthetic surface water matrix. The recorded photodegradation kinetics and half-lives of targeted compounds in mixture and as individual are shown in **Table 3.2**.

3.2.1. Effect of Mixture in Ultra-Pure Water and Simulated Surface Water

The photodegradation of diclofenac, diuron and EE2 were the most affected among other compounds due to the presence in mixture. The photolysis half-life of DCF in DW increased from 113 min as maximum value reported in the literature for DCF as individual to 577 min in the mixture, and from 40 min to 64 min in the SSW matrix. This decline in the photolysis rate of DCF due to the presence in mixture is in accordance with another study that have examined the photolysis of Diclofenac in a mixture with naproxen using various water matrices irradiated by natural sunlight [24]. Diuron exhibited no photodegradation with the mixture in DW compared to a half-life of 235 min as individual, while in the SSW, the mixture had a relatively less decreasing impact in the photolysis half-life of diuron (65 min to 96 min). [226] have also observed the decline in the photolysis rate of diuron with a mixture of 4 different pesticides in the real water matrix. As observed in this study (Section 4.2.4.2), the presence of diuron and Diclofenac in the mixture with SSW had hugely increased its photolysis rate constant from no degradation in DW to a half-life of 96 min in SSW for diuron and 577 min in DW to 64 min in SSW, therefore, organic matter seems to

have a dominant impact over the mixture for the photodegradation of diuron and DCF. However, the photolysis rate of terbutryn and ciprofloxacin in mixture were in the range of single compound indicating the negligible effect of mixture on their photodegradation behavior.

Table 3.2: Photolysis rate constants and half life time for selected ECs.

Compound	Milli-Q water				Simulated surface water			
	Mixture		Individual (Literature)		Mixture		Individual	
	k1 (min ⁻¹)	t _{1/2} (min)	k1 (min ⁻¹)	t _{1/2} (min)	k1 (min ⁻¹)	t _{1/2} (min)	k1 (min ⁻¹)	t _{1/2} (min)
DCF	0.0012	577	0.006 - 0.056	10 - 113	0.0108	64	0.0172	40
Diuron	No degradation		0.0022 - 0.0113	61- 235	0.0072	96	0.0106	65
Terbutryn	0.0005	1386	0.0000 - 0.0055	125 – 12120	No degradation		No degradation	
EE2	No degradation		0.035	23	0.0248	28	Complete removal	
CIP	0.0159	43.6	0.0099 - 0.32	2.14 – 70	0.0068	102	0.007	98

The drop in the photolysis rate of all compounds in both DW and SSW matrices as a result of existing in mixture could be generally attributed by the competition on light photons between different compounds in the solution, the light scattering effect due to the presence of various other molecules, in addition to the initial concentration effect which is known to cause a decrease in photolysis rate as a result of photon limitation at higher initial concentrations of contaminants [327], [328]. Furthermore, the possible reason for the significant decline in the photolysis rate of DCF, EE2 and diuron compared to terbutryn and ciprofloxacin can be explained by UV absorption spectra of the contaminants that is related to their chemical structure and the corresponding molar absorption coefficient (MAC) for each wavelength of UV light. The wavelength used in this study is in the UV-A range (360 nm), the UV light absorption by diuron was found to be maximum at 247 nm with MAC value of 17600 M⁻¹ cm⁻¹, and negligible at the wavelength range of 320 nm to 370 nm [329], DCF recorded the highest absorption at 275 nm with MAC of 10300 M⁻¹ cm⁻¹ [330], while MAC for DCF decreased to 1113 M⁻¹ cm⁻¹ at 310 nm [331]. In addition to EE2 that have a

relatively low maximum MAC value between 240 and 330 nm ($2026 \text{ M}^{-1} \text{ cm}^{-1}$) that is linked mainly to its photoactive phenolic group [332]. The maximum MAC values that are recorded for diuron, EE2 and DCF along the UV spectrum and particularly in the wavelength range emitted from the photoreactor of this study are significantly lower than the MAC of ciprofloxacin which is found to be $1.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 310 nm [333], [334]. As the MAC illustrates the strength of a molecule to absorb UV light at a certain wavelength, therefore in the mixture studies, the compounds that have the highest MAC near the applied UV light wavelength, are expected to have a minor variation in their photolysis rate, absorbing the light more efficiently, and being dominant over the compounds with low MAC values which will exhibit a considerable declining in their photodegradation rate due to the competition with the compounds that have higher affinity to absorb the light in the solution.

3.2.2. Comparison between Ultra-Pure Water and Simulated Surface Water

Compared to the results with mixture of selected compounds in distilled water. The synthetic surface water has enhanced the photolysis rate of diuron and EE2 from no degradation within 480 min to a photolysis half-life of 96 min and 28 min respectively. In addition, the photodegradation of Diclofenac was also significantly accelerated from a half-life of 577 min with DW to 64 min in SSW. This enhancement in the photolysis rate due to the effect of surface water matrix is also reported in another studies such as [335], [336]. The increase in photolysis rate could be due to the ionic composition of surface water which contain nitrates and chloride that could be the responsible factor in enhancing the photodegradation. In addition to the tendency of the organic matter to produce active species under sunlight irradiation such as triplet DOM* and $\bullet\text{OH}$ which play a major role in degradation of compounds [337]. However, the surface water inhibited the photodegradation of terbutryn that did not recorded any photodegradation in the matrix within 480 min, this could be due to the adsorption of terbutryn to the organic matter presence in the surface water by its C-S bond that present in its chemical structure [236]. Moreover, the presence of some components in surface water such as bicarbonate might compete with terbutryn for the absorption of light photons [338]. Therefore, surface water matrix can have dual effect depends on the experiment condition such as light wavelength and the type of pollutants presence in the solution.

3.2.3. Effect of PP-MPs, Ag₂S-NP and their Combination

The photodegradation of all compounds best fit with the pseudo-first-order kinetic model (**Figure 3.2**). Addition of PP-MPs or Ag₂S-NPs to the irradiated solution of ECs mixture resulted in different trends including the increase/decrease or no change in the photodegradation rates of ECs; however, the trends were same for the addition of PP-MPs or Ag₂S-NPs. Terbutryn in the mixture was not degraded during 8 hours and addition of PP-MPs or Ag₂S-NPs did not affect its persistency (**Table 3.3**). The addition of PP-MPs to the irradiated solution had substantially inhibited the photodegradation rates of EE2 (0.0248 min⁻¹ to 0.0058 min⁻¹, $p < 0.0001$), ciprofloxacin (0.0068 min⁻¹ to 0.0028 min⁻¹, $p = 0.0002$) and diuron (0.0072 min⁻¹ to no degradation). This inhibition suggests that adsorption of ECs on PP-MPs might reduce their exposure to UV irradiation, decreasing their availability for photodegradation and subsequently lowering their photolysis rates. Some organic contaminants have a strong affinity for adsorption onto the surface of MPs through various mechanisms, including electrostatic interactions, pore filling, van der Waals forces, hydrogen bonding, and, primarily, hydrophobic interactions [52]. EE2 and diuron are hydrophobic compounds [339], [340] with relatively low water solubility [94], [105], making them more likely to adsorb onto the hydrophobic surface of MPs.

As we saw previously, terbutryn is highly resistant to photodegradation by sunlight, and its persistence was unaffected by the presence of PP-MPs and Ag₂S-NPs. Ciprofloxacin, and EE2 exhibited similar reductions in photolysis rates in the presence of Ag₂S-NPs as for PP-MPs (**Figure 3.3**). While diclofenac was not significantly affected by the presence of Ag₂S-NPs alone the effect of Ag₂S-NPs on photodegradation of ECs has not been previously reported. However, Ag₂S-NP are known to absorb and scatter light efficiently across a broad wavelength range (200 nm to 800 nm) [341]–[343], which may partially reduce the available light for ECs photolysis. The molar absorption coefficient (MAC) of diclofenac is relatively low near the tested wavelength in this study (1113 M⁻¹ cm⁻¹ at 310 nm) [331], with a maximum value at 275 nm (10300 M⁻¹ cm⁻¹) [330]. In contrast, ciprofloxacin has a high MAC value of 45×10^4 M⁻¹ cm⁻¹ at 310 nm [333], [334],), while EE2 has a nearly constant MAC value of 2026 M⁻¹ cm⁻¹ between 240 and 330 nm [332]. Therefore, compounds with less MAC near the tested wavelength like diclofenac is expected to be less sensitive for the light scattering effect posed by the presence of Ag₂S-NPs. For

the combined presence of Ag₂S NPs and PP-MPs, the trend in photodegradation rates of EE2 was similar to those observed for their individual presence (**Figure 3.3** and **Table 3.3**).

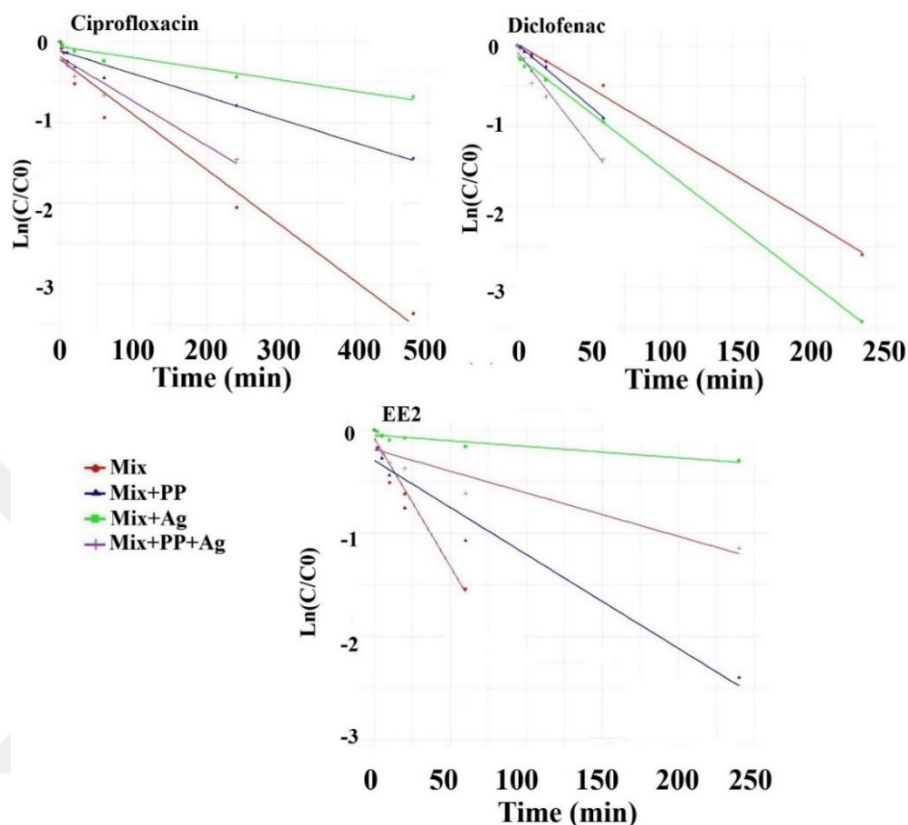


Figure 3.2: Pseudo-first-order kinetic model for ciprofloxacin, diclofenac, and EE2 in the mixture, with and without polypropylene microplastic (PP-MPs) and silver sulfide nanoparticles (Ag₂S-NPs) in synthetic surface water matrix.

Table 3.3: Photolysis kinetics and half-lives of selected ECs in the presence of PP MPs and Ag₂S-NP.

Compound	Mixture*		Mixture + PP-MPs		Mixture + Ag ₂ S-NPs		Mixture + PP-MPs + Ag ₂ S-NPs	
	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)
Diclofenac	0.0108	64	0.0151	42	0.0137	50.5	0.0233	30
Diuron	0.0072	96	N.D		N.D		N.D	
Terbutryn	N.D		0.0012	577	N.D		N.D	
EE2	0.0248	28	0.0058	119	0.0061	113.6	0.0077	90
Ciprofloxacin	0.0068	102	0.0028	247.5	0.0014	495	0.003	231

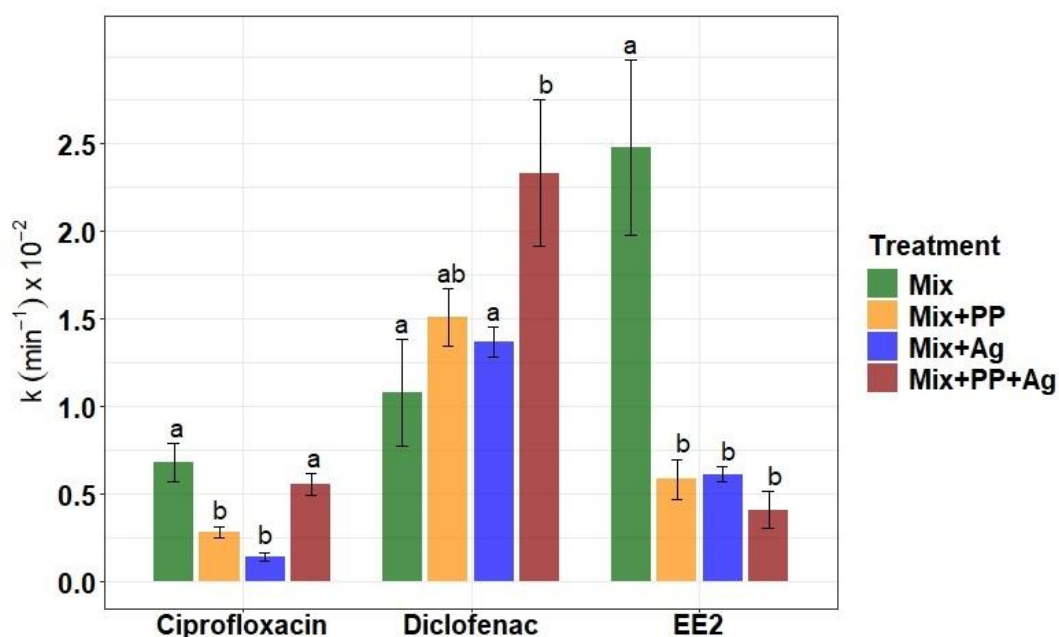


Figure 3.3: Photolysis rate constants of ciprofloxacin, diclofenac, and EE2 in the mixture (with diuron and terbutryn), with and without polypropylene microplastics (PP-MPs) and silver sulfide nanoparticles (Ag_2S -NPs) in a synthetic surface water matrix with low TOC content and temperature (25 °C). Error bars represent standard errors of the mean, and different letters above the bars indicate significant differences between treatments ($p < 0.05$).

The presence of PP-MPS and Ag_2S -NPs alone did not affect the photolysis of diclofenac. In contrast, the photodegradation rate of diclofenac increased in the presence of PP-MPs+ Ag_2S -NP, with its half-life decreasing from 64 min to 30 min, $p=0.001$ (**Figure 3.3**). This result is consistent with previous studies reporting accelerated photolysis rates for various micropollutants in the presence of MPs and NPs [50], [344]. The enhancement in photodegradation may be attributed to the generation of reactive oxygen species (ROS) upon light irradiation of MPs, as observed in earlier studies [345]–[347]. Diclofenac contains electron-rich aromatic rings and an anilide moiety, making it highly susceptible to attack by photo-generated reactive oxygen species (ROS) such as singlet oxygen ($^1\text{O}_2$) and hydroxyl radicals ($\bullet\text{OH}$) [348]. In contrast, the steroid structure of EE2 and the zwitterionic, fluorinated structure of ciprofloxacin are generally less reactive toward $^1\text{O}_2$ under similar conditions [349], [350]. Therefore, the increased photodegradation of diclofenac, in contrast to the decreased rates for EE2 and ciprofloxacin in the presence of particulate contaminants, suggests that both ROS selectivity and differential adsorption based on

molecular properties may determine ECs persistence, potentially leading to imbalanced contaminant profiles in natural waters. It is worth to investigate these expected mechanisms in the further studies.

In conclusion, both individually and in combination, PP-MPs and Ag₂S-NPs reduced the photolysis rates of the target ECs, except for diclofenac, which exhibited an increased photodegradation rate in the presence of PP-MPs+ Ag₂S-NP. These findings highlight the complex interactions between ECs and coexisting MPs and NPs, which underscore the urgent need for studies investigating the mechanism of these complex interactions.



4. ADSORPTION OF EMERGING CONTAMINANTS UNDER NORMAL CLIMATIC CONDITIONS

4.1. Experimental Plan and Procedure

The adsorption of the five contaminants mixture (Diuron (DIU), Terbutryn (TER), Diclofenac (DCF), Ciprofloxacin (CIP) and 17 α -ethynyl estradiol (EE2)) were tested using Lufa soil with pH 5-6 and organic carbon content of 1.5-2%. The experiments were conducted in three different sets as shown in **Table 4.1**. The selected concentrations were 0.1 mg/kg for the studied contaminants, 1 g/kg for PP microplastics and 5 mg/kg for Ag2SNP. These concentrations are chosen near to the detected terrestrial environmental values of these contaminants in order to reflect the environmental relevant conditions [182], [191], [193], [194], [351]–[353].

All of the experiments were performed in duplicates. The targeted pollutants stock solution was prepared in methanol in a concentration of 10 mg/L. Ag2SNP were prepared in distilled water in a concentration of 100 mg/L and ultrasonicated for 10 min prior to use. PP-MPs were added in the powder form (0.1% of soil weight) and homogenized with the solution. The sets containing the soil and contaminants solution were prepared in 100 mL dark conical flasks (**Figure 4.1**). The appropriate soil: water ratio for adsorption study were selected according to an experimental trial with three different ratios (10g : 20mL, 3g : 30mL and 20g : 20mL). According to the obtained solution volume (8 – 15 mL) after shaking at 200 rpm and centrifuge at 5000 rpm for 15 min, the ratio of 10 g : 20 mL were chosen for further experiments.

Table 4.1: The tested sets components and concentrations of contaminants used for the study.

Components	Set A	Set B	Set C
Mixture	0.1 mg/kg	0.1 mg/kg	0.1 mg/kg
PP	-	1 g/kg	1 g/kg
PP + Ag2S-NP	-	-	5 mg/kg



Figure 4.1: The shaker and dark flasks used for the adsorption experiments.

To determine the possible adsorption equilibrium time point for the targeted contaminants, the three sets were shaken in different time points including (15, 30, 45, 60, 120, 300, 480, 960, 1440 and 2880 min). Afterward, the samples were centrifuged at 5000 rpm for 15 min, and the supernatant was separated by syringe and filtered using PVDF hydrophilic welded syringe filters (0.22 μm). Then, the filtered samples were measured by LC-MS/MS. According to the obtained results, all of the tested sets reached equilibrium at 1440 min, thus, it was selected as the equilibrium time point for the following experiments. However, EE2 exhibited complete adsorption in the first shaking time point (15 min) in addition to ciprofloxacin which had an adsorption amount of around 90 % at 15 min. Therefore, lower shaking time points were added to the next experiments, including (2 min, 5 min and 10 min). Therefore, the experiments were conducted at the following time points: 2, 5, 10, 15, 30, 45, 60, 120, 300, 480, 960 and 1440 min.

4.2. Results and Discussion

The adsorption results of all the targeted compounds were best fitted the non-linear second order kinetic model (**Figure 4.2**). EE2 has recorded the highest amount of adsorbed molecules at equilibrium with q_e value of 94 $\mu\text{g/kg}$ and >98% adsorption in

45 min, which indicate a very high affinity to adsorb on the soil surface (**Figure 4.3**). The adsorption rate of EE2 as single compound was difficult to obtain in many studies due to its high affinity to be adsorbed on the natural soil organic matter, not only due to the high hydrophobicity of EE2, but also as a result of the chemical structures of the soil organic matter that could facilitate the attachment of the aliphatic compounds such as EE2 [254]. For example, [47] and [354] recorded extensive adsorption of EE2 molecules on the natural soil containing organic carbon content of 1.2 - 2 % with an adsorption percentage of 90% to 100%, in addition, [41] also observed a high adsorption amount of EE2 (62%) within 1440 min with only 250 mg of natural soil.

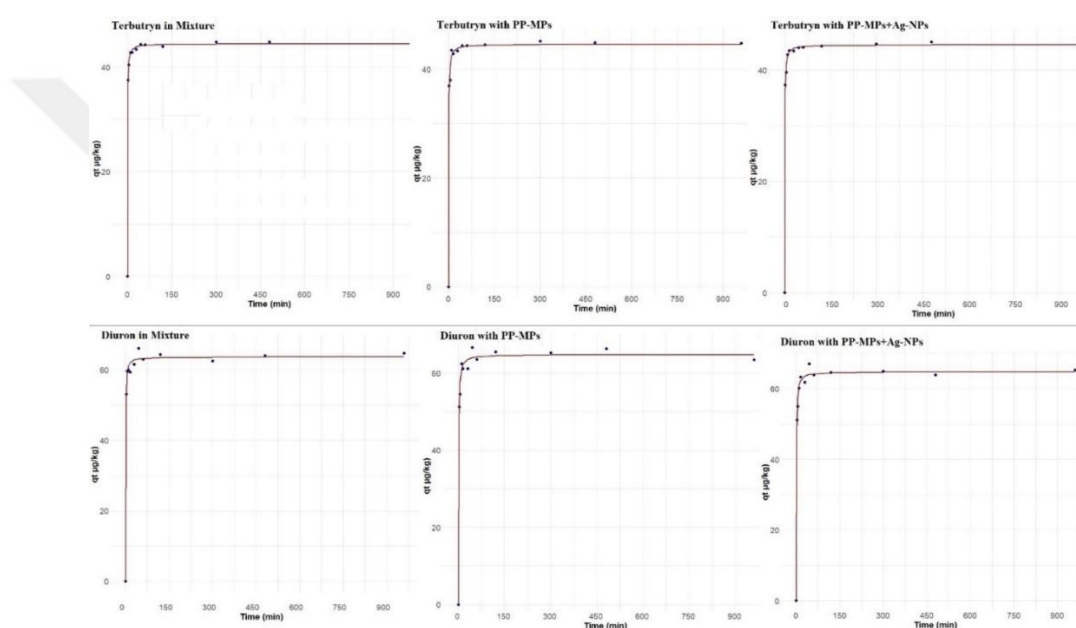


Figure 4.2: Non-linear second order rate fit of terbutryn and diuron with and without the presence of polypropylene microplastics (PP-MPs) and silver sulfide nanoparticles (Ag₂S-NP).

The adsorption rates of tested ECs as single compound on the surface of natural soil are not sufficiently reported in the literature, while the available values varied widely depending on the soil properties and reaction conditions which could be difficult to compare with our study. Nevertheless, as all the compounds in this study had a comparable adsorbed amount at equilibrium (q_e), the competitive relation among the studied compounds is expected to be limited. However, terbutryn and ciprofloxacin have recorded an equal decrease in their q_e value compared to other compounds. This result is also observed previously for ciprofloxacin that has recorded a decrease in its

adsorbed amount to soil when it was in a mixture with tetracycline [253]. This can be due to the relatively similar adsorption mechanisms of ciprofloxacin and terbutryn on the surface of natural soil compared to other compounds in the solution. For instance, the adsorption of terbutryn and ciprofloxacin was not significantly affected by the organic matter type and fraction of natural soil, rather, they were adsorbed to the soil in neutral or cationic forms which made the pH of the soil the most affective parameter in their adsorption rate [115], [355]. Therefore, the cation exchange capacity of the adsorbent soil is the key factor that could influence TER and CIP adsorption rate, Thus, a competitive relation between CIP and TER is expected to be created in the solution leading decreasing their adsorption amount at equilibrium.

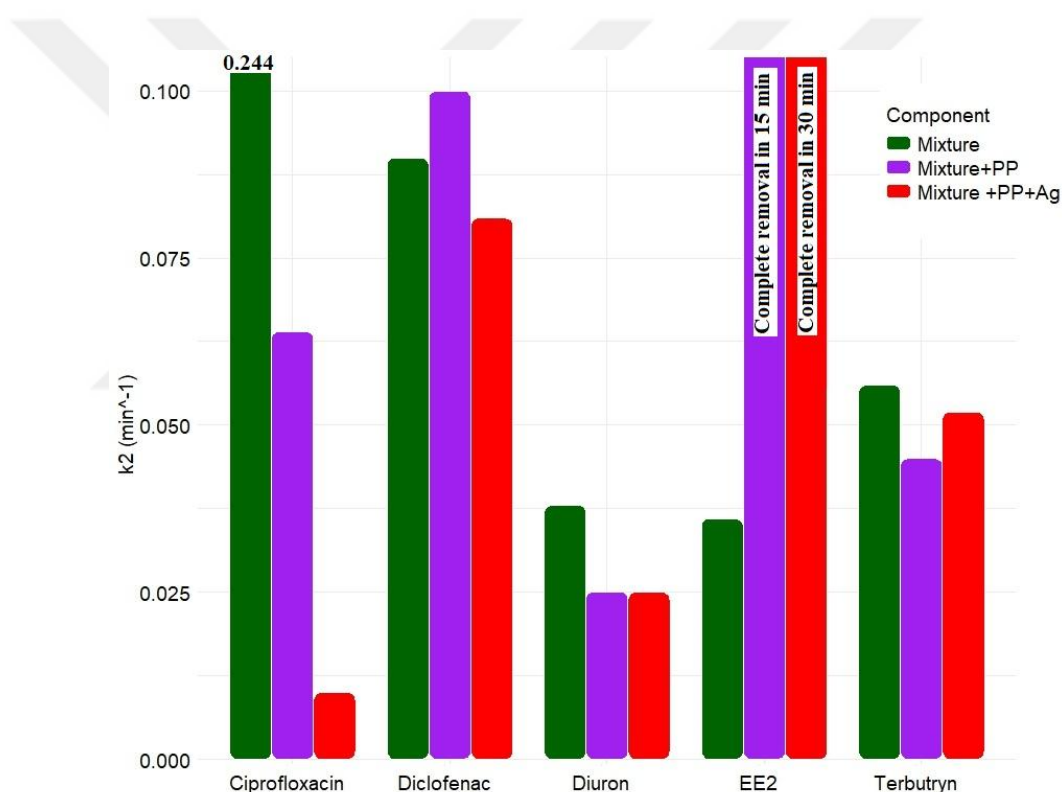


Figure 4.3: Adsorption rates of selected ECs in mixture, with PP-MPs and Ag₂S-NP.

As illustrated in **Table 4.2**, the presence of PP-MP had hugely inhibited the adsorption rate of ciprofloxacin (0.244 min⁻¹ to 0.064 min⁻¹), while the adsorption rates of diuron and terbutryn were slightly decreased due to the presence of PP-MPs. The potential of microplastics to reduce the adsorption of organic micropollutants when they co-exist in the same solution in natural soil was also observed in other studies such as [52], [53]. Microplastics might compete with other compounds for the easily available

adsorption sites on the surface of soils. In addition to the tendency of microplastics to interact with the hydrophobic compounds which might cause their desorption from the surface of soil, hence decreases the soil capability to retain the attached molecules. Although hydrophobic organic contaminants have a high tendency to get adsorbed to non-polar surfaces, including sediments and soil organic matter, however, it often has a greater affinity for plastic surfaces [356], [357].

Table 4.2: The second-order non-linear kinetic parameters for the tested ECs.

Compound	Component	k ₂ (min ⁻¹)	t _{1/2} (min)	q _e (µg/kg)	R ²
Diuron	Mixture	0.038	24.75	63.72	0.999
	Mixture + PP	0.0251	36.89	64.8	0.999
	Mixture + PP + Ag ₂ S-NP	0.025	36.95	64	0.999
Terbutryn	Mixture	0.056	24	44.46	1
	Mixture + PP	0.045	29.6	44.5	0.999
	Mixture + PP + Ag ₂ S-NP	0.052	25.8	44.55	0.999
Diclofenac	Mixture	0.09	10	66	0.999
	Mixture + PP	0.1	171	66.3	0.999
	Mixture + PP + Ag ₂ S-NP	0.081	211.6	65.82	0.999
Ciprofloxacin	Mixture	0.244	6.11	40.2	1
	Mixture + PP	0.064	23.6	39.5	1
	Mixture + PP + Ag	0.01	171	35	0.999
EE2	Mixture	0.036	17.3	94	0.999
	Mixture + PP	Complete removal in 30 min			
	Mixture + PP + Ag ₂ S-NP	Complete removal in 15 min			

However, the adsorption rate of EE2 was significantly increased in the presence of PP-MPs. EE2 was not detectable in the solution within 30 min of reaction with soil and PP-MP. On the contrary to the strong acidic nature of diclofenac, diuron, terbutryn and ciprofloxacin that are expected to be present in the solution in ionic forms (with pK_a values of 4.15, 3.7, 4.4 and 5.56 respectively) [79], [89], [108], [115], EE2 is a weak Lewis acid with pK_a of 10.33 [358], it exists in non-dissociation form at pH range of 4.8-9.1 [94], thus, the electrostatic attraction will not be effective for its interaction with MPs present in the solution. Therefore, the desorption of ECs from the surface of

natural soil that could occur due to the effect of electrostatic attraction with MPs, as observed with CIP, DIU, TER and DCF would not be valid in the case of EE2, which could justify the absence of decreasing effect in its adsorption rate in the presence of MPs compared to other compounds in the solution.

The addition of Ag₂S-NPs to the mixture and PP-MP had slightly decreased the adsorption rate of diclofenac, while it significantly inhibited the adsorption of ciprofloxacin. The adsorption of organic micropollutants onto the natural soil in the presence of Ag₂S-NP was not reported in the literature previously. Nevertheless, silver nanoparticles were found to be strongly retained on the surface of natural soil [359], thus it has the high potential to hamper the adsorption of other pollutants by occupying the soil's adsorption sites. However, the adsorption of EE2 was highly promoted with the addition of Ag₂S-NP with complete removal in 15 min of reaction. EE2 was found to have high tendency to be adsorbed on the surface of Ag₂S-NP [360]. Therefore, the presence of Ag₂S-NP which have a considerable affinity to attach to the surface of natural soil is expected to substantially increase the adsorption capacity of soil to EE2 by creating an additional binding mechanism with soil surface.

5. EFFECT OF CLIMATE CHANGE ON THE PHOTOLYSIS AND ADSORPTION OF EMERGING CONTAMINANTS

5.1. Introduction

The extreme climatic conditions due to the alteration in the temperature and organic matter content of surface water and natural soil can have a substantial influence on the fate and toxicity of ECs. Some studies have estimated the variation of temperature and organic matter in the natural environment due to human activities and climate change. A model study for a natural lake that is conducted by [54], have anticipated a significant modification in the mixing regimes of 635 lakes around the world that could result from the increase in the temperature of the lake surface water (2.5 °C- 5.5 °C) and the diminish of water ice cover with being permanently ice-free by the year 2080–2100, and subsequently affecting the distribution and OM concentration in the lake due to the disturbance and less frequently of mixing areas. Similarly, [55] have estimated an increase of 2°C to 4°C in the temperature of surface water by the year 2080 due to climate change effect under the anthropogenic medium emissions scenarios. In addition, the chemical properties of organic matter including its preservation and degradation patterns are altered in the natural lakes and rivers depending on the location, water column and sediments. For instance, [56] observed a decline in the OM concentration in a river stream by 60% and 70% after 160 m and 600 m respectively away from an effluent discharge point of a wastewater treatment plant. Furthermore, the temperature of high-latitude soils was found to be warmer than the ambient air during winter (up to 25°C), and cooler in summer (up to 10°C) at 0 cm to 15 cm soil depths [57]. Due to the positive offset between air and soil temperatures in cold environments, a declining of 17% was observed in the annual soil mean temperature in most of the cold environments. In addition, the land-use alteration is continuously modifying the amount and velocity of natural organic matter in agriculture soils. For example, the forest soils contained three times more of soil organic carbon compared to crop fields, and the fraction of particulate organic matter varied widely between plowing tillage, conservation tillage and the forest soil that had

recorded 8.24, 30.08 and 6.54 w/w per fraction, respectively [58]. Which indicates the significance of investigating various temperatures and organic matter concentrations on the fate of ECs in the terrestrial environment.

The previous studies have quantified the change in photolysis rate of ECs by examining the effect of one factor variation at a time (temperature or organic matter) [59]–[61], which could give a false estimation for their photodegradation rate in the natural environment. For instance, in a model study done by [62] for a number of ECs that were supported by actual lab experiments for comparison, most of the recorded photodegradation rates by the simulation was either underestimated or overestimated mainly due to not taking into account many of the probable indirect photodegradation pathways that could occur in the experimental solution. Furthermore, temperature alteration could influence the process of indirect photolysis in the presence of organic matter. For example, the kinetic reactions in the aquatic environment are influenced by the ambient temperature, and the rate of DOM decomposition in addition to the production of reactive species due to sunlight absorption by photosensitizers in surface water were found to be temperature dependent processes [63]. Furthermore, many studies have recorded a substantial variation in the concentration of monitored ECs depending on seasonal variations and sampling location sites such as [64], [65], which could indicate the strong influence of the combined interplay effect of temperature and organic matter on the fate of ECs in the natural environment. Moreover, the variation in temperature and organic matter could influence the interactions between ECs and other environmental components (micro/nano particles) which may substantially alter their ultimate environmental fate. For instance, the hydrophobic partitioning between the organic contaminants and the surface of micro/nano materials would determine their attachment or detachment in the ambient water [66]. However, [67] implied that the presence of dissolved organic matter (DOM) in the aqueous solution could disturb the interaction between the contaminants and MPs, which could inhibit the long-range transport of ECs by microplastics in natural surface water. In contrary, the attachment of some types of ECs (e.g. hormonal steroid compounds) to MPs could be enhanced by the presence of DOM due to the probable established complexations between MPs and DOM in the solution as reported by [68]. Therefore, the influence of the variation in the key environmental conditions (organic matter and temperature) with the presence of micro and nanoparticles that were not covered collectively in the previous

studies, must be evaluated for the fate and toxicity of ECs in the natural environment, in order to support the environmental risk assessment studies with accurate data obtained in environmentally relevant conditions. Thus, the objective of this study is to reveal the complex combined interaction of mixture, temperature and organic matter conditions, along with the presence of MPs and Ag₂SNPs in the surface water and soil matrices on the photodegradation, adsorption rates, and microbial toxicity of various types of ECs.

5.2. The Effect of Climate Change on the Photolysis of Emerging Contaminants

5.2.1. Experimental Setup

Previous researchers have identified organic matter as a significant participant in the photochemical degradation of hydrophobic organic ECs in surface waters [361]–[364]. Therefore, the effect of higher concentration of organic matter in the synthetic surface water on the photodegradation of the targeted compounds mixture was tested by adding three times higher amount of humic acid (19.5 mg/L) which corresponds to a concentration of around 13 mg/L of total organic matter content.

To study the influence of solution temperature, the photodegradation of selected compounds mixture was investigated in two different temperatures (25 °C and 35 °C) with distilled water and synthetic surface water matrices. The temperature was maintained during the experiment by adjusting the irradiated solution temperature using a cooler air pump system to reduce the sample temperature and a heater placed under the sample, while the sample temperature was monitored through the experiment time using a thermometer.

5.2.2. Results and Discussion

5.2.2.1. The Effect of Higher Organic Matter Concentration

Compared to the results of lower organic matter content (TOC: 4.5 mg/L, **Table 5.1**), the addition of higher OM concentration (TOC: 13 mg/L) has further enhanced the photodegradation rate of diuron (from no degradation in DW to a photolysis rate of

0.0072 min⁻¹ with low OM and 0.0514 min⁻¹ with high organic matter content). This confirms the positive effect of organic matter on the indirect photodegradation of diuron by the produced reactive species as a result of OM photodegradation in the tested solution. In addition, as seen previously in the surface water matrix with low amount of OM content which have prohibited the photolysis of terbutryn compared to distilled water, the photolysis rate of terbutryn was enhanced by the addition of higher amount of organic matter, from no degradation with low OM to 0.0002 min⁻¹ with higher organic matter, however, it is still significantly lower than the terbutryn photolysis rate in the absence of OM (0.0005 min⁻¹). Therefore, the effect of organic matter content is dependent on the counterbalance between the various OM photolysis inhibiting and promoting mechanisms such as the adsorption to OM, photo shielding effect which diminish the amount of light available for the photodegradation of the compound's presence in the sample, and the generation of reactive species that can enhance the photodegradation of compounds. The photolysis rate of EE2 had slightly decreased with the addition of the higher organic matter content (0.024 min⁻¹ to 0.022 min⁻¹) compared to the significant enhancement recorded in its photolysis rate from no degradation with DW to 0.024 min⁻¹ with the lower OM content. Therefore, OM can play a positive role in the photodegradation of EE2 if it does not exceed a certain concentration that might result in the decreasing effect (e.g light scattering) outweighing its increasing effect (indirect photolysis). This result is compatible with other studies that tested the photolysis of EE2 with different OM concentrations [31], [234].

Table 5.1: Photolysis rate constants and half life time for selected emerging compounds in the presence of low and high organic matter (OM).

Compound	Low OM		High OM	
	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)
Diclofenac	0.0108	64	0.0058	119
Diuron	0.0072	96	0.0514	13.48
Terbutryn	No degradation		0.0002	3465
EE2	0.0248	28	0.0222	31.2
Ciprofloxacin	0.0068	102	0.0063	110

The elevated temperature in distilled water matrix had a substantially increasing effect on the photodegradation rate of diclofenac, terbutryn, and EE2 and a moderate increase in the photolysis rate of ciprofloxacin **Table 5.2**. The amplified effect of higher

temperature for the photodegradation rate of organic compounds is also reported in other studies such as [365]–[369]. The accelerating influence of the temperature on the rate of chemical reactions is well known, as the kinetic energy of the organic pollutant molecules increases with increasing temperature [370]. Therefore, rising the temperature of the irradiated solution is expected to increase the photodegradation efficiency of the targeted compounds. However, increasing the temperature from 25 °C to 35 °C in the surface water matrix had hampered the photolysis rate of all the targeted compounds especially for diuron and EE2 from a half-life of 96 min and 28 min with 25 °C respectively to a half-life of 2310 min for diuron and 169 min for EE2 at 35 °C, which reflect the inhibition effect of higher temperature on the photolysis rate of the selected organic ECs in surface water. As discussed in the previous report (with low OM content), the organic matter had recorded a substantial promoting impact on the photolysis rate for most of the selected analytes, specifically for diuron and EE2.

Table 5.2: Photolysis rate and half life time for selected emerging compounds in the mixture in the low and high temperature.

Compound	SW (25 °C)		SW (35 °C)		DW (25 °C)		DW (35 °C)	
	k1 (min ⁻¹)	t _{1/2} (min)	k1 (min ⁻¹)	t _{1/2} (min)	k1 (min ⁻¹)	t _{1/2} (min)	k1 (min ⁻¹)	t _{1/2} (min)
Diclofenac	0.0108	64	0.0064	108	0.0012	577	0.0023	301
Diuron	0.0072	96	0.0003	2310	No degradation		No degradation	
Terbutryn	No degradation		No degradation		0.0005	1386	0.0115	60
EE2	0.0248	28	0.0041	169	No degradation		0.0515	13
Ciprofloxacin	0.0068	102	0.0033	210	0.0159	43.6	0.0168	41

The humic acid which is used in this study for the synthetic surface water is a substantial constituent of natural organic matter, accounts for approximately 90% of the total organic carbon (TOC) and contain abundant olefins C = C aromatic structures [371]. The irradiation of organic matter results in the formation of the dissolved inorganic carbon (DCF) which is found to increase the photolysis pseudo-first order rate constants of the organic ECs due to the formation of some reactive species such as •CO₃⁻ [25], [372]. The previous studies had shown the strong dependency of the photochemical transformation of organic matter on the temperature of the solution. The direct transformation of dissolved organic carbon (DOM) to DCF that result from

the light absorption by the olefins double bonds in DOM is found to be optimum at low temperatures (15 °C – 25 °C) [373], [374]. Thus, the indirect photodegradation pathway in the presence of organic matter in the solution is expected to be maximum at lower temperatures, which could justify the significant inhibition of diuron and EE2 photolysis rate in surface water matrix at high temperature as recorded in this study. Therefore, the temperature alone can contribute only to a certain extent in speeding up the photolysis reaction rate, and the maximum photodegradation rate of any compound is not always acquired at higher temperatures, while it depends primarily on other factors such as the water components (e.g. Chloride, humic acid, phosphate and nitrate) and the dominant photodegradation pathway for each compound.

5.2.2.2. Effect of Temperature with High and Low Organic Matter Concentrations.

As it was observed for the media with low organic matter concentration in Section 5.1.2.1, increasing the temperature with higher concentration of organic matter had the similar decreasing impact for the photolysis rate of DCF, diuron and ciprofloxacin, which emphasize on the importance of the photodegradation of OM at lower temperatures that substantially contribute to the indirect photolysis pathway of organic ECs (**Table 5.3**). However, in the opposite to the rest of compounds in the mixture, terbutryn had recorded an increase in its photolysis rate with elevated temperature in HOM concentration with a half-life of 3465 min at 35 °C and 577 min at 25 °C. As seen from the results in Section 5.1.2.1, the anticipated adsorption of terbutryn to the low concentration of OM presence in the SSW by its C-S bond have totally hindered its photolysis rate (1386 min in DW to no degradation), while a higher concentration of OM had decreased the photolysis rate of terbutryn to a certain extent from 1386 min in DW to 3465 min with HOM. Therefore, after a specific amount of OM, the fraction of adsorbed terbutryn to OM can reach equilibrium and the excess amount of OM could serve for the indirect photolysis of terbutryn that could justify the slight decrease in its photolysis rate with HOM compared to DW after the total prohibition with LOM, which indicate the domination influence of adsorption to OM in determining the photolysis rate of terbutryn over the indirect photolysis. Previous studies have partitioned the adsorption process into high-affinity reactions that would be regulated by the equilibrium thermodynamics, and low affinity reactions that is controlled by diffusion [375]. Terbutryn is known to have high-affinity to adsorb to natural organic

matter [376], hence the equilibrium thermodynamics would control its adsorption to OM. Since the desorption process of organic ECs onto the surface of natural organic matter is endothermic in nature [377], the desorption of terbutryn from the natural organic matter is expected to increase at higher temperature, while it is also was found to have higher mobilization in rivers at summer times due to elevated water temperatures [378]. Therefore, the increasing temperature with HOM concertation is expected to cause desorption of terbutryn from the OM and increase its mobilization in the irradiated solution, hence increasing its photolysis rate.

Table 5.3: Photolysis rate and half-life for selected ECs in the mixture at low and high temperature in the presence of low and high organic matter.

Compound	LOM (25 °C)		LOM (35 °C)		HOM (25 °C)		HOM (35 °C)	
	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)
Diclofenac	0.0108	64	0.0064	108	0.0058	119	0.0051	135.8
Diuron	0.0072	96	0.0003	2310	0.0514	13.48	N.D	
Terbutryn	N.D		N.D		0.0002	3465	0.0012	577
EE2	0.0248	28	0.0041	169	0.0222	31.2	0.0303	22.8
Ciprofloxacin	0.0068	102	0.0033	210	0.0063	110	0.0026	266

5.2.2.3. Effect of Higher Organic Matter with PP-MPs and Ag₂SNP

The photodegradation of ciprofloxacin, diclofenac, and EE2 was best described by a pseudo-first-order model (**Figure 5.1**). The effect of higher organic matter content (13 mg/L) in the presence of PP-MPs and Ag₂SNP was also investigated. In contrary to the effect of the presence of PP-MPs and Ag₂S-NP (Section 3.1.7) in which it significantly declined the photolysis rate of ciprofloxacin and EE2 due to the probable attachment between these particles and the tested ECs, the addition of higher OM concentration in the presence of PP-MPs and Ag₂S-NP have promoted the photodegradation rate of these two compounds in the solution (**Table 5.4**).

The organic matter has a crucial role as photosensitizer for the indirect photo-transformation of ECs by the generation of reactive species, which could justify the general enhancement in EE2, terbutryn and ciprofloxacin photolysis rate as we saw previously with low OM content.

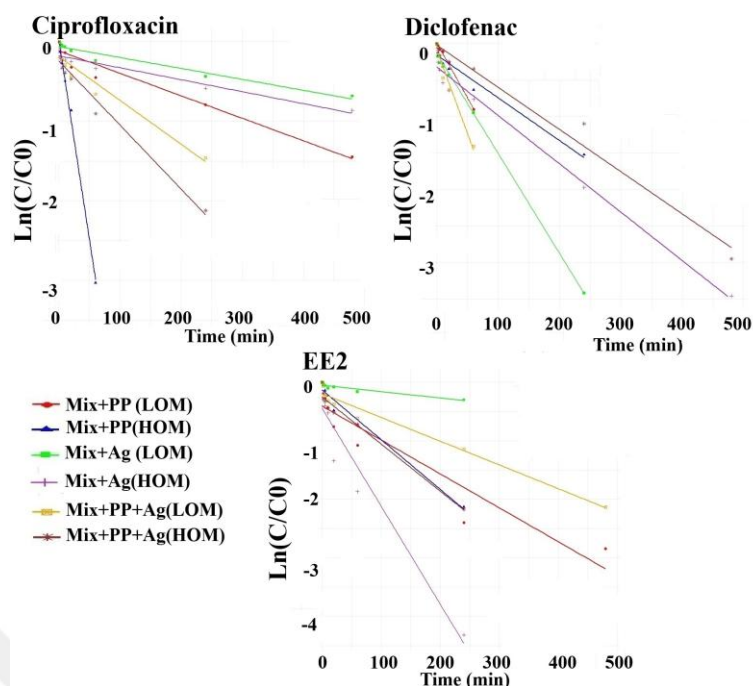


Figure 5.1: Pseudo-first-order kinetic model for ciprofloxacin, diclofenac, and EE2 in a mixture (with diuron and terbutryn), with polypropylene microplastic (PP-MPs). and silver sulfide nanoparticles (Ag₂S-NPs) in synthetic surface water matrix at low and high organic matter concentrations (4.5 mg/L and 13 mg/L).

Table 5.4: The photolysis rate and half-lives of targeted ECs in the presence of PP-MPs and Ag₂S-NPs at various organic matter concentrations.

Compound	PP-MPs (LOM)		PP-MPs (HOM)		Ag ₂ SNP (LOM)		Ag ₂ SNP (HOM)		PP-MPs and Ag ₂ SNP (LOM)		PP-MPs and Ag ₂ SNP (HOM)	
	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)
DCF	0.0151	42	0.0059	154	0.0137	50.5	0.0066	105	0.0233	30	0.0077	40
Diuron	N.D		N.D		N.D		N.D		N.D		N.D	
Terbutryn	0.0012	577	0.0043	161	N.D		N.D		N.D		0.0011	630
EE2	0.0047	147	0.0085	81.5	0.0061	113	0.1749	3.9	0.0077	90	0.004	173
CIP	0.0028	247.5	0.0051	13.8	0.0014	495	0.0015	462	0.0031	231	0.0081	85.5

Moreover, the DOM in aqueous solution was found to have the potential to alter the sorption of ECs on the surface of MPs via complex interactions [379]. In addition, OM can change the surface morphology and functional groups of MPs leading to new adsorption characteristics [380], [381]. Due to its non-specific functional groups, PP-MPs are well defined as non-polar polymers that interact with organic compounds via hydrophobic interactions [382]. The reactive species that are generated from the absorption of sunlight by the natural OM (especially $^1O_2$) are found to enhance the oxygen-containing functional groups on the surface of MPs (e.g. carbonyl groups), subsequently decreasing their hydrophobicity [383]–[385]. Therefore, the organic contaminants that are attached to MPs dominantly via the hydrophobic interactions (e.g. EE2, and ciprofloxacin) [386], [387] are expected to desorb from the surface of MPs in the presence of irradiated OM, that will make them more available for degradation by sunlight. Furthermore, natural OM was found to interact with Ag₂S-NP forming a coat of organic molecules on its surface [388], [389]. This behavior of OM is expected to decrease the inherent scattering effect of light by the surface of Ag₂S-NP which is discussed in Section 3.1.7. Thus, the ECs in the solution will be exposed to higher amount of sunlight that will increase their direct photodegradation rate.

However, the addition of OM in the presence of PP-MPs and Ag₂SNP had decreased the photolysis rate of Diclofenac (**Figure 5.2**), while the addition of these particles (Section 3.1.7) in fixed OM concentration had promoted the photolysis rate of diclofenac. The chemical structure of NSAIDs including Diclofenac is characterized with the presence of the carboxylic acid functional group (COOH), which is anticipated to cause an electrostatic repulsion between MPs and NSAIDs at neutral pH [390], [391], thus, having low affinity to be attached on the surface of PP-MPs, and the addition of OM concentration in the presence of PP-MPs is not expected to have the same increasing photodegradation rate due to reducing the interactions with PP-MPs as in the case of EE2 and ciprofloxacin with LOM. Although increase in OM slightly decreases the photodegradation of diuron in the presence of PP-MPs or Ag₂SNP, diuron becomes highly persistent to photodegradation in the presence of PP-MPs or Ag₂SNP (see Section 3.2.3).

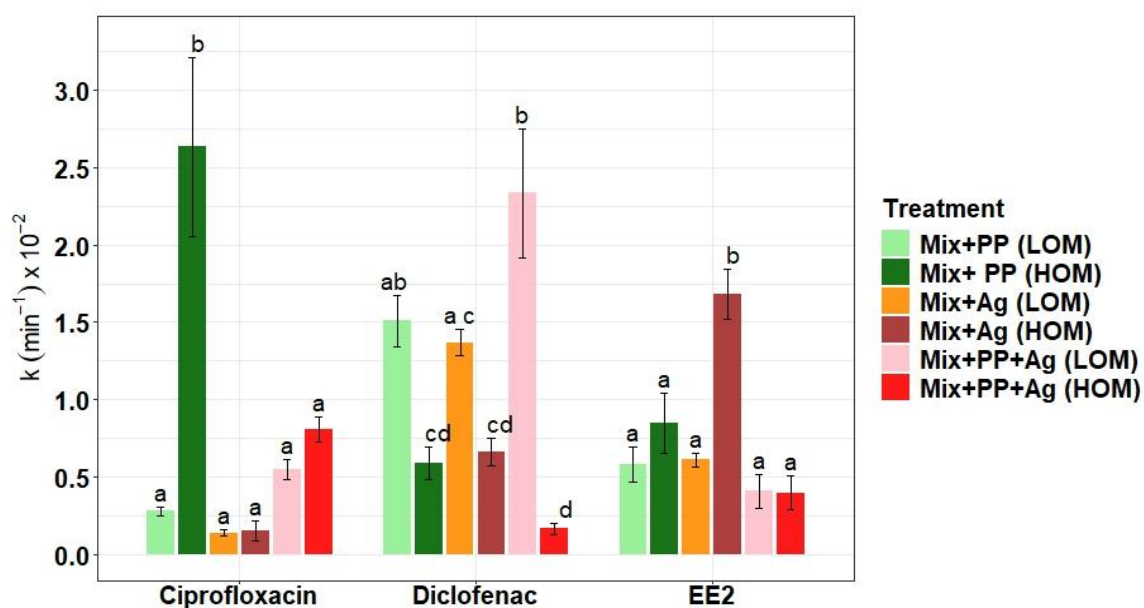


Figure 5.2: Photolysis rates constants for ciprofloxacin, diclofenac, EE2 in a mixture (with diuron and terbutryn), with polypropylene microplastic (PP-MPs) and silver sulphide nanoparticles (Ag_2S -NPs) in synthetic surface water matrix at low and high organic matter concentrations (4.5 mg/L and 13 mg/L). Error bars represent standard errors of the mean, and different letters above the bars indicate significant differences between treatments ($p < 0.05$).

5.2.2.4. Effect of Higher Temperature with PP-MPs and Ag_2SNPs

The photodegradation of all compounds was best described by a pseudo-first-order kinetic model (**Figure 5.3**). The elevated temperature in the synthetic surface water matrix with LOM concentration in the presence of PP-MPs had hindered the photolysis rate of ECs except EE2 under all conditions and ciprofloxacin in the presence of Ag_2SNPs at low OM. The presence of OM in the solution can serve as an indirect photolysis agent by the generation of reactive species by sunlight absorption such as triplet DOM^* and $\bullet\text{OH}$ which could significantly enhance the degradation of targeted ECs [337]. The absorption of irradiance by natural OM leads to the formation of dissolved inorganic carbon (DCF), which play a dominant role in accelerating the pseudo-first order rate constants of organic contaminants by the formation of reactive species (e.g. $\bullet\text{CO}_3^-$) [25], [372]. The direct photochemical transformation of DOM to DCF have been found to be strongly dependent on the temperature of water, and the maximum transformation rate was recorded at low temperature values of 15 $^{\circ}\text{C}$ – 25 $^{\circ}\text{C}$ [373], [374]. Therefore, the indirect photolysis pathway in the presence of OM is

anticipated to be optimum at lower temperatures, that could explain the decline in the photolysis rate at higher temperatures. Similar results were observed for the presence of Ag₂SNP except for ciprofloxacin in the case of Ag₂SNP alone and in a mixture with PP-MPs at low OM (Table 5.5).

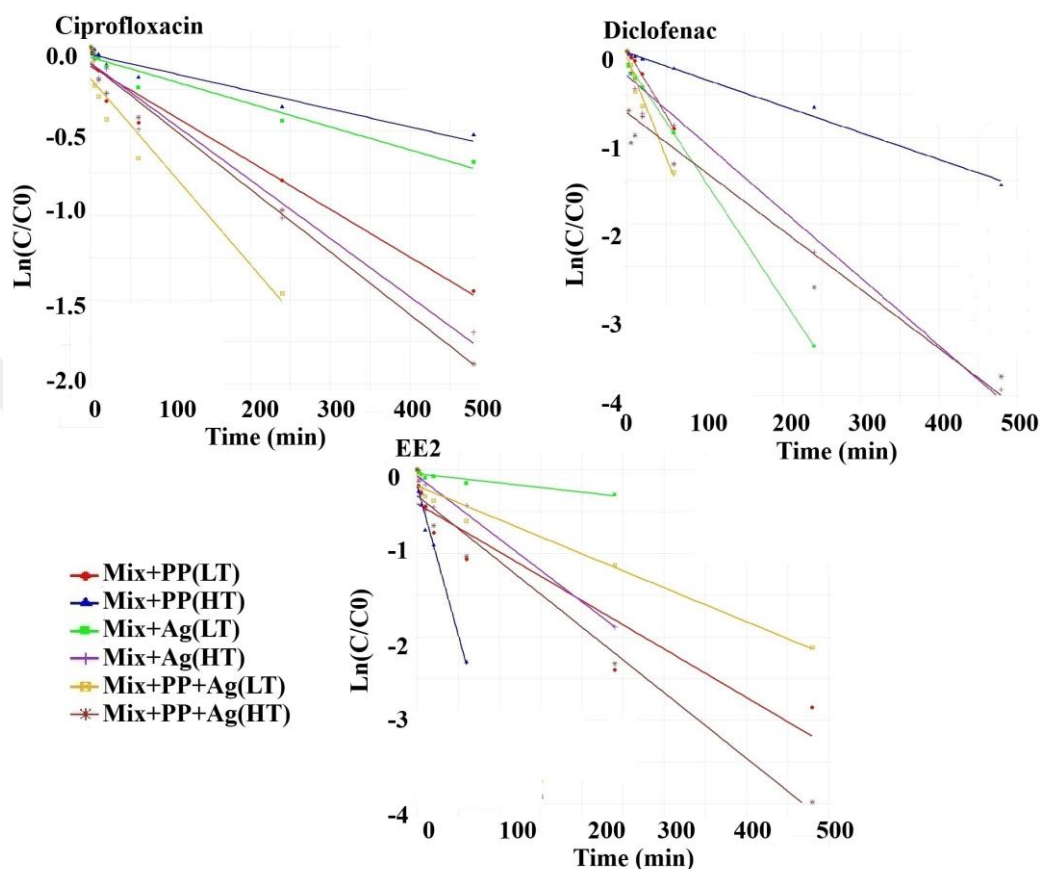


Figure 5.3: Pseudo-first-order kinetic model of ciprofloxacin, diclofenac, and EE2 in a mixture (with diuron and terbutryn), with polypropylene microplastic (PP-MPs) and silver sulfide nanoparticles (Ag₂S-NPs) in synthetic surface water matrix at low and high temperatures (25 °C and 35 °C).

As observed in Section 5.2.2.1 of this study, that is also in accordance with other studies in the literature such as [21], [237], the addition of higher OM concentration in the synthetic surface water matrix had recorded negligible or slight decrease in its photodegradation rate of ciprofloxacin. Therefore, the indirect degradation by photo-generated reactive species by OM is not affective in degrading ciprofloxacin, thus, the change in the solution temperature in the presence of OM is not expected to add a significant change in its degradation as observed in this study, while the dominant

effect will be for its interaction with the present PP-MPs and Ag₂SNP by various mechanisms at multiple temperatures as will be illustrated in the following discussion.

Table 5.5: The photolysis rate and half-lives of studied ECs in the presence of PP-MPs and Ag₂SNP at various temperatures.

Compound	PP-MP (25 °C)		PP-MP (35 °C)		Ag ₂ SNP (25 °C)		Ag ₂ SNP (35 °C)		PP-MP and Ag ₂ SNP (25 °C)		PP-MP and Ag ₂ SNP (35 °C)	
	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)	k ₁ (min ⁻¹)	t _{1/2} (min)
Diclofenac	0.0151	42	0.0031	223	0.0137	50.5	0.0078	81	0.0233	30	0.0068	101.9
Diuron	N.D		N.D		N.D		N.D		N.D		N.D	
Terbutryn	N.D		N.D		N.D		N.D		N.D		0.0015	462
EE2	0.0058	119	0.0357	19.4	0.0061	113	0.0075	92	0.0029	238	0.0079	87.7
Ciprofloxacin	0.0028	247.5	0.0011	630	0.0014	495	0.003	231	0.0055	116	0.0037	187

According to the previous observation in this study (Section 3.2.3), the presence of PP-MPs and Ag₂SNP is expected to substantially reduce the photolysis rate of the studied contaminants which resulted possibly from light scattering and the affinity of particles to adsorb the organic micropollutants by various mechanisms such as electrostatic interactions, Van der Waals forces, hydrogen bonding [52], making the contaminants less available for direct photodegradation by sunlight. Temperature can strongly influence the interaction of particles with existing organic micropollutants, the thermodynamic studies in the temperature range of 15 °C – 35 °C have demonstrated that the adsorption of organic micropollutants on the surface of micro and nanoparticles are spontaneous and endothermic processes [392]–[394], therefore, increasing the temperature is expected to favor the adsorption of targeted contaminants on the presence PP-MPs and Ag₂SNP which will result in decreasing its photodegradation rate. Moreover, electrostatic interactions are one of the most

common mechanisms for the affinity of certain particles to attach organic molecules [395]. The ionization of MPs is found to get promoted by high temperature [396] which increase its adsorption efficiency, and subsequently hindered the photolysis rate of adsorbed compounds as in the case of diclofenac, diuron, terbutryn and ciprofloxacin. However, increasing temperature in the presence of PP-MPs and Ag₂SNP had accelerated the photolysis rate of EE2 from 0.0047 min⁻¹ to 0.0357 min⁻¹ with PP-MP, 0.0061 min⁻¹ to 0.0075 min⁻¹ with Ag₂SNP, and 0.0077 min⁻¹ to 0.0079 min⁻¹ with PP-MP and Ag₂SNP (**Figure 5.4**).

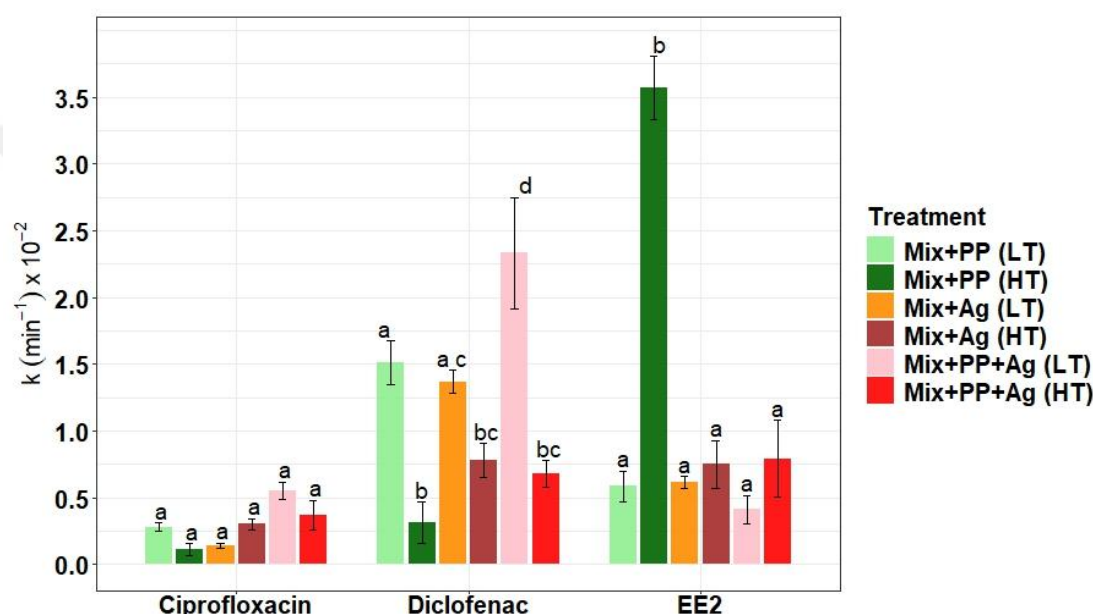


Figure 5.4: Photolysis rates constants of ciprofloxacin, diclofenac, and EE2 in a mixture (with diuron and terbutryn), with polypropylene microplastic (PP-MPs) and silver sulfide nanoparticles (Ag₂S-NPs) in synthetic surface water matrix at low and high temperatures (25 °C and 35 °C). Error bars represent standard errors of the mean, and different letters above the bars indicate significant differences between treatments ($p < 0.05$).

On the contrary to the strong acidic nature of diclofenac, diuron, terbutryn and ciprofloxacin that are expected to be present in the solution in ionic forms (with pKa values of 4.15, 3.7, 4.4 and 5.56 respectively) [79], [89], [108], [115], EE2 is a weak Lewis acid with pKa of 10.33 [358], it exists in non-dissociation form at pH range of 4.8-9.1 [94], thus, the electrostatic attraction will not be effective for its adsorption to the particles present in the solution, while the Van der Waals forces would be the dominant mechanisms for EE2 attachment to these particles. As rising temperature

increase the kinetic energies and instability of molecules, which reduce the effect of intermolecular forces of attraction [397], thus, the strength of Van der Waals adhesive forces to bring different molecules together are anticipated to decrease with higher temperatures. Therefore, the compounds that are not at the ionic form to create electrostatic interaction with the present micro and nanoparticles will depend mainly on Van der Waals mechanism, and subsequently their adsorption to PP-MPs and Ag₂SNP is expected to be lower at higher temperature, which will make them more available for photodegradation by light. Hence, varying temperature in the presence of various particles in the irradiated solution can have multiple outcomes on the photolysis rate of existing contaminants depending on the physicochemical properties of the compounds, the presence of water photosensitizers (e.g. organic matter), and the possible interaction mechanisms that could be established between the ECs and the coexisting particles in the aqueous solution. In the presence of both PP-MPs and Ag₂SNP, the results were similar to the effect of Ag₂SNP, photodegradation rates were decreased except for EE2 and ciprofloxacin (**Figure 5.5**). The percentage removal of all compounds at different treatments and time points in presented in **Figure 5.6**

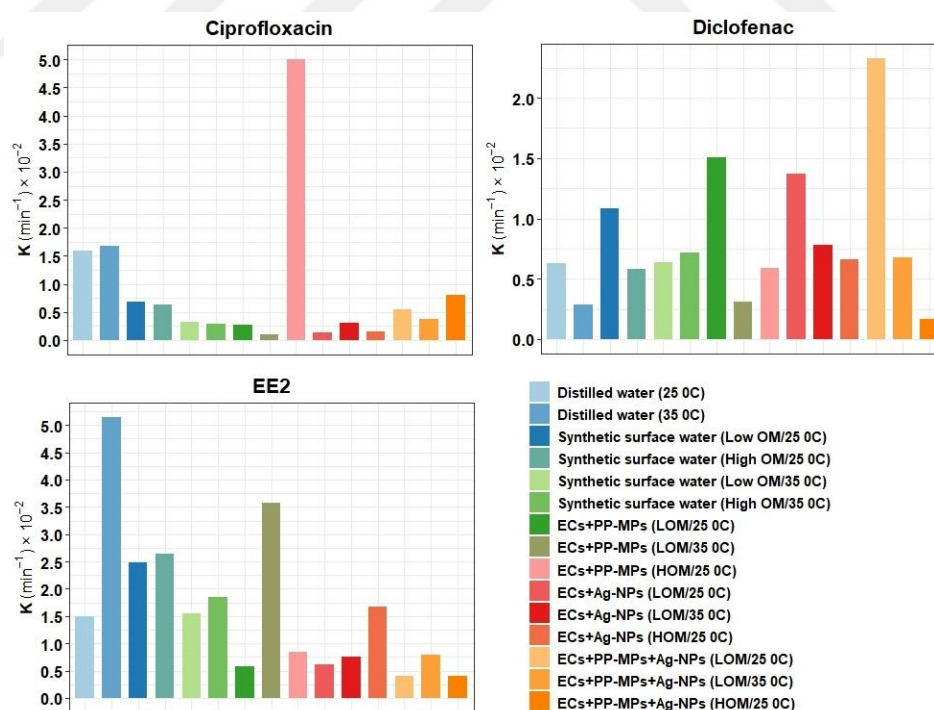


Figure 5.5: Photolysis rates constants of ciprofloxacin, diclofenac, and EE2 in a mixture (ECs) (with diuron and terbutryn), with polypropylene microplastic (PP-MPs) and silver sulfide nanoparticles (Ag₂S-NPs) in synthetic surface water matrix at low and high temperatures (25 °C and 35 °C), and with low and high TOC content (4.5 and 13.5 mg/L).

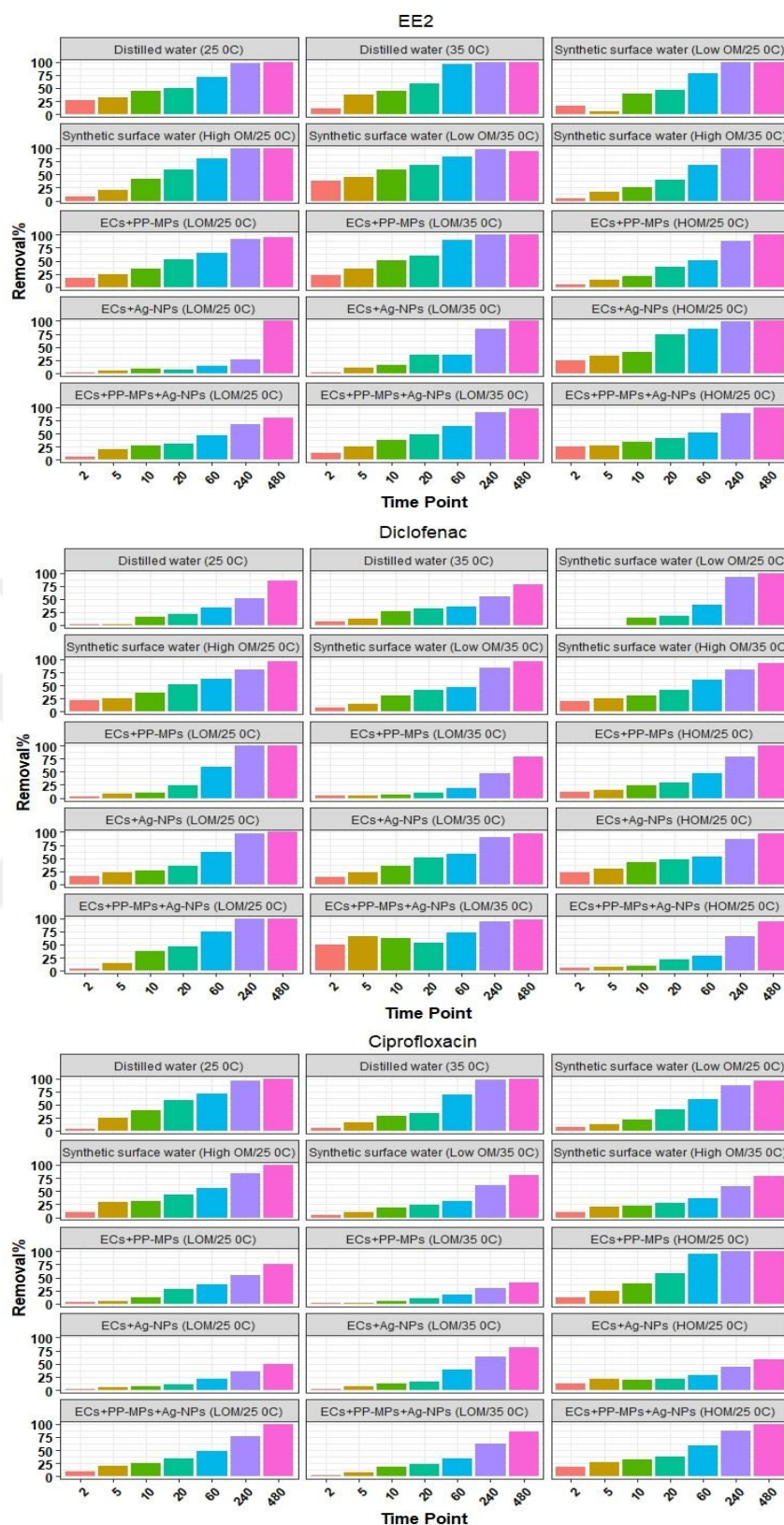


Figure 5.6: Removal rate percentage for ciprofloxacin, diclofenac, and EE2 in a mixture (ECs) (with diuron and terbutryn), with polypropylene microplastic (PP-MPs) and silver sulfide nanoparticles (Ag₂S-NPs) in synthetic surface water matrix at low and high temperatures (25 °C and 35 °C), and with low and high TOC content (4.5 and 13.5 mg/L).

5.3. The Effect of Climate Change on the Adsorption of Emerging Contaminants.

5.3.1. Experimental Setup

The effect of extreme climatic conditions on the adsorption behavior of ECs to the surface of natural soil was examined at higher temperature (35 °C) and soil organic matter content (TOC increased by 10%). The temperature was maintained by using a closed shaker with temperature system, while the soil TOC concentration was adjusted by the addition of biosolid. The experiments were conducted with and without the presence of PP-MPs and Ag₂SNPs, at similar concentrations used in Section 3.7.1.

5.3.2. Results and Discussion

5.3.2.1. Effect of Higher Temperature

As observed from the comparison between the adsorption rate of selected compounds at low and high temperatures (**Table 5.6**), the higher temperature had dramatically accelerated the adsorption rates of diuron, terbutryn and diclofenac by 2, 3 and 5 folds respectively, in addition to increasing the adsorption of EE2 which could not be detected in the solution after 2 min of reaction. As observed in the previous studies, the relation between temperature variation and the adsorption of organic micropollutants on the surface of natural soil is not consistent, it can be affected by multiple factors including the type of adsorption (physical or chemical), the soil and contaminants properties, and the thermodynamic nature of reaction which can predict the final state of contaminants in natural soil, in addition to the predominant adsorption mechanism i.e molecular interaction between contaminants and soil surface [398]. For instance, some studies recorded increase in adsorption rate of micropollutants with natural soil when the thermodynamic analysis revealed a spontaneous and endothermic adsorption process. Whereas other studies have concluded that physical adsorption also favor the elevated temperatures, as they recorded a variation in soil pore volume with higher temperatures which could increase the available sites for adsorption, consequently, promote the adsorption of contaminants which physical adsorption to soil is their dominant mechanism. This could be the justification for the remarkable increase in the adsorption rates of diclofenac, terbutryn and EE2 with higher

temperature. However, the high temperature had significantly decreased the adsorption rate of ciprofloxacin by 8 folds. The adsorption process of ciprofloxacin to the surface of natural soil was found to be a spontaneous exothermic process [399]. The thermodynamic analysis showed that contaminants which had an exothermic adsorption process with chemisorption (e.g. hydrogen bonding or ligand-exchange interactions) being the predominant binding mechanism with natural soil, have recorded a significant decrease in their adsorption rates with higher temperatures [400]. Moreover, the prohibition effect of high temperature to the adsorption of organic contaminants was found to increase with increasing the compound molecular weight [401]. Ciprofloxacin has the highest molecular weight among the tested compounds (331.34 g/mol), compared to 233, 242, 296.4, and 296 g/mol for diuron, terbutryn, EE2 and diclofenac respectively. Therefore, due to the exothermic adsorption process of CIP and its high molecular weight, its adsorption rate to the natural soil is anticipated to remarkably decrease with higher temperature.

Table 5.6: The second-order non-linear kinetic parameters for the tested ECs at high temperature (35 °C).

Compound	Component	k2 (min ⁻¹)	t _{1/2} (min)	q _e (µg/kg)	R ²
Diuron	Mixture	0.09	10.07	66.2	0.999
	Mixture + PP	0.1	9.17	65	0.999
	Mixture + PP + Ag2S-NP g	0.09	10.17	65.5	0.999
Terbutryn	Mixture	0.183	7.43	43.97	1
	Mixture + PP	0.274	4.99	43.83	1
	Mixture + PP + Ag2S-NP	0.24	5.72	43.62	1
Diclofenac	Mixture	0.5	1.88	63.79	0.999
	Mixture + PP	3.5	0.263	65.13	0.999
	Mixture + PP + Ag2S-NP	2	0.47	63.78	0.999
Ciprofloxacin	Mixture	0.03	50.8	39.36	0.999
	Mixture + PP	0.09	20.83	32	0.999
	Mixture + PP + Ag2S-NP	0.022	72.04	37.5	0.999

The presence of PP-MP as single component and in a mixture with Ag2S-NP at high temperature had further accelerated the adsorption rate of all the tested compounds (**Figure 5.7**). Which is in contrary to the results observed at low temperature, where the presence of PP-MP and Ag2S-NP had mostly a decreasing effect on the adsorption

rate of co-existing ECs in the solution (Section 4.3.2). The interaction mechanism of chemical contaminants and microplastics is more complicated in the matrix of natural soil compared to the aquatic matrix, which could be mainly due to the competitive relation between soil particles and MPs for the adsorption of organic contaminants molecules, in addition to other factors such as soil texture, physical properties, organic matter, ambient temperature, and pH [402]. Temperature can strongly influence the interaction of MPs with existing organic micropollutants, the thermodynamic studies in the temperature range of 15 °C – 35 °C have demonstrated that the adsorption of organic micropollutants on the surface of micro and nanoparticles are spontaneous and endothermic processes [392]–[394], therefore, increasing the temperature is expected to favor the adsorption of targeted contaminants on the PP-MPs and Ag₂SNP present in soil.

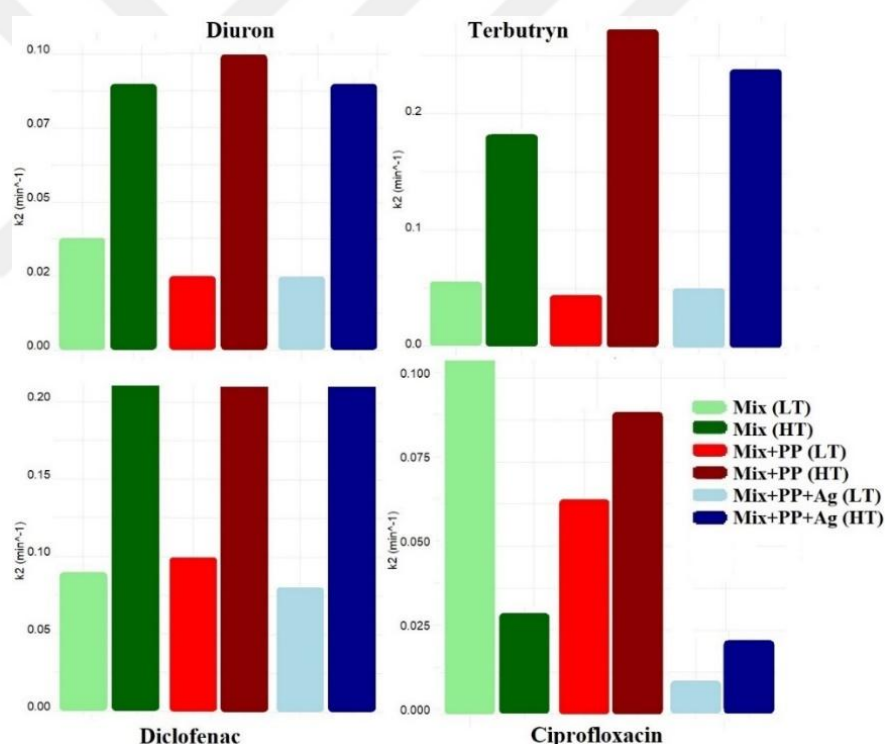


Figure 5.7: Adsorption rate diuron, terbutryn, diclofenac and ciprofloxacin at high and low temperatures (25 °C and 35 °C) with and without the presence of polypropylene microplastics (PP), silver sulfide nanoparticles (Ag₂S-NP) and their combination (PP+ Ag₂S-NP).

Moreover, electrostatic interactions are one of the most common mechanisms for the affinity of certain particles (e.g. MPs) to attach organic molecules [395]. The electrostatic and hydrophobic interactions were found to be the main adsorption

mechanism between natural soil and microplastics [403]. As the ionization of MPs was found to get promoted by high temperature [396], thus the higher ambient temperature is expected to increase the adsorption efficiency of MPs towards both the organic contaminants and the charged surface of natural soil. Therefore, MPs can play a major role in increasing the soil surface area and establishing additional binding sites on the surface of soil at higher temperature, that would facilitate the attachment of organic contaminants and increase their adsorbed amount as observed in this study.

5.3.2.2. Effect of Higher Organic Matter

For diuron and terbutryn, the adsorption kinetics were well described by the pseudo second-order non-linear model (**Figure 5.8**), which provided consistent and reasonable rate constants. In contrast, diclofenac did not follow the pseudo second-order kinetic model when organic matter content was high. Instead, its adsorption was better represented by a biphasic kinetic model. Such behavior indicates that diclofenac adsorption under these conditions cannot be described by a single homogeneous process but rather involves at least two distinct phases: a fast initial sorption to readily available surface sites, followed by a slower phase associated with diffusion into less accessible domains of soil organic matter. The adsorption of diclofenac under low organic matter content have fitted well with the pseudo second-order non-linear kinetic model suggesting that in this case adsorption is dominated by more homogeneous interactions, likely controlled by electrostatic attraction to mineral surfaces. While the non-linear second-order model does not capture the complexity of diclofenac adsorption under high organic matter conditions, where biphasic kinetics provide a more appropriate description.

The adsorption behavior of the tested ECs varied depending on the soil organic matter content and the presence of microplastics and nanoparticles (**Figure 5.9**). EE2 and ciprofloxacin were completely removed from solution in soils with higher organic matter in all of the treatments. This can be explained by the strong affinity of EE2 for hydrophobic domains of soil organic matter, as reported by [404] and [405]. Furthermore, the complexations with organic matter tends to enhance the adsorption of ciprofloxacin [355], [406]. In contrast, the adsorption of diuron and terbutryn was not influenced by organic matter in the ECs mixture alone in addition to the treatments with only PP-MPs. This suggests that microplastics alone do not significantly alter the

partitioning of moderately hydrophobic herbicides, consistent with studies showing limited effects of microplastics in the absence of other modifying agents [407].

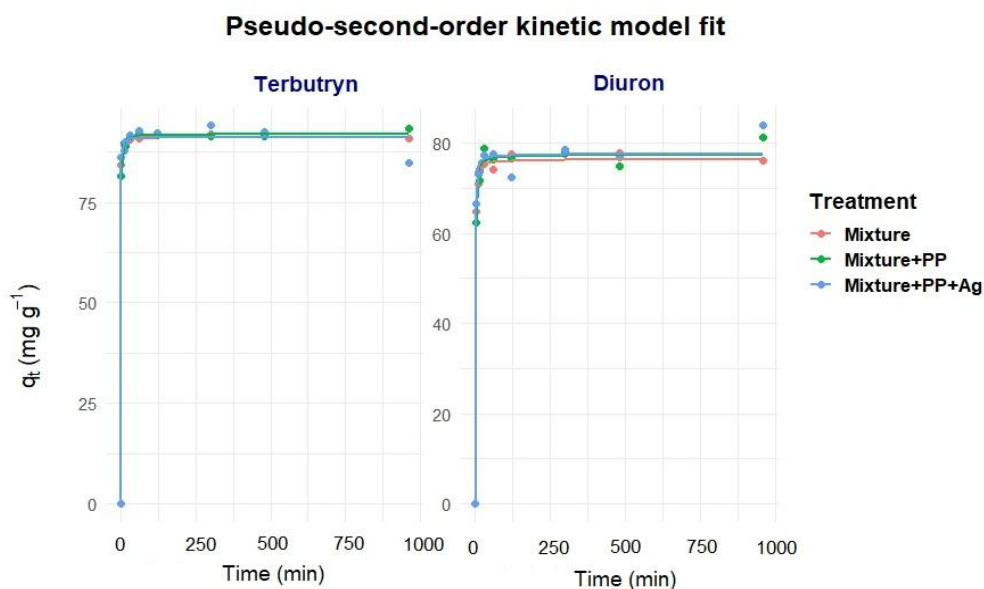


Figure 5.8: Pseudo second-order non-linear kinetic model for terbutryn and diuron at three different treatments at high organic matter content and low temperature (25 °C).

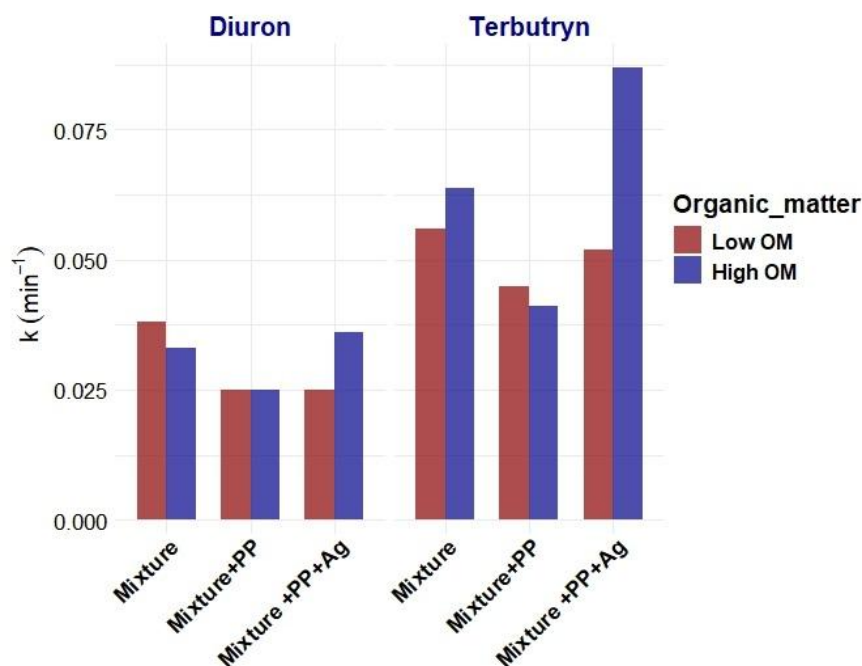


Figure 5.9: Adsorption rate constants for terbutryn and diuron at three different treatments at high organic matter content and low temperature (25 °C).

However, when both PP-MPs and Ag₂SNPs were present, the adsorption of ECs increased in soils with higher organic matter. This indicates a combined effect in which organic matter provides sorption domains, while microplastics act as additional hydrophobic surfaces, and silver nanoparticles alter soil surface reactivity and organic matter conformation. The synergistic effect of microplastics and silver sulphide nanoparticles is consistent with reports that nanoparticles can modify contaminant-soil interactions by changing organic matter binding capacity and providing reactive surfaces [408]. Together these findings suggest that adsorption of moderately hydrophobic herbicides such as diuron and terbutryn depends not only on soil organic matter but also on interactions between organic matter and coexisting particles in the soil. The obtained adsorption kinetic for tested treatments of different organic matter content, low and high temperature, as well as the presence of PP-MPs and Ag₂SNPs for every contaminant are presented in **Figure 5.10**.

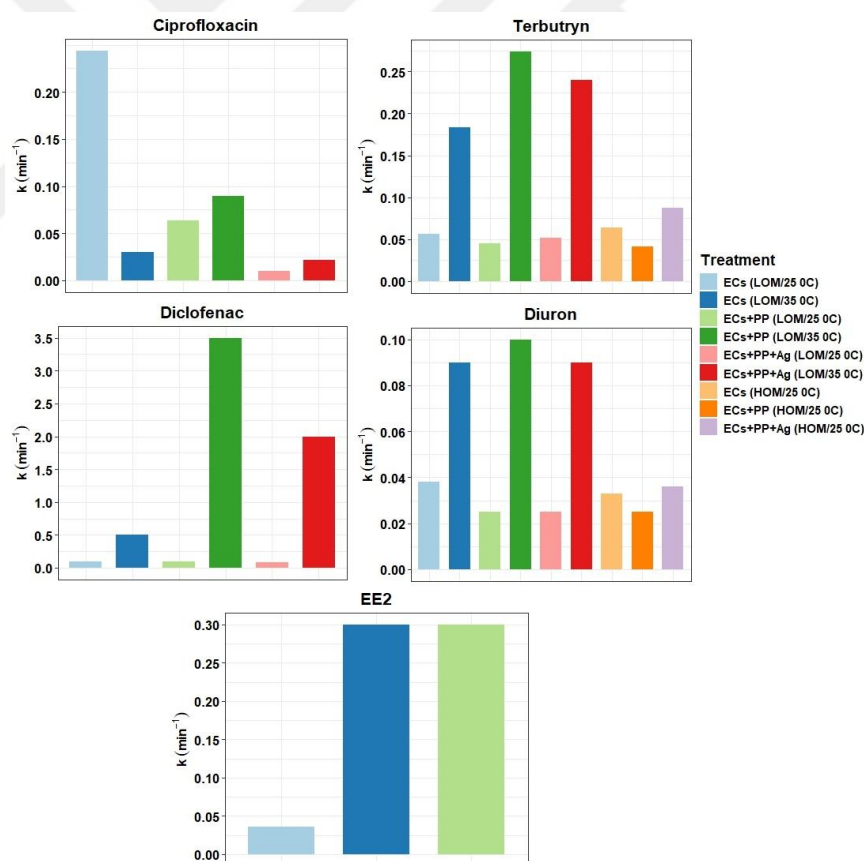


Figure 5.10: Adsorption rate constants for ciprofloxacin, terbutryn, diclofenac, EE2 and diuron at three different treatments at low and high organic matter temperature.

6. THE EFFECT OF EMERGING CONTAMINANTS AND PP-MPS ON SOIL MICROBIAL COMMUNITY AND MAIZE PLANTS

6.1. The Effect of ECs on Soil Microbial Community

6.1.1. Soil Sampling

Soils were collected in August 2024 from 5 different spots in an ecological site with a natural microbial community in Wageningen, the Netherlands. Soil cores were collected at 5 – 20 cm and were combined to represent the entire field. Soil was sieved at the same day after collection using a 5 mm mesh, and stored at 4 °C for 24 hrs. The original soil microbial community was kept and the soil was incubated at 20 °C and 60% of soil water holding capacity for 15 days to stabilize the microbial community prior to the experiments.

6.1.2. Experimental Set-Up

500 mL air-tight pots (with gas-sampling lids, **Figure 6.1**) were filled with 20 gr of dried-weight equivalent soil, and incubated at 20 °C with 60% of soil WHC. Half of the collected soil was sterilized at 120 °C for 15 min, the sterilization was repeated for 3 times during 72 hrs. Thereafter, the selected Mix and PP-MPs were added to the appropriate pots at environmentally relevant concentrations, ranging from 100-500 µg/kg for Mix and 0.1% for PP-MPs, and the soil was homogenized by mixing with sterilized tools. The experiments were done with 5 replicated for each treatment.

6.1.3. Soil Respiration Rate

The soil microbial activity was evaluated by measuring soil respiration rate which is an essential indicator to the total soil microbial activity [409], and a highly sensitive factor to alteration in environmental stressors in the soil matrix (e.g. the addition of chemical contaminants and microplastics) [410].



Figure 6.1: 500 mL plastic pots with gas sampling lids used for soil treatments incubation and CO₂ collection.

The lids of the soil's air-tight pots were closed for 24 hours before the first sample collection. The accumulated CO₂ in the headspace of the pots were sampled on days 1, 2, 3, 7, 12, and 15. The pots were kept closed and flushed after each sampling point with fixed CO₂ concentration air. The sampling was done by taking a 12 mL of headspace gas sample using a syringe and 0.6 mm needle. Samples were kept in pre-evacuated 6 mL GC vials (**Figure 6.2**). The CO₂ concentration in the vials was measured by gas chromatography with thermal conductivity detector (GC-TCD) (**Figures 6.3**). Standards with known CO₂ concentrations (0 – 8600 ppm) were made to create a calibration line.

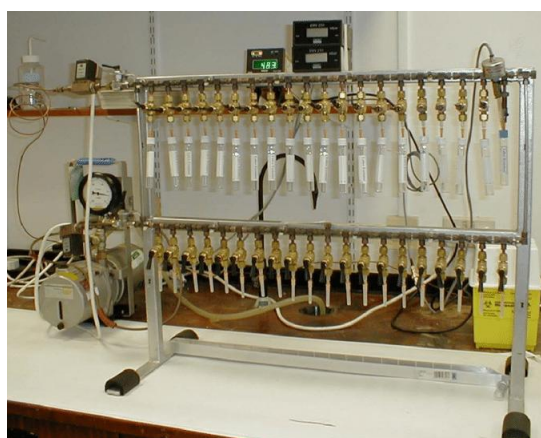


Figure 6.2: The 6 mL GC vials and evacuation system using pure nitrogen.

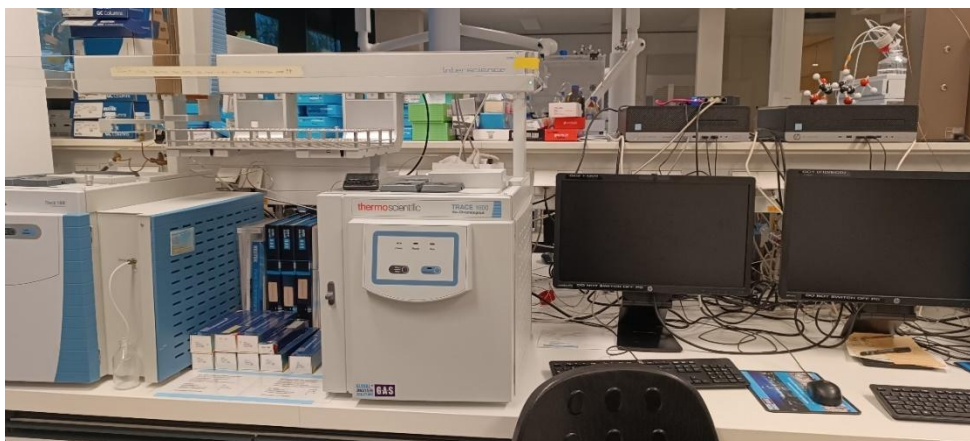


Figure 6.3: GC-TCD used for CO₂ measurement.

6.1.4. Soil Microbial Community Analysis

Sequence pre-analysis consisted of removal of staggered primers with cutadapt v 4.3. Quality screening, chimera removal, generation of the amplicon sequence variant (ASV) abundance matrices, and taxonomic classification were performed with the dada2 package v.1.34 of the R version 4.4. Owing to the binned quality scores, error rate calculation was performed with a modified loess function by GuillemSalazar. Silva SSU taxonomic dataset v 138.1 formatted for dada2, and UNITE general fasta release version 8.2 were used for the classification of the V3V4 16S rRNA and ITS2 amplicons respectively.

Microbial diversity coverage was assessed through rarefaction curves prepared with the vegan package v. 2.6.4. and the percentage of total species represented in a sample estimated with the entropart package v. 1.6.13. The microbiome package v. 1.24.0 was used to calculate the α -diversity indices: observed richness (S), Pielou's evenness, Shannon's diversity, and inverse Simpson. Analysis of variance of the α -diversity indices between treatments for each time point was evaluated via the parametric ANOVA or the non-parametric Kruskal-Wallis tests after performing Shapiro-Wilk test of normality. Tukey's or Fisher's least-significant-difference (LSD) post hoc tests were used after performing ANOVA and Kruskal-Wallis respectively. Kruskal-Wallis test was performed with the agricolae package v. 1.3.7. Redundancy analysis was carried out with the vegan package to estimate the β -diversity between treatments for each time point. Lastly, ASV's differential abundance analysis was performed with the non-parametric Kruskal-Wallis test on outlier-free relative abundance of each

ASV. Outliers were determined with Dixon's outlier test from the package dixonTest v. 1.0.4.

6.1.5. Extraction of Chemical Residuals from Soil and LC-MS/MS Analysis

To investigate the contaminant degradation, we monitored the chemical residual in both sterile and non-sterile soils at 0, 7, and 15 days of incubation, with and without the presence of PP-MPs using 4 replicates. For this, an extraction and measurement method was optimized for the simultaneous detection of targeted chemicals in the soil, based on a previous method by (Ramadan and Ozturk, 2024), with the following modifications:

Soil samples were extracted using an Omni Beadruptor 12 (Kennesaw, GA, USA) homogeniser. To achieve this, 1 g (dw) of soil sample was transferred to 7 mL beadruptor tubes, spiked with 25 µL internal standard and homogenized with vortex shaker. Afterwards, 3 mL of acidified acetonitrile (0.1% TFA) were added to the samples. The beadruptor was run for ~7 min [speed=6m/s, cycles=3, time=2min, resting time=0.3min] while cooled using liquid nitrogen (Air Liquide, Paris, France) using a Biotage (Uppsala, Sweden) Cryo unit. After which the samples were transferred to 50 mL tubes where 6 mL of MTBE:ethylacetate (1:1, v/v) solvent mixture was added and the tubes were shaken vigorously for 5 min, followed by ultrasonication for 5 min, and head over head shaking for 15 min. Thereafter, the samples were centrifuged for 10 min at 3500g and transferred to glass tubes for evaporation to dryness at 40 °C under a gentle stream of nitrogen. The samples were reconstituted with 100 µL of acetonitrile, ultrasonicated for 30 sec, vortexed for 60 sec, after which 2.9 mL of ultrapure water (0.1% TFA) was added and ultrasonication and vortexing steps were repeated. Extracts were cleaned up using SPE.

Phenomenex (Torrance, CA, USA) Strata-X RP SPE cartridges were used for the extraction and clean-up of samples. The cartridges were conditioned with methanol and acidified ultrapure water (0.1 %TFA). The samples were percolated through the conditioned cartridges under vacuum. Following percolation, the cartridges were washed with 4 mL of ultrapure water and left to dry for 20 min, and were eluted by successively adding 3 mL of acetonitrile, MTBE, and ethylacetate. After elution, 20 µL of DMSO was added to the samples, and evaporated with nitrogen until only

DMSO remains. 180 μ L of 10% methanol were added to the samples and homogenized.

After SPE, the compounds were detected using Shimadzu (Kyoto, Japan) Nexera LC coupled to a Sciex (Darmstadt, Germany) 6500+ Q-Trap tandem mass spectrometer (LC-MS/MS). Separation of the target analytes was achieved using a Waters (Milford, MA, USA) Acquity CSH C18 UPLC column (2.1 $\times$ 100mm, 1.7 μ m pore diameter). The autosampler temperature was maintained at 10 $^{\circ}$ C, and the injection volume was set at 10 μ L. The mobile phase consisted of methanol containing 5 mM ammonium fluoride (Phase A) and ultrapure water containing 1 mM ammonium fluoride (Phase B). The gradient started with 10% Phase A, which was maintained for 0.2 min, increased to 70% within 2 min, then to 90% between 2 and 5 min, and remained at 90% for 2 min before returning to the initial conditions within 2 min. The mobile phase flow rate was 0.3 mL/min, and the column temperature was maintained at 40 $^{\circ}$ C.

The MS conditions were as follows: Curtain gas flow of 35 L/h, collision gas (Argon) at the medium setting, ion spray voltage of 5500 V for positive polarity and -4500 V for negative polarity, ion source gas 1 and 2 a flow 60 L/h and a source temperature of 500 $^{\circ}$ C. Analytes were measured using multiple reaction monitoring (MRM) as mentioned in **Table 6.1**. All using an entrance potential (EP) of 10 for positive polarity and -10 for negative polarity.

Table 6.1: The m/z values of the main substance and ionization products of the targeted analytes.

Analyte	[M+H] Mw (DP)	Product ion 1 (CE, CXP)	Product ion 2 (CE, CXP)
Diclofenac	296.0 (36)	215.0 (27, 16)	151.0 (85, 16)
Ciprofloxacin	332.0 (66)	231.0 (49, 20)	288.0 (25, 22)
Diuron	233.1 (76)	160.0 (31, 22)	145.2 (43, 38)
Terbutryn	242.2 (131)	186.1 (27, 42)	91.2 (31, 14)
EE2	295.1 (-220)	145.0 (-62, -15)	159.0 (-44, -13)

DP; Declustering Potential, CE; Collision Energy, CXP; Collision Cell Exit Potential.

6.1.6. Results and Discussion

6.1.6.1. Soil Respiration Rate

Respiration rates of the microbial community depended on the type of contaminants added. The addition of ECs mixture (Mix) had no significant effect on the soil respiration rate. As it was observed by previous studies, the addition of the same compounds at low environmentally relevant concentrations as used in this study, had no significant effect on the soil respiration rate [411], which could be due to the high biodegradability of these pollutants. While the influence started to appear at higher concentrations i.e., 10 mg/kg – 150 mg/kg [412]–[417]. Moreover, the addition of PP-MPs as a single contaminant had no significant effect on the soil respiration rate compared to the none contaminant treatment. While there was strong interaction between the Mix and the plastics (PP-MPs) added to the soils (t-test: $t = 2.3$, $df = 8$, $p = 0.0005$), indicating that respiration was higher in soils with both Mix and PP-MPs addition, than in soils where only PP-MPs or Mix were added (**Figure 6.4**). These effects were particularly apparent at day 1 and day 3. Starting from day 7, the difference in the soil respiration rate between the treatments was less clear. Nevertheless, the addition of PP-MPs tended to reduce, while the combination of Mix+PP-MPs continued to increase the soil respiration rates (**Figure 6.4**). The presence of ECs can be considered as additional carbon or energy source for the soil microorganisms to fuel their growth and increase their functional activity [418]. Although the amount of added ECs is negligible compared to the soil carbon content, and the addition of ECs did not affect the soil respiration rate when it was added alone. However, the aggregation of ECs in the surface of MPs could increase their bioavailability, hence, facilitating its degradation and usage by soil microbial community as additional carbon source for respiration. Moreover, the presence of ECs and MPs combination could impose a mild abiotic environmental stress to the soil microbial community. This stress can promote the metabolic activity of soil microbes in an attempt to adapt to the new conditions [419]. Therefore, the respiration rate can increase as microorganisms expend higher energy on adaptation processes. Furthermore, when the microorganisms start to decompose the adsorbed ECs presence in soil and surface of MPs, it might also start breaking down other types of organic matter. This phenomenon is known as priming effect in which the microbes can

stimulate the decomposition of more resistant organic matter by the introduction of an easily degradable organic compound [420], thus, amplifying the soil respiration rate. After day 7, the soil respiration rate decreased from day 7 to day 12 and was almost stagnant until the end of the experiment at day 15, where there was no significant difference recorded in the soil respiration rate between the different treatments.

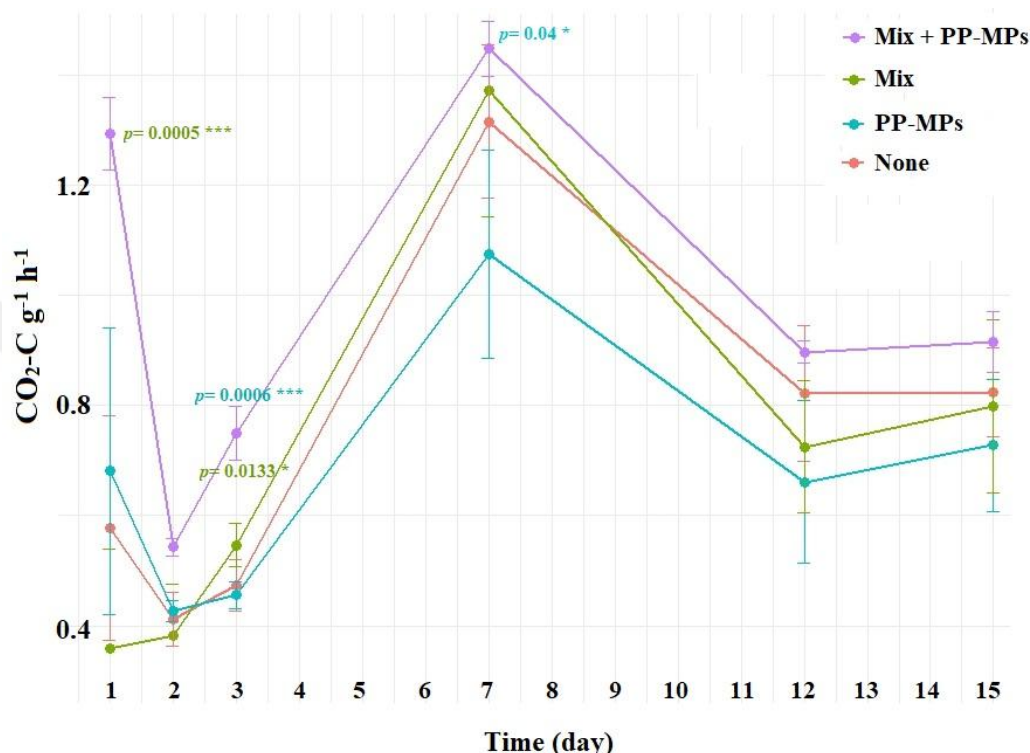


Figure 6.4: Respiration rate of soil microbial community after 1, 2, 3, 7, 12, and 15 days of inoculation with None (no contaminants addition), contaminants mixture (Mix), polypropylene microplastics (PP-MPs), and contaminants mixture with microplastics combination (Mix+PP-MPs).

6.1.6.2. Biodegradation of ECs in the Soil.

We observed considerable variability in the measured degradation of emerging contaminants (ECs) within treatments, as indicated by the error bars in **Figure 6.5**. In sterile soils, no significant degradation of any compound was detected across treatments, confirming that abiotic processes such as hydrolysis or photolysis played only a minor role under the tested conditions. In contrast, in unsterilized soils where microbial activity was present, all compounds except terbutryn showed a pronounced reduction in concentration by day 15 (**Figure 6.5**). This highlights microbial activity

as the primary driver of degradation, consistent with previous findings that biodegradation is the dominant pathway for many ECs in soils [421].

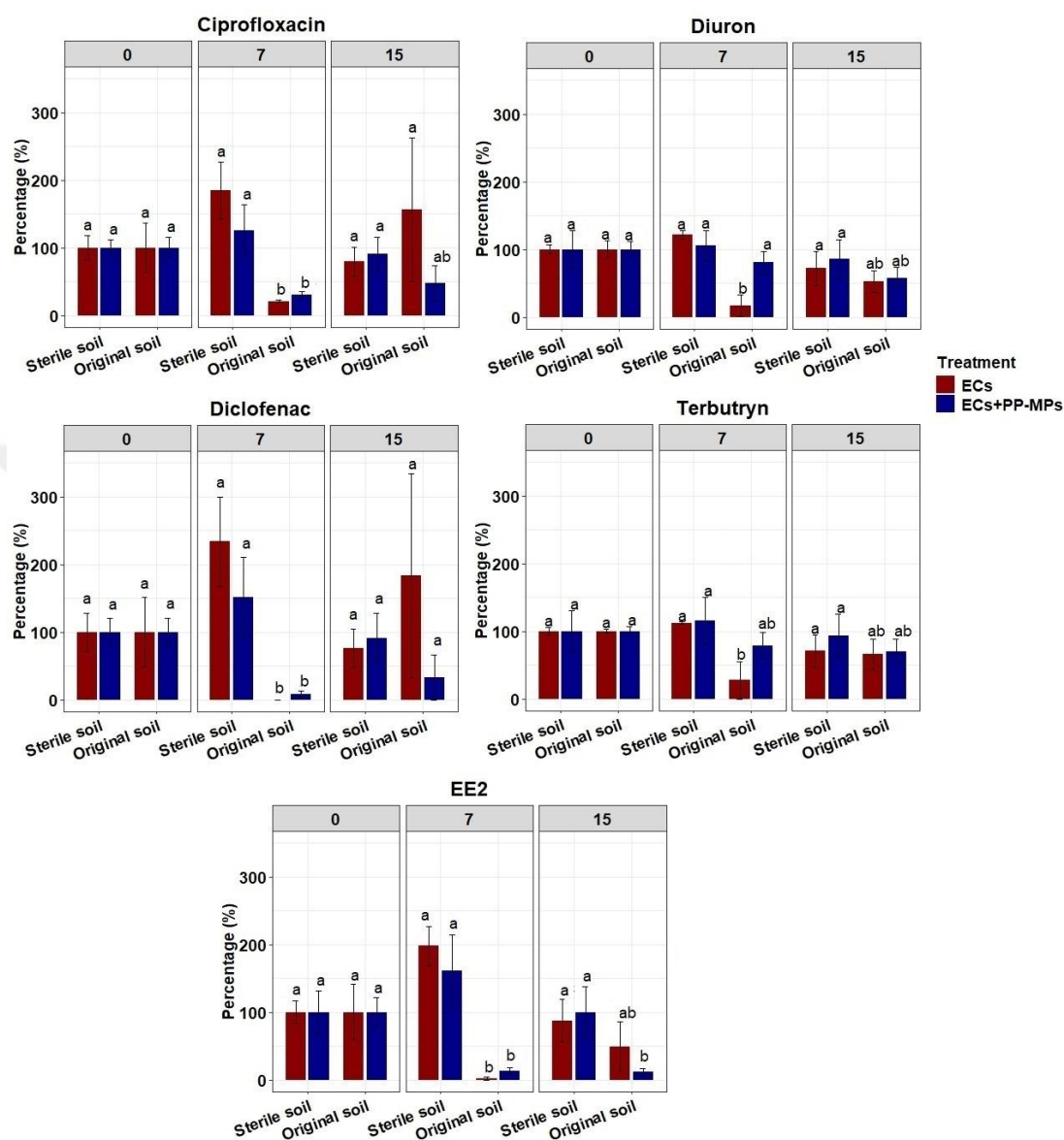


Figure 6.5: The residual ($\mu\text{g/kg}$) of ciprofloxacin, diuron, terbutryn, diclofenac and EE2 in the soil at 0, 7, and 15 days of inoculation with and without the presence of polypropylene microplastics (ECs and ECs+PP respectively).

Significant differences between sterile and non-sterile soils were observed for ciprofloxacin, diuron, and EE2 in the ECs treatments, with degradation ranging from 50–80% (**Figure 6.5**). Ciprofloxacin has been reported to undergo slow biodegradation due to its stable quinolone structure, but partial microbial transformation is possible under favorable conditions [422]. The observed reductions suggest that the soil microbial communities were able to partially metabolize

ciprofloxacin. For diuron, degradation in non-sterile soil is consistent with earlier reports that microbial hydrolysis and demethylation are key transformation pathways [423]. EE2 degradation in both ECs and ECs+PP treatments further supports the role of microbial metabolism, as steroid hormones are known to be susceptible to microbial enzymatic attack, often leading to hydroxylated or conjugated metabolites [424].

Interestingly, in the ECs+PP treatment, only EE2 showed significant degradation in non-sterile soils ($\approx 90\%$), while ciprofloxacin, diclofenac, and diuron exhibited limited or no degradation compared to the ECs treatment. This suggests that the presence of PP-MPs reduced the efficiency of microbial degradation for most compounds. Microplastics have been reported to alter microbial community composition and reduce microbial access to contaminants by providing additional sorption surfaces or by physically shielding compounds [425], [426]. The persistence of ciprofloxacin and diuron in the presence of microplastics is consistent with this mechanism, as both compounds are known to adsorb strongly to polymeric surfaces, limiting their bioavailability [407]. The effect of PP-MPs on diuron was also observed in Section 4.2, where the presence of microplastics decreased the attachment of ECs to soil.

Diclofenac, which is often microbially degraded in soils through hydroxylation and ring cleavage [427], similarly showed reduced degradation in the presence of microplastics, further suggesting decreased microbial accessibility. The exception of EE2 may be related to its high hydrophobicity, which promotes strong sorption to organic matter where microbial communities can still access and degrade it, thereby reducing the inhibitory effect of microplastics on its transformation. Terbutryn remained comparatively stable across all treatments, showing little to no degradation over the experimental period (**Figure 6.6**). This indicates low biodegradability and/or strong sorption stability, consistent with earlier studies reporting high persistence of triazine herbicides in soils due to their chemical stability and limited microbial metabolic pathways [428].

In summary, microbial activity was the main driver of degradation for ciprofloxacin, diclofenac, diuron, and EE2, with significant reductions detected by day 7. The presence of PP-MPs increased the persistence of these compounds by limiting their bioavailability to soil microbes, except in the case of EE2, where degradation remained high. Terbutryn demonstrated strong persistence, reflecting its resistance to microbial breakdown. These results highlight the complex interplay between soil organic matter,

microbial activity, and microplastic interactions in determining the environmental fate of ECs.

6.1.6.3 Soil Microbial Community Composition

The inverse Simpson index significantly increased in the bacterial community under the combined treatment (ECs+PP) after 15 days of incubation ($F_{3,12} = 9.714$, $p = 0.002$) (**Figure 6.6**), while richness (ASVs) and Shannon diversity did not differ between treatments or time points. This indicates that the combined exposure altered bacterial community evenness rather than overall species richness. Such changes are consistent with previous studies showing that exposure to microplastics and chemical mixtures can selectively favor certain microbial taxa, thereby altering community structure without necessarily changing richness [429].

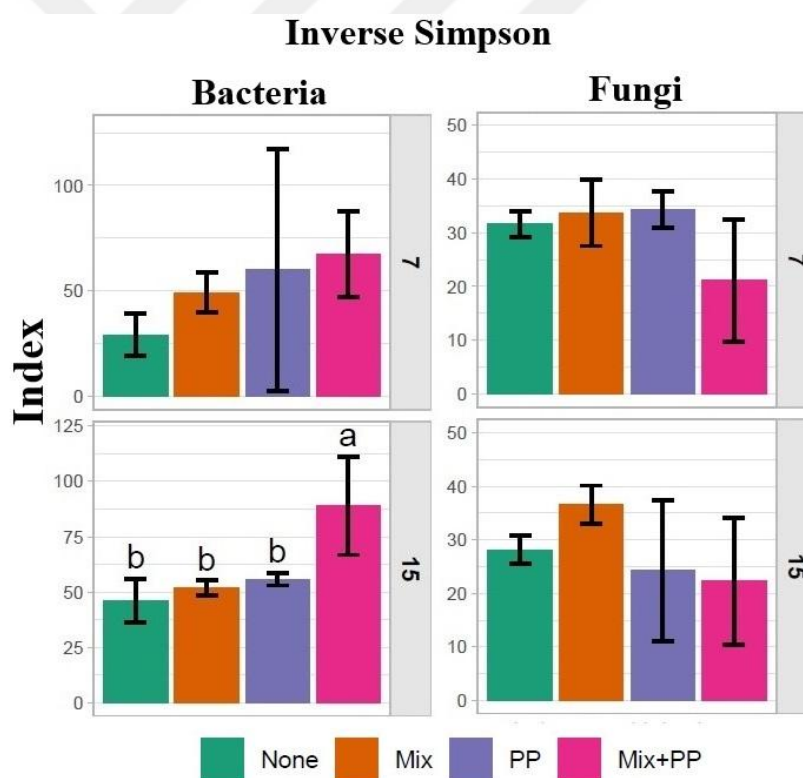


Figure 6.6: Inverse Simpson diversity index for soil bacterial (left graph) and fungal (right graph) communities with chemical mixture (Mix), polypropylene microplastics (PP), and their combination (ECs+PP) at 7 (top) and 15 (bottom) days of incubation.

Redundancy analysis (RDA) (**Figure 6.7**) further confirmed treatment effects on bacterial community composition. At day 7, bacterial communities across treatments

were partially overlapping, suggesting that treatment effects were still emerging, although the separation of PP and control groups indicated early treatment-specific responses. By day 15, community shifts became more distinct, with the ECs+PP treatment forming a clear cluster separated along both RDA axes, indicating a stronger combined effect of microplastics and chemical mixture. This aligns with evidence that microplastics can act as vectors or stressors that modulate microbial community responses to co-occurring contaminants [407], [425]. The distinct clustering of 15 Mix and 15 PP groups compared to the control (15 None) further demonstrates that both chemicals and microplastics individually exert selective pressures on bacterial communities over time.

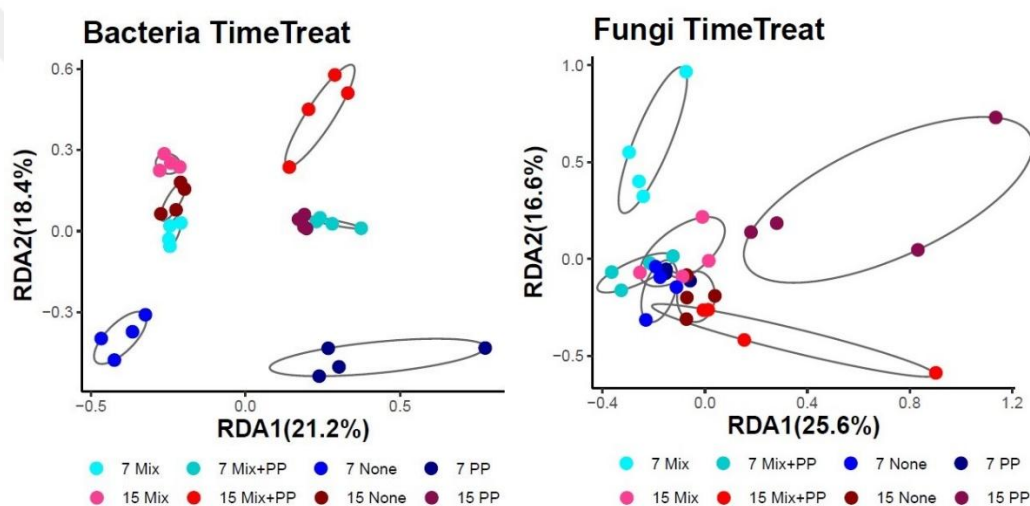


Figure 6.7: Redundancy analysis for soil microbial and fungal communities with chemical mixture (Mix), microplastics (PP), and their combination (Mix+PP) at day 7 and 15 of incubation.

In contrast, fungal communities were less responsive to treatments, as indicated by their overlapping clustering in RDA (**Figure 6.7**). Only the Mix treatment at day 7 and the PP treatment at day 15 clustered separately from the other groups. The relatively weak response of fungi suggests greater resilience or lower sensitivity to both chemical mixtures and microplastics compared to bacterial communities, consistent with previous reports that bacteria often respond more rapidly to environmental disturbances due to their shorter generation times and metabolic versatility [430].

Overall, these findings demonstrate that bacterial communities are more strongly and rapidly affected by ECs, microplastics, and particularly their combination, while fungal communities remain comparatively stable under the same conditions.

The heatmaps (**Figures 6.8** and **Figure 6.9**) reveal clear shifts in soil bacterial community composition in response to the mixture of emerging contaminants (Mix) and microplastics (PP), both individually and in combination. Several taxa appeared or disappeared under different treatments, indicating that exposure to these stressors altered the relative abundance and presence of specific bacterial groups. The most pronounced effects occurred in the combined treatment (Mix+PP), where unique taxa were introduced while others were eliminated, highlighting strong selective pressures exerted by the combined contaminants.

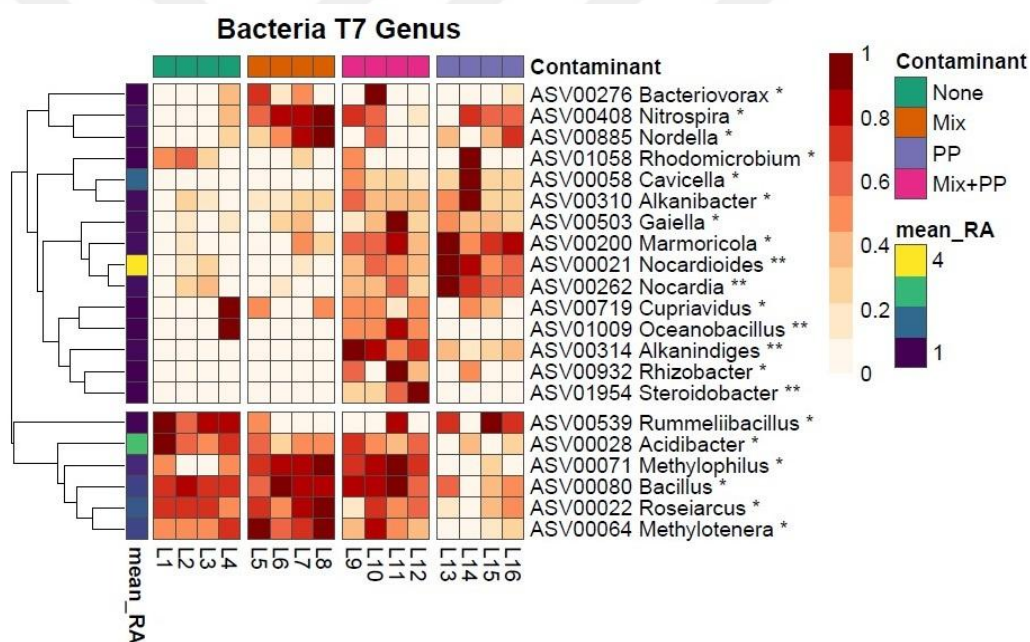


Figure 6.8: Heatmap of soil microbial community composition at day 7 of inoculation with None (no contaminants added), Mix (the mixture of ECs including EE2, terbutryn, diuron, diclofenac and ciprofloxacin), and mixture of ECs with polypropylene microplastics (Mix+PP).

At day 7 (**Figure 6.8**), changes in community composition were already visible, with several genera such as *Cupriavidus*, *Oceanobacillus*, *Rhizobacteria* and *Alkanindiges* becoming more dominant under Mix+PP compared to controls. Early shifts suggest that certain taxa rapidly respond to chemical stressors and microplastics, consistent with reports that bacterial communities can adjust within days to contaminants by

favoring resistant or metabolically flexible groups [431]. By day 15 (**Figure 6.9**), treatment effects were even stronger, with genera such as *Marmoricola*, *Nocardioides*, *Cavicella*, and *Phenylobacterium* enriched in Mix+PP soils, while others were reduced or absent. The enrichment of these groups suggests their potential tolerance to both microplastics and xenobiotic compounds, possibly linked to hydrocarbon or pesticide degradation capabilities [432].

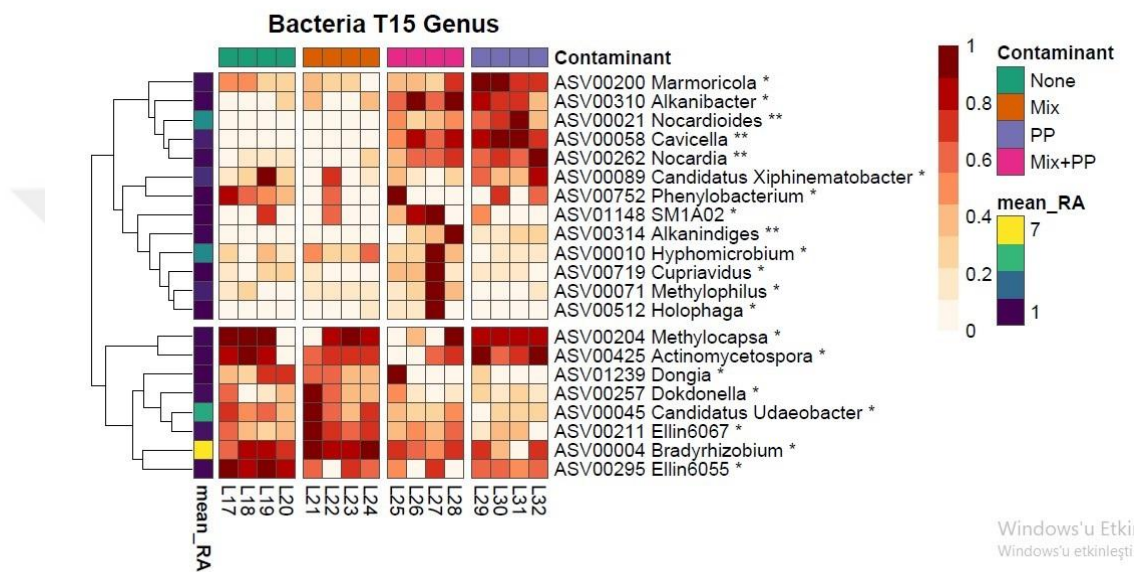


Figure 6.9: Heatmap of soil microbial community composition at day 15 of inoculation with None (no contaminants added), Mix (the mixture of ECs including EE2, terbutryn, diuron, diclofenac and ciprofloxacin), and mixture of ECs with polypropylene microplastics (Mix+PP).

The observed disappearance of sensitive taxa in Mix and Mix+PP treatments suggests that contaminant mixtures and plastic particles may inhibit certain microbial groups by generating toxic stress, reducing nutrient availability, or altering soil microhabitats. Microplastics can modify soil porosity, water retention, and oxygen diffusion, thereby restructuring ecological niches [425]. At the same time, microplastics can act as sorption surfaces, concentrating organic contaminants and making them less bioavailable to some taxa while creating microhabitats that support others [433]. This dual role of microplastics, as pollutant carriers and as ecological surfaces, likely explains the distinct clustering and compositional changes observed in the Mix+PP treatments. The increase in diversity evenness (Inverse Simpson index) under Mix+PP treatment further supports the hypothesis that the combined stressors promote a

restructuring of bacterial communities, where formerly less abundant taxa increase in relative importance. Overall, our results demonstrate that the mixture of ECs and PP-MPs significantly reshaped soil bacterial community composition, introducing resistant taxa while eliminating sensitive ones.

6.2. The Effect of ECs and PP-MPs on Maize plants

6.2.1. Experimental Set-Up

6.2.1.1. Growth Conditions and Materials

12 kg of soil were collected from a field in Wageningen, The Netherlands, sieved (5 mM), homogenized and kept in the incubator for 2 weeks at 20 °C for soil microbes stabilization. Afterwards, a pot experiment was conducted in the greenhouse with a photoperiod of 12 h day/12 h night at 20°C and 60% relative humidity. 3 Maize seeds (*Zea mays* cultivar PR39F58) were cultivated in each soil pot. Plants were watered every 2 days and supplemented weekly with a 0.5 Hoagland solution (1 ml per 80 cc of the soil, 0.5 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 1 M KNO_3 , 1M KH_2PO_4 , 0.5 M $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 98.6 mM ferric EDTA).

Two types of plastics were used in this study: the mulch films biodegradable plastics (BioPs) provided by Unifarm, Wageningen University, The Netherlands. A macro-sized BioPs pieces were made by cutting plastic mulch films into 5 mm × 5 mm squares by hand, in addition to the polypropylene microplastics (PP-MPs), supplied from a factory in Turkey with a size distribution of 40-100 µm. A total of 30 soil pots were cultivated using 5 replicates for each treatment. Contaminants were applied to soil in a full-factorial design with six treatments: ECmix, BioPs, PP-MPs, ECmix+PP-MPs, ECmix+BioPs and a control without any chemicals added. ECs were added to the plants successively with the feeding water to resemble the irrigation of maize crops with treated wastewater, while the BioPs and PP-MPs were added to the soil prior to cultivation in a concentration of 1% and 0.1% respectively.

6.2.1.2. Plant Growth and Biomass

After 7 weeks of cultivation, the length of plants was measured and recorded (**Figure 6.10**). Afterwards, the plants were harvested and the excess of soil was shaken off, the roots were cleaned with water, and plants were separated into shoots and roots. The plants were dried for 48 hr at -80°C to -90°C under a pressure of 550 mbar using a christ freeze dryer (Alpha 1-2 LDplus) (**Figure 6.11**), and the dry biomass were recorded.

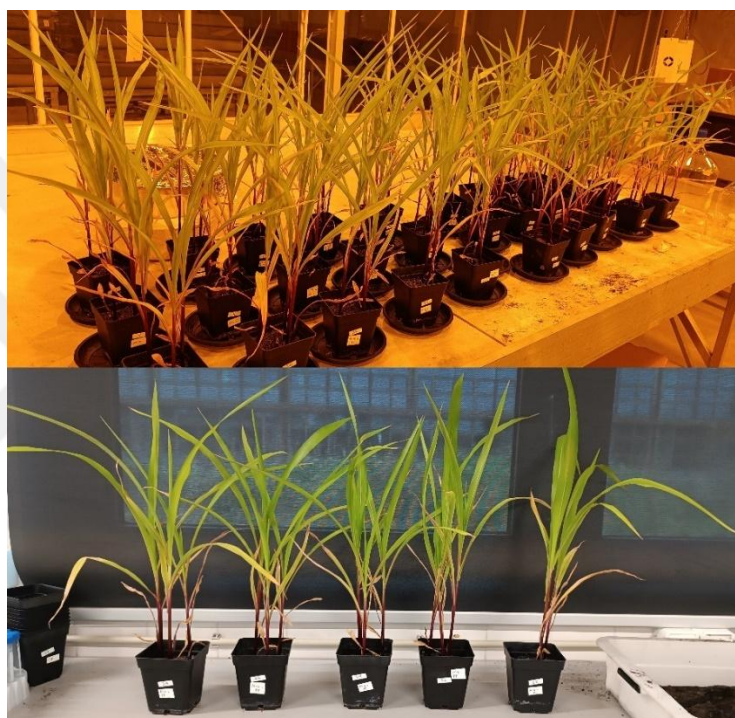


Figure 6.10: The cultivated pots of maize plants with various treatments.



Figure 6.11: The Christ Alpha 1-2 LDplus freeze drier used to dry the harvested maize leaves, shoots and roots.

6.2.1.3. Volatile Trapping and Measurement

The volatile organic compounds (VOCs) emitted by the rhizosphere microbial community were collected using polydimethylsiloxane (PDMS)-silicone tubes. The tubes were conditioned and buried in the wheat rhizosphere for 3 hours before final harvest (**Figure 6.12**). The PDMS tubes were stored at -20°C before analysis. An automated thermal desorption unit (model UnityTD-100, Markes International Ltd., United Kingdom) was used to desorb the trapped volatiles in the PSMD tubes at 210°C for 12 min, using a helium flow of 50 ml/min. Thereafter, the volatile compounds were trapped on a cold trap at 10°C . The trapped organic volatile compounds were introduced to Gas Chromatography Quadrupole Time-of-Flight Mass Spectrometry (GC-QTOF), (model Agilent 7890B GC and the Agilent 7200A QTOF, USA). The cold traps were heated to 280°C for 3 min. The GC used column was a 30×0.25 mm ID RXI-5MS, film thickness $0.25\ \mu\text{m}$ with a split ratio of 1:20. The temperature program was: 39°C for 2 min, from 39°C to 95°C , and to 160°C at $6^{\circ}\text{C}\cdot\text{min}^{-1}$, upto 250°C at $15^{\circ}\text{C}\cdot\text{min}^{-1}$ and, to 300°C at $40^{\circ}\text{C}\cdot\text{min}^{-1}$, which was held for 20 min as final step. The separated VOCs were detected by MS at 70 eV and EI mode. The detected mass spectra were extracted by MassHunter Qualitative Analysis Software,

using GC-Q-TOF qualitative analysis module. The extracted VOCs were identified by their mass spectra via the deconvolution function (Local- Maximum algorithm) in combination with two libraries including National Institute of Standards and Technology (NIST 2014 V2.20) and Wiley 9th edition, and their linear retention indexes (LRI). The calculated LRI were compared with both NIST and in LRI database of The Netherlands Institute of Ecology (NIOO-KNAW).

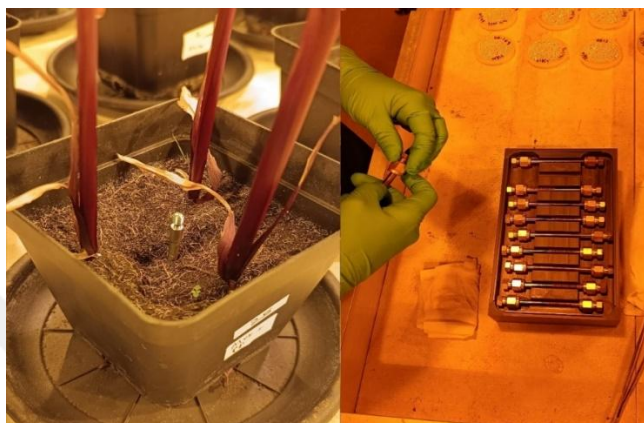


Figure 6.12: PDMS tubes used for VOCs trapping from plants rhizosphere.

6.2.2. Results and Discussion

6.2.2.1. Plant Growth and Biomass

The leaves dried biomass varied depending on the treatment added. We have observed a significant variation in the dried biomass when the combination of Mix and PP-MPs were added to the soil ($P= 0.032$) (**Figure 6.13**), while the decrease in biomass for Mix alone was not statistically significant. As was observed in the effect on soil microbial community, where the combination of Mix+PP-MPs had the most significant effect. The dried biomass of the roots with BioPs and Mix+BioPs treatments were not obtained due to the strong attachment of large plastics particles between the roots, therefore, it was difficult to separate and measure the precise weight of roots. The toxic effect of Mix+PP-MPs combination was also predominant in the maize roots (**Figure 6.14**). The addition of Mix+PP-MPs had the most significant effect in decreasing the root biomass ($P= 0.0021$).

The decreasing in the maize plants biomass can also be linked to the effect on soil and rhizosphere microbial community. The presence of PP-MPs can decrease the uptake of Mix by the plants which make it more persistent in the soil. Thus, the longer stay and accumulation of Mix in the soil could adversely affect the soil and rhizosphere microbial community. The beneficial-root associated microorganisms play a crucial role in plants growth and health [434]. According to the obtained results in this section, it is very important to consider the presence of microplastic particles and their possible interactions while investigating the effect of soil chemical contamination on plants health.

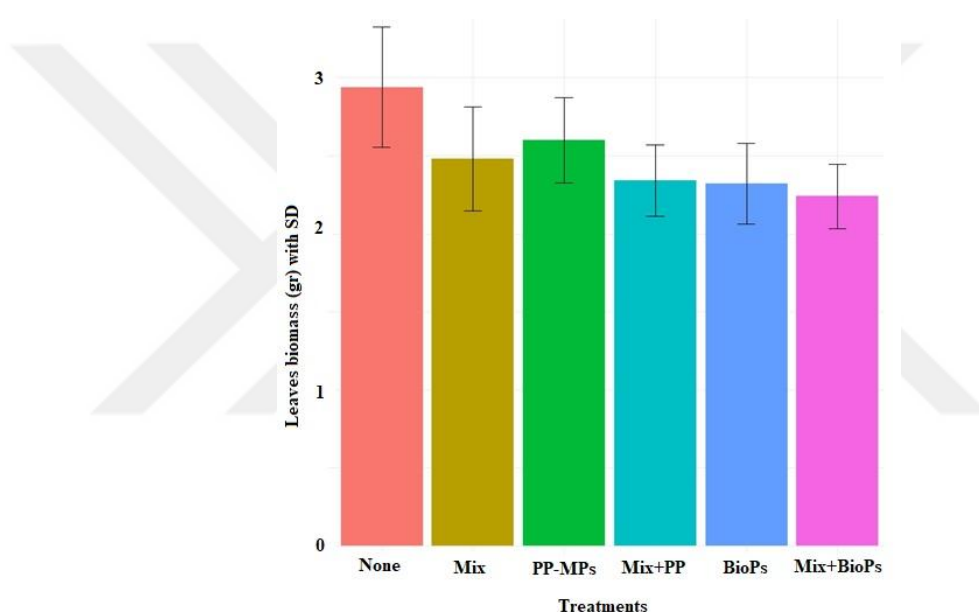


Figure 6.13: The dried biomass of maize plant leaves for different treatments.

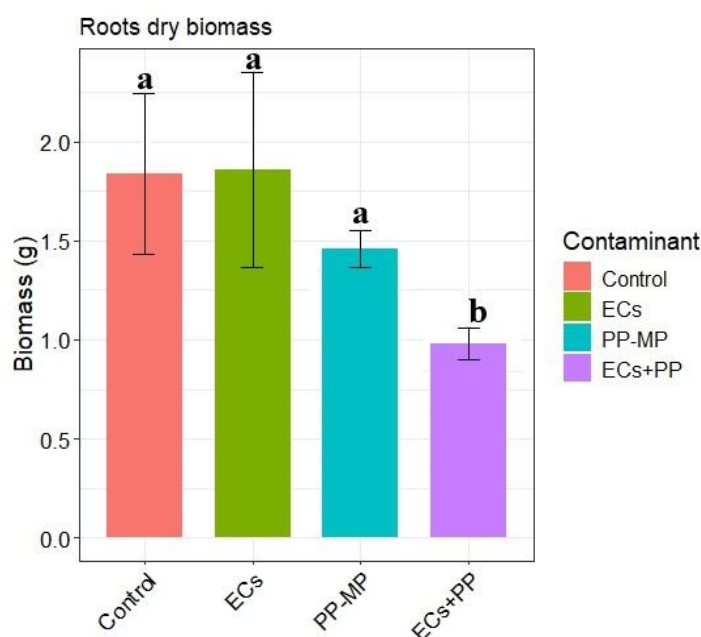
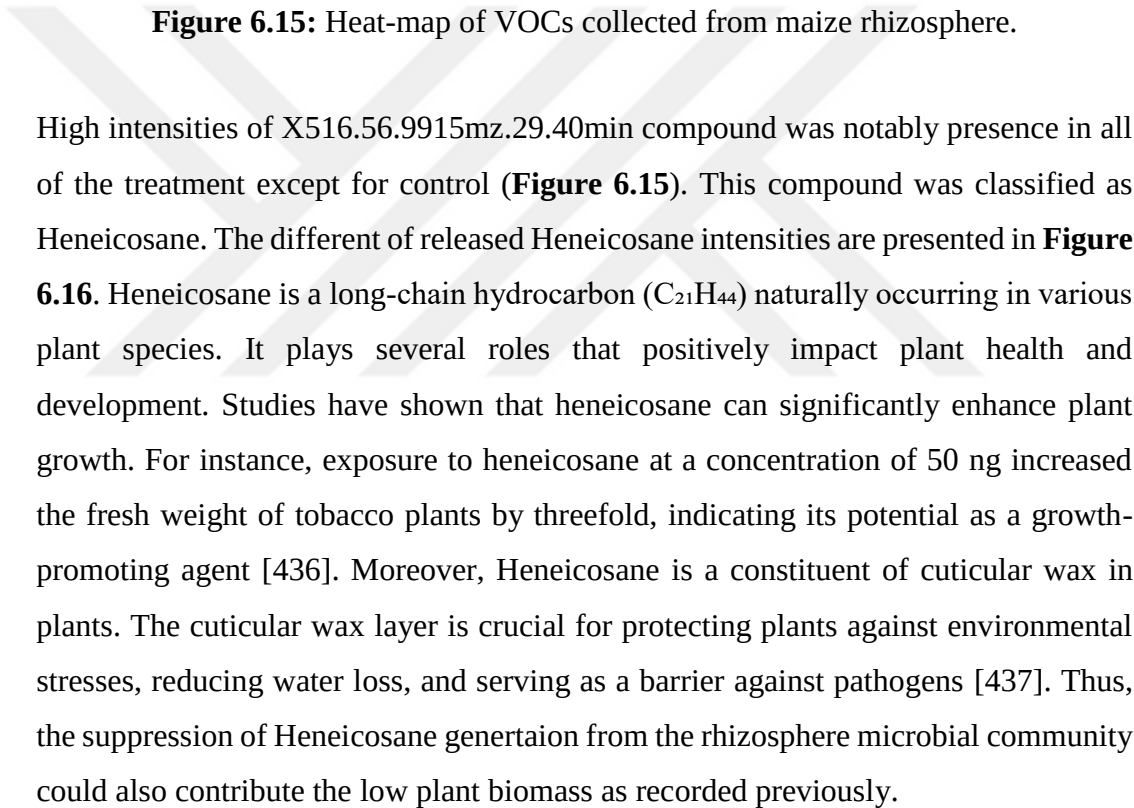


Figure 6.14: The dried biomass of maize roots at different treatments.

6.2.2.2. The Effect of ECs and Microplastics on Rhizosphere VOCs.

Secondary metabolites such as VOCs, play significant roles in plant-microbe interactions. Specifically, the chemical composition of volatile metabolites in the rhizosphere is critical for below-ground interactions with soil [435]. In this study, we collected and analyzed the volatiles emitted in the maize rhizosphere at the end of the experiment. Our results showed that the addition of ECs and plastic residues have markedly altered the blend of some volatiles emitted in the rhizosphere (**Figure 6.15**). The VOCs which showed the highest differences among the treatments were identified. The heatmap revealed that certain compounds were exclusively generated in treatments involving BMP and PP-MPs contaminants. Additionally, differences in volatile compounds were detected between the control and all other added contaminants.



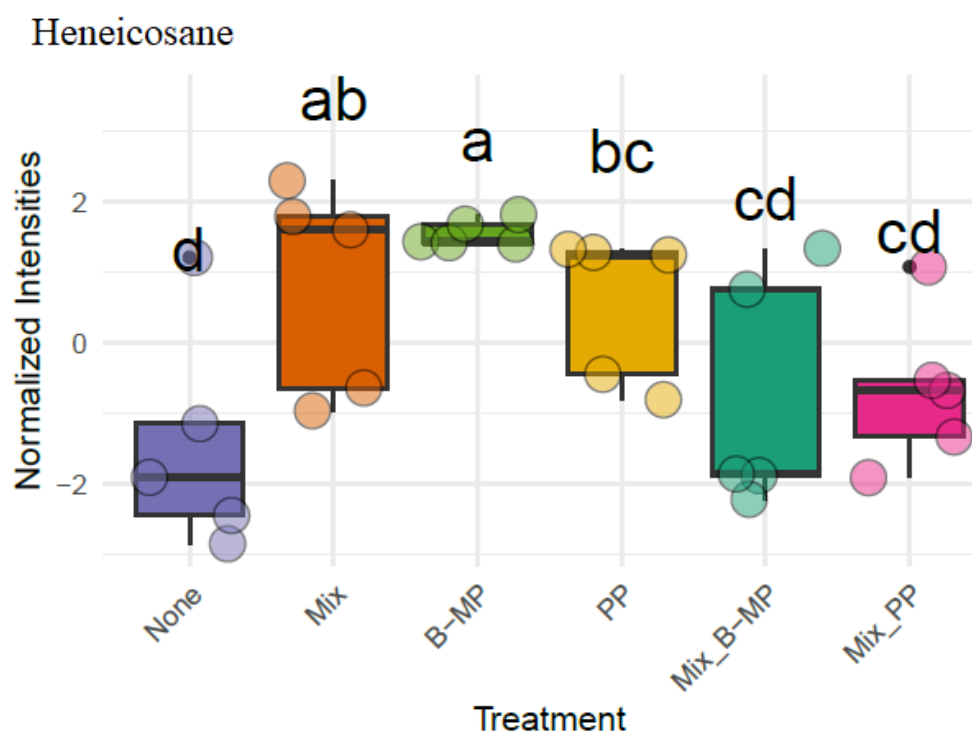


Figure 6.16: Boxplot of detected Heneicosane intensities in different treatments.

Notably, distinct volatiles were identified exclusively in the Mix+PP treatment, including X90.44.9690mz.5.29min which was identified as 2-Methoxyphenol (**Figure 6.17**). 2-Methoxyphenol (also known as guaiacol) is a naturally occurring phenolic compound found in plant biomass. It has both positive and negative impacts on plant growth and health, depending on its concentration, environmental conditions, and the plant species involved. At lower concentrations, 2-methoxyphenol may have antioxidant properties that can protect plants from oxidative stress [438]. This could contribute to enhanced seed germination and growth in certain plant species. However, at higher concentrations (occurrence intensities), 2-methoxyphenol can be toxic to plants, inhibiting seed germination, root elongation, and overall plant growth [439]. This is attributed to its role in disrupting cellular processes, including oxidative damage to plant cells, and disruption of nutrient uptake in the roots [440]. Moreover, while direct studies on 2-methoxyphenol are limited, insights can be drawn from related phenolic compounds. Phenolic compounds, in general, are known to influence soil microbial dynamics by promoting the growth of specific phenol-degrading microorganisms. For instance, certain bacteria can utilize phenolic compounds as carbon sources, leading to shifts in microbial community composition [441]. Such

alterations can disrupt beneficial plant-microbe interactions, potentially affecting plant health. While these findings pertain to phenolic compounds broadly, they suggest that 2-methoxyphenol may similarly alter soil microbial communities and indirectly impact plant health. Therefore, the presence of this compound at higher intensities in the Mix+PP-MPs combination could justify the observed significant decrease in the biomass of maize roots.

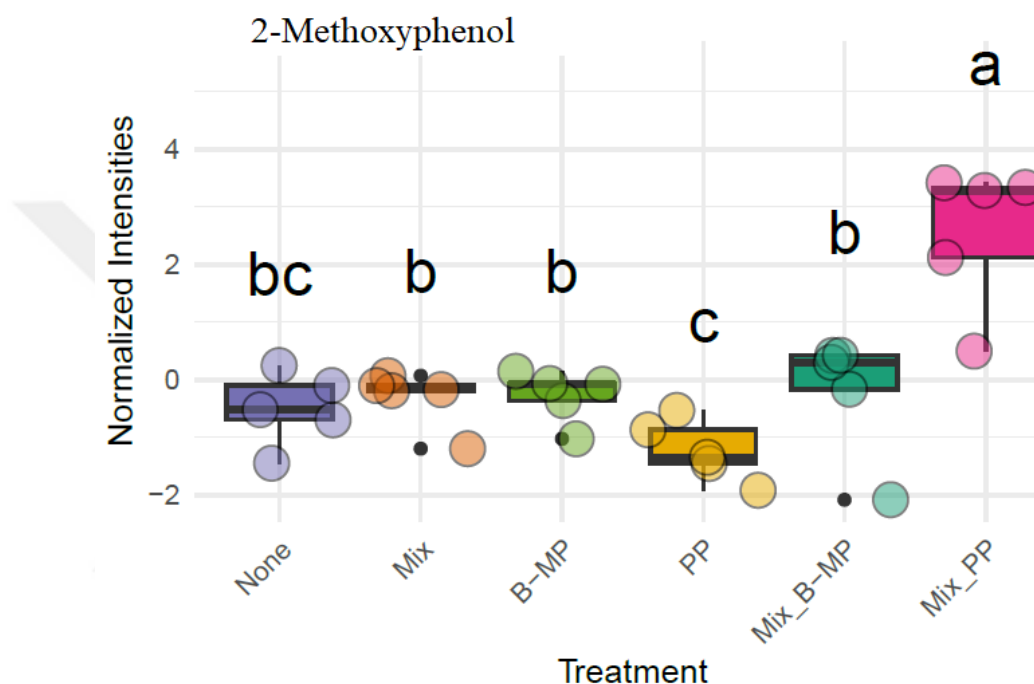


Figure 6.17: Boxplot of detected 2-Methoxyphenol intensities in different treatments.

Furthermore, X405.191.0186mz.19.99min was found with significantly higher intensity in PP and Mix+PP treatment (**Figure 6.18**). This compound was identified as 2,4-Di-tert-butylphenol (2,4-DTBP). 2,4-DTBP is a phenolic compound commonly found in various plants and microorganisms. It is often a significant component of volatile or essential oils and exhibits strong toxicity against a wide range of organisms, including its producers [442]. 2,4-DTBP demonstrates notable phytotoxic effects, adversely affecting plant health and development. It has been observed to significantly inhibit seed germination and seedling growth in various plant species. For instance, it caused severe chlorosis and necrosis in *Hedyotis verticillata* and *Leptochloa chinensis*, indicating strong phytotoxic activity [443]. Furthermore, Exposure to 2,4-DTBP can suppress the plant immune system, making plants more susceptible to diseases [442].

This immunosuppressive influence is expected to further compromise plant health and resilience. Therefore, the presence of ECs and PP-MPs combination in the soil contributed significantly in producing high intensities on VOSs that are known to be toxic for the plants.

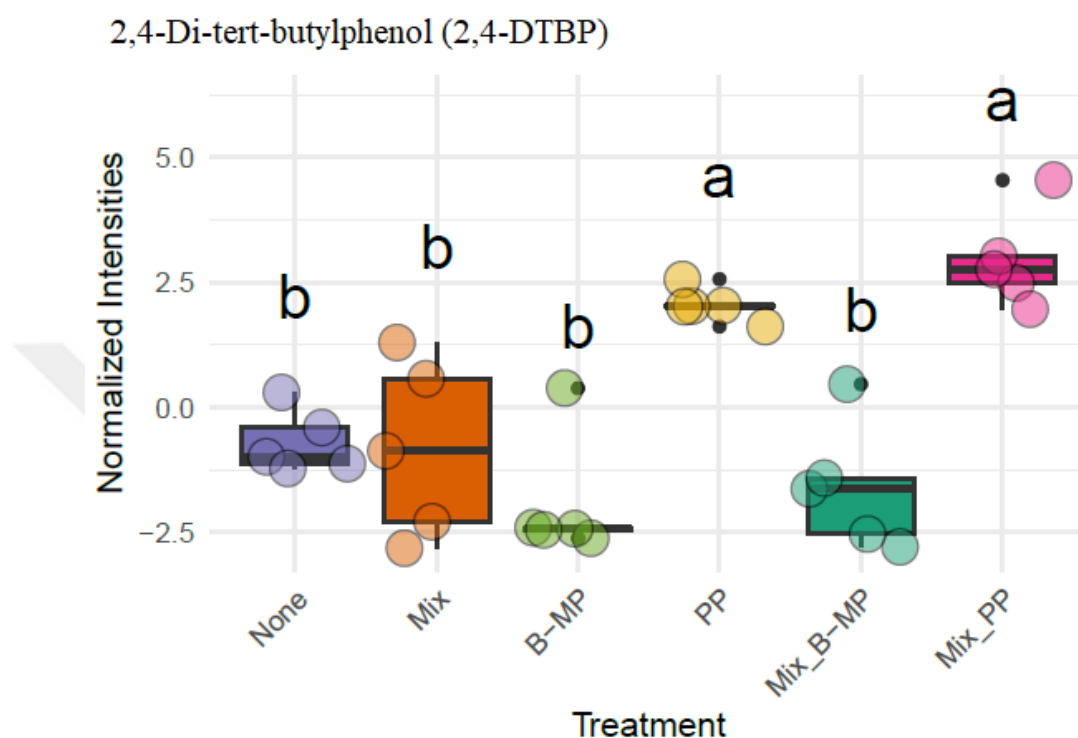


Figure 6.18: Boxplot of detected 2,4-DTBP intensities in different treatments.

The presence of PP-MPs as a single compound had registered high release of X526.84.9415mz.29.88min compound, which was identified as γ -Palmitolactone. The difference in detected intensities are shown in **Figure 6.19**. γ -Palmitolactone is a lactone compound identified as a significant component in the essential oils of various plants species, where it contributes to the plants bioactive properties [444]. Currently, there is limited information regarding the direct negative impacts of γ -Palmitolactone on plants. Most studies focus on its beneficial properties. While the presence of PP-MPs had shown to record a significant decrease in the plant biomass, further research is needed to elucidate any potential adverse effects of high concentrations of γ -Palmitolactone on plant health.

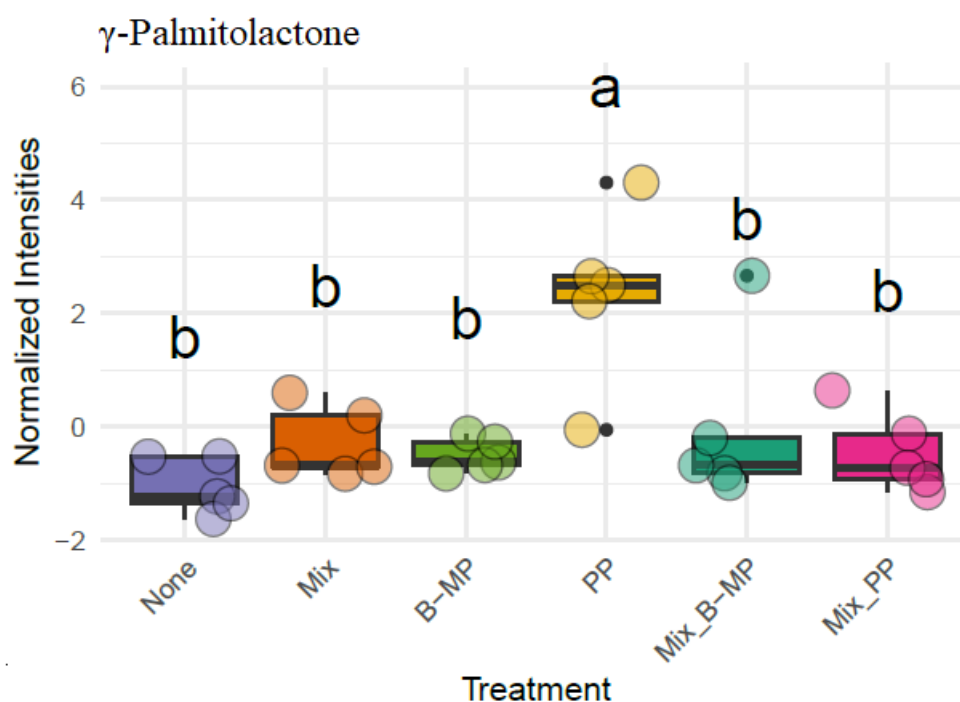


Figure 6.19: Boxplot of detected γ -Palmitolactone intensities in different treatments.

Therefore, the combination of ECs and PP-MPs alters the synthesis and release of specific VOCs, such as suppression of heneicosane, a beneficial VOC, in treatments involving mixed contaminants (Mix+PP-MPs), and the elevated presence of phytotoxic VOCs, such as 2-Methoxyphenol and 2,4-Di-tert-butylphenol (2,4-DTBP), in treatments involving ECs and PP-MPs highlights a major mechanism behind the observed reduction in plant biomass. Furthermore, the capacity of phenolic compounds like 2-Methoxyphenol to reshape microbial community composition introduces secondary impacts that disrupt beneficial plant-microbe interactions in the rhizosphere. Interestingly, the presence of γ -Palmitolactone in the PP-MP treatment points to its possible contribution to the observed biomass reduction, though its specific effects at high concentrations require further investigation. Overall, these findings underscore the cumulative impacts of ECs and PP-MPs on soil VOCs profiles, which significantly affect the rhizosphere environment and plant health. This disruption leads to a feedback loop where plant growth and resilience are compromised, further altering soil-plant-microbe dynamics. Future research should prioritize understanding the long-term implications of VOC shifts, particularly in soils exposed to mixed contaminants, and explore mitigation strategies to restore plant and soil health in contaminated environments.

7. CONCLUSION

Emerging contaminants (ECs) are a growing environmental concern due to their widespread presence, persistence, and ecological impacts. Their complex interactions with environmental factors and co-contaminants have raised significant challenges for predicting their fate and managing their risks. Due to the lack of regulations and limited understanding of the behavior of these contaminants, particularly under the influence of climate change and in the presence of co-contaminants like microplastics and silver sulfide nanoparticles (Ag₂SNP), this thesis explored multiple dynamics of ECs in the environment, focusing on their environmental fate by investigating their photodegradation under natural sunlight, and adsorption behavior in soil, under various climate conditions, and in the presence of co-contaminants. Furthermore, the mixture effect of ECs on soil microbial communities and plant systems were investigated to obtain a comprehensive view for their fate and potential toxicity in the terrestrial environment. Therefore, an integrated experimental approach was used in this study for a robust framework that enabled a thorough exploration of ECs dynamics across aquatic and terrestrial environments. The experimental design includes:

- The integration of climate variables (temperature, organic matter) and co-contaminants (microplastics, and silver-nanoparticles) into the study design.
- The accurate methods for photolysis and adsorption experiments, ensuring reliability and environmental relevance.
- Assessing the soil microbial activity and plant response for the studied ECs and the relevant co-contaminants.

The findings contribute to addressing critical gaps in understanding the environmental risks posed by ECs under real-world scenarios and provide insights for improving environmental management practices.

7.1. Detection of ECs Mixture at Trace Concentrations

An optimized analytical method was successfully developed for the simultaneous extraction and quantification of a mixture of ECs from aquatic matrices in Chapter 3. ECs for this study were chosen based on their distinct physicochemical properties such

as different solubilities in water and organic solvents, and the chemical structures including phenylacetic acid (Diclofenac), carbonyl diamide (Diuron), heterocyclic N,S triazines (Terbutryn), quinolinecarboxylic acid (Ciprofloxacin) and steroids (EE2), in addition to their diverse sources and applications (anti-inflammatory drugs, pesticides, herbicides, antibiotics and estrogens). The measurement method is based on solid-phase extraction (SPE) coupled with liquid chromatography-mass spectrometry (LC-MS/MS), providing high precision, selectivity, and sensitivity for the targeted analytes. The method was optimized through systematic SPE trials, that included the optimization of parameters such as pH, conditioning solvents, washing steps, drying time, and elution solvents. The final SPE method which gave the highest recovery rates for all of the tested compounds involved:

- pH 2 for sample preparation.
- Conditioning with methyl tert-butyl ether (MTBE), acetonitrile, ethyl acetate.
- Washing with a 20% acetonitrile-80% UPW mixture.
- Drying for 20 mins.
- Stepwise elution with acetonitrile, ethyl acetate and MTBE (4 mL each).

These conditions ensured efficient extraction of the analytes, minimizing losses while preventing contamination from interfering with compounds of different water matrices (lake water and synthetic surface water). Moreover, to confirm the suitability of the optimized method for routine analysis, the analytical quality parameters were evaluated. The method demonstrated excellent selectivity by effectively separating the targeted analytes from other organic compounds in the surface water matrix. Recovery rates for spiked analytes ranged between 90% and 114%, while blank samples showed no interference (0–0.05% recovery). This confirms the method's ability to distinguish analytes from potential interferences in real and synthetic water matrices. The stability and robustness parameters were also examined, targeted analytes remained stable during storage under dark conditions at 4°C for up to 72 hours, with consistent recovery rates between 85% and 115%. Moreover, the method performed reliably across different matrices (distilled water and synthetic surface water with varying organic matter concentrations of 4.5 mg/L and 13.6 mg/L). Recovery rates were unaffected by matrix variability, confirming the method's robustness for use in diverse environmental conditions. The optimized method exhibited strong linearity, as demonstrated by correlation coefficients (R^2 values ranging from 0.988 to 0.999)

across a concentration range of 10–750 µg/L. This indicates the method's ability to produce accurate results for varying concentrations of the analytes. Finally, the method demonstrated excellent sensitivity with concentration factors of 500 due to SPE preconcentration. Limits of detection (LOD) were 0.01 µg/L for ciprofloxacin, diuron, terbutryn, and diclofenac, and 0.05 µg/L for EE2. Limits of quantification (LOQ), 5 µg/L for ciprofloxacin, diuron, terbutryn, and diclofenac, and 25 µg/L for EE2. These LODs and LOQs values indicate the method's capability to detect and quantify ECs at trace levels in aquatic environments.

Therefore, the optimized SPE-LC-MS/MS method is highly suitable for the monitoring of selected ECs in various aquatic matrices, including synthetic and real water samples. Its high selectivity, sensitivity, and robustness ensure accurate quantification of these contaminants in complex matrices, which highlight its utility in environmental monitoring programs. The ability to detect ECs at trace levels provides a powerful tool for environmental monitoring and risk assessment of these contaminants. This is critical for understanding the behavior, persistence, and ecological impacts of ECs in natural environment. Future studies could extend its applicability to broader classes of contaminants and further optimize it for high accuracy analysis to address growing concerns regarding water pollution and ecosystem health.

7.2. Mixture and Water Matrix Impacts on the Photodegradation of ECs

Chapter 3 focused on investigating the photolysis behavior of selected emerging contaminants (ECs) as individual compounds and in mixtures under controlled conditions of temperature and organic matter in distilled water (DW) and synthetic surface water (SSW) matrices. The experiments revealed that photolysis rates and degradation patterns of ECs were strongly influenced by their physicochemical properties, environmental conditions, and the nature of the water matrix.

7.2.1. The Photolysis of Individual ECs in Distilled Water

The photolysis rates of individual ECs in DW were primarily determined by their ability to absorb light at specific wavelengths and their quantum yields. For example, compounds with high molar absorption coefficients, such as diclofenac and

ciprofloxacin, exhibited rapid degradation under UV light. The temperature of water matrix played a significant role, with elevated temperatures accelerating photolysis rates for most ECs due to enhanced molecular excitation and reaction kinetics. However, the absence of natural water constituents in DW such as DOM and salts, which are present in SSW led to a more predictable photodegradation behavior, providing a baseline for comparing ECs degradation under more complex conditions of SSW. However, the presence of these natural components in SSW provided a more realistic representation of environmental conditions. Therefore, this study demonstrated that relying solely on distilled water experiments can lead to an overestimation of ECs photolysis rates in natural systems.

7.2.2. The Photolysis of Individual ECs in Synthetic Surface Water

A synthetic surface water matrix was prepared according to an environmentally relevant concentrations of salts and organic matter recorded at real river water in Türkiye. In SSW matrices, the presence of dissolved organic matter (DOM), salts, and other constituents significantly altered photolysis behavior of targeted contaminants. DOM served as both a photosensitizer, enhancing indirect photolysis through reactive oxygen species generation, and an inhibitor by competing for light absorption or scavenging reactive species. Salts, such as bicarbonates and nitrates, were also predicted to influence the degradation pathways. For instance, nitrates can enhance indirect photolysis by producing reactive radicals. In contrary to DW, increasing temperature of SSW had an huge inhibitory effect for the photodegradation of all the tested compounds, especially for the contaminants which are affected by indirect photodegradation such as EE2 and diclofenac. The generation of reactive oxygen species from DOM that have a fundamental role in the degradation of organic contaminants was found to be optimum at lower temperatures. Therefore, it is highly recommended to consider the impact of different water components when evaluating the photolysis behavior of ECs in the natural environment under various conditions.

7.2.3. The Mixture Effect on Photolysis Behavior

The behavior of ECs in mixtures demonstrated a persistence effect, where photolysis rates were often slower than those observed for individual compounds. This inhibition

was attributed to competitive light absorption and interference between ECs. Specific interactions, such as the enhancement of ciprofloxacin photodegradation rate in the presence of other compounds, highlighted the potential for complex synergistic effects in mixtures. The maximum MAC values that are recorded for diuron, EE2 and diclofenac along the UV spectrum and particularly in the wavelength range emitted from the photoreactor of this study (UV-A range (360 nm)) are significantly lower than the MAC of ciprofloxacin which is found to be $1.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 310 nm. Thus, the variance in MAC among the co-existing ECs could significantly contribute to their photolysis behavior in natural surface water.

7.2.4. The Presence of Co-Contaminants

Chapter 3 demonstrates the complex dynamics governing the photodegradation of ECs in aqueous systems containing co-contaminants such as polypropylene microplastics (PP-MPs) and silver sulfide nanoparticles (Ag₂S-NPs). The results revealed a dual influence of co-contaminants on the photodegradation rates of ECs, characterized by both inhibitory and enhancing effects, depending on the specific chemical properties of the contaminants and the co-contaminants involved. The addition of PP-MPs significantly inhibited the photodegradation rates of hydrophobic compounds such as diuron, EE2, and ciprofloxacin. This inhibition can be attributed to the strong affinity of these contaminants for attachment to hydrophobic surface of PP-MPs via mechanisms such as electrostatic interactions, hydrogen bonding, and Van der Waals forces. The adsorption of these contaminants onto PP-MPs reduces their exposure to UV irradiation, effectively limiting their availability for photolysis and thereby decreasing their degradation rates. This highlights the importance of considering microplastic-contaminant interactions in environmental risk assessments, as these interactions can significantly alter contaminant persistence in aquatic environment. Conversely, the presence of PP-MPs enhanced the photodegradation rates of terbutryn and diclofenac. This acceleration is likely due to the generation of reactive oxygen species (ROS) upon light irradiation of PP-MPs, as supported by previous studies. Therefore, the study shows that the photodegradation behavior of ECs in the presence of PP-MPs depends on the chemical structure and properties of the contaminants, such as chemical structure and hydrophobicity.

The inclusion of Ag₂S-NPs in the aqueous solution further modified the photodegradation rates of ECs, predominantly inhibiting the photolysis of diuron, EE2, and ciprofloxacin. This inhibition is attributed to the strong light absorption and scattering properties of Ag₂S-NPs, which effectively reduce the availability of UV light for photodegradation processes. However, the photodegradation of diclofenac was enhanced in the presence of Ag₂S-NPs, potentially due to their ability to shift the wavelength of scattered light and interact with compounds exhibiting variable molar absorption coefficients (MACs) across the light spectrum. Diclofenac's relatively low MAC near the tested wavelength (310 nm) and high MAC at 275 nm make it particularly susceptible to wavelength shifts induced by metallic nanoparticles. The coexistence of PP-MPs and Ag₂S-NPs further complicated the photodegradation dynamics. While the combined presence of these co-contaminants completely inhibited the photolysis of diuron, it further enhanced the degradation of diclofenac. These findings confirm the synergistic or antagonistic interactions between multiple co-contaminants, which can amplify or diminish their individual effects on the photochemical behavior of ECs.

7.2.5. Key Implications

The findings of Chapter 3 underline the complexity of ECs photolysis in real-world conditions. The interplay between environmental factors, matrix constituents, and the chemical nature of ECs strongly dictates their photodegradation patterns. These results emphasize the importance of conducting photolysis studies under environmentally relevant conditions to improve the accuracy of risk assessments and predictions for ECs persistence in aquatic systems. Furthermore, the observed mixture effects highlight the necessity of incorporating multi-compound studies in future research to better understand the collective behavior of ECs in natural environments. While the inhibitory effects of co-contaminants like PP-MPs and Ag₂S-NPs on photodegradation emphasize the potential for prolonged persistence of certain ECs in natural waters, which could amplify their environmental risks. Conversely, the observed enhancement in photodegradation for other ECs suggests that co-contaminants can also play a role in promoting contaminant removal under specific conditions. Therefore, the environmental risk assessment studies need to take the possible interaction of ECs and co-contaminants considering the variable factors of environmental conditions and the

distinct physicochemical characteristics of each ECs into account when developing the relevant environmental models.

7.3. Mixture and Co-contaminants Effect on Adsorption of ECs to Natural Soil

The adsorption behavior of selected ECs onto natural soils under normal controlled conditions, focusing on their retention and mobility were investigated in Chapter 3. The study provided critical insights into the mechanisms governing the interaction between ECs and soil matrix, emphasizing the role of physicochemical properties of both the contaminants and the soil. The adsorption process followed pseudo-second-order kinetics for most ECs, suggesting chemisorption mechanisms involving covalent or ionic bonding. The rapid initial phase of adsorption was attributed to abundant available adsorption sites, followed by a slower phase as these sites became saturated. The adsorption of ECs onto soil was strongly influenced by their physicochemical properties such as hydrophobicity, molecular structure, and ionization potential. For example, hydrophobic ECs (e.g., Diclofenac and terbutryn) showed higher adsorption due to their strong affinity for soil organic matter (SOM), while polar or ionizable ECs (e.g., ciprofloxacin) exhibited variable adsorption kinetics depending on the condition.

The presence of multiple ECs in the soil solution reduced the adsorption efficiency of individual compounds due to competition for available adsorption sites. Hydrophobic ECs often outcompeted polar ECs for binding sites on SOM, demonstrating preferential adsorption patterns in multi-contaminant scenarios. The study also highlighted the complex interactions between ECs, polypropylene microplastics (PP-MPs), and silver nanoparticles (Ag-NPs) in soil adsorption processes. For example, the presence of PP-MPs markedly inhibited the adsorption of ciprofloxacin, reducing its rate from 0.244 min^{-1} to 0.064 min^{-1} . This observation aligns with previous studies, which have shown that microplastics can compete with organic micropollutants for adsorption sites on soil surfaces. While the hydrophobic nature of PP-MPs can interact strongly with hydrophobic ECs, potentially causing desorption from the soil surface and reducing soil retention capacity. Interestingly, diuron and terbutryn exhibited only slight decreases in adsorption rates, suggesting that their chemical structures and interactions with PP-MPs mitigate desorption effects compared to ciprofloxacin. Unlike other ECs, the adsorption rate of EE2 increased significantly in the presence of

PP-MPs, resulting in its complete removal from the solution within 30 minutes. The differing behavior of EE2 is attributed to its weak Lewis acidic nature (pK_a 10.33), allowing it to remain undissociated in the pH range of 4.8–9.1. This minimizes electrostatic interactions with PP-MPs. The lack of ionic interactions and its high affinity for non-polar surfaces explain why PP-MPs enhance EE2 adsorption, contrary to their inhibitory effect on other ECs. The addition of Ag2SNPs influenced the adsorption of ECs variably. Ciprofloxacin adsorption was significantly inhibited, suggesting that Ag-NPs' strong soil binding hampers ciprofloxacin's access to adsorption sites. While Ag2SNPs promoted the adsorption of EE2, achieving complete removal within 15 minutes of interaction. This is attributed to the strong affinity of EE2 for Ag-NPs, which serve as additional adsorption sites. Ag2SNPs, when retained on the soil surface, create new binding mechanisms that enhance the soil's overall capacity to retain EE2.

These findings highlight the importance of accounting for competitive adsorption and mixture effects when assessing the environmental fate of ECs. It also demonstrates the critical role of co-contaminants such as PP-MPs and Ag2SNPs in modifying the adsorption behavior of ECs, with significant implications for understanding their environmental fate and transport. This emphasizes the necessity of considering co-contaminants when developing predictive models for the transport and risk assessment of ECs in terrestrial environments. Furthermore, the study highlights that the chemical nature of each EC (e.g., pK_a , hydrophobicity) plays a crucial role in determining its interaction with co-contaminants and soil matrices. The contrasting effects of PP-MPs and Ag2SNPs on different ECs reveal the complexity of contaminant behavior in real-world scenarios, where multiple stressors interact simultaneously. Thus, these results emphasize the critical need for multifactorial studies to predict the environmental behavior of ECs accurately and to develop targeted strategies for mitigating their impacts. Future research should extend these investigations to field-scale studies to validate these findings under natural conditions.

7.3.1. Environmental Implications of Adsorption Behavior

The degree of adsorption directly influences the mobility and bioavailability of ECs in the soil environment. Strongly adsorbed ECs are more likely to accumulate in the topsoil, potentially posing risks to soil-dwelling organisms and plants. Conversely,

weakly adsorbed ECs are more prone to leaching, increasing the risk of groundwater contamination. Moreover, adsorption onto soil can shield ECs from microbial degradation and photolysis, prolonging their environmental persistence. This persistence raises concerns about chronic exposure risks to soil ecosystems. The results underline the need for soil-specific risk assessments to evaluate ECs behavior in different environments accurately. Incorporating soil texture, SOM content, pH variability, the distinct physicochemical properties of each ECs, and the possible existing co-contaminants into environmental models can improve predictions of ECs transport, retention and exposure. This incorporation would aid in the development of effective mitigation strategies to sustainably maintain soil and groundwater resources.

7.4. The Complex Interaction of Climate Change and Co-contaminants

The influence of key climate variables, such as temperature and organic matter content, on the photolysis and adsorption of ECs was systematically evaluated in Chapter 5. The effect of extreme climatic conditions were examined with high and low temperatures (25 °C and 35 °C), and the variation in the water organic matter content was studied with 2 different total organic carbon (TOC) concentrations including 4.5 mg/L and 13 mg/L that corresponds to the TOC concentration in real surface water in Turkey. The results revealed that elevated temperatures and variations in organic matter significantly modulate the degradation kinetics of ECs, highlighting the complexity of their environmental persistence in a changing climate. Elevated temperatures, a key factor associated with climate change, were shown to accelerate the photolysis of several ECs, thereby reducing their persistence in aquatic environments. However, this effect was not uniform across all compounds and water matrices, as interactions with other variables, such as organic matter concentration, altered degradation pathways. The dynamic role of organic matter was particularly noteworthy; while it facilitated indirect photolysis through the production of reactive oxygen species, its presence at high concentrations sometimes inhibited degradation due to light attenuation or competitive interactions. Furthermore, the presence of co-contaminants, such as microplastics and silver sulphide nanoparticles (Ag₂SNPs), introduced an additional layer of complexity to EC behavior. Varying the temperature and organic matter content in the presence of co-contaminants had different impact on

the photolysis rate that were recorded for co-contaminants as single factor. For instance, according to the observation in Chapter 3, the presence of PP-MPs and Ag₂SNP is expected to substantially reduce the photolysis rate of the studied contaminants which resulted possibly from light scattering and the affinity of particles to adsorb the organic micropollutants by various mechanisms such as electrostatic interactions, Van der Waals forces, hydrogen bonding. EE2 has shown strong affinity to present co-contaminants due to its hydrophobicity. However, the temperature had strongly influenced the interaction of co-contaminants with existing EE2. Increasing temperature in the presence of PP-MPs and Ag₂SNP had accelerated the photolysis rate of EE2 from 0.0047 min⁻¹ to 0.0357 min⁻¹ with PP-MP, 0.0061 min⁻¹ to 0.0075 min⁻¹ with Ag₂SNP, and 0.0077 min⁻¹ to 0.0079 min⁻¹ with PP-MP and Ag₂SNP. On the contrary to the strong acidic nature of diclofenac, diuron, terbutryn and ciprofloxacin that are expected to be present in the solution in ionic forms (with pKa values of 4.15, 3.7, 4.4 and 5.56 respectively), EE2 is a weak Lewis acid with pKa of 10.33, it exists in non-dissociation form at pH range of 4.8-9.1. Therefore, the electrostatic attraction will not be effective for its adsorption to the co-contaminants particles present in the solution, while the Van der Waals forces would be the dominant mechanisms for EE2 attachment to these particles. As rising temperature increases the kinetic energies and instability of molecules, which reduce the effect of intermolecular forces of attraction, thus, the strength of Van der Waals adhesive forces to bring different molecules together are anticipated to decrease with higher temperatures. Therefore, the compounds that are not at the ionic form to create electrostatic interaction with the present micro and nanoparticles will depend mainly on Van der Waals mechanism, and subsequently their adsorption to PP-MPs and Ag₂SNP is expected to be lower at higher temperature, which will make them more available for photodegradation by light. Hence, varying temperature in the presence of various co-contaminants in the irradiated solution can have multiple outcomes on the photolysis rate of existing contaminants depending on the physicochemical properties of the compounds, the presence of water photosensitizers (e.g. organic matter), and the possible interaction mechanisms that could be established between the ECs and the coexisting particles in the aqueous solution.

These findings reveal that the interplay of climate-driven variables and co-contaminants can significantly modify the environmental persistence, mobility, and

bioavailability of ECs, often in ways that are unpredictable under static or single-variable scenarios. These insights emphasize the critical need for multifactorial and holistic approaches in environmental risk assessment to account for the synergistic effects of these variables. As climate change intensifies, and variable contaminants are being continuously introduced to the natural surface water, understanding these interactions will be essential for predicting ECs behavior in natural systems and developing effective mitigation strategies to protect ecosystems and human health.

7.4.1. Environmental Implications

The observed interplay between climate variables, organic matter, and co-contaminants emphasizes the need for dynamic and real-time environmental monitoring frameworks. These protocols should consider temporal and spatial variations in temperature, organic matter, and the presence of co-contaminants to accurately predict ECs behavior in natural environment. Moreover, risk assessments strategies should move beyond fixed evaluations to incorporate multifactorial analyses that include the synergistic and converse effects of temperature, organic matter, and co-contaminants. This will help predict the persistence, bioavailability, and toxicity of ECs under varying climatic and environmental conditions. The findings of Chapter 5 could help in developing predictive models to assess the future fate of ECs under projected climate scenarios, integrating data on elevated temperatures, organic matter variations, and co-contaminant dynamics. Therefore, it can contribute in establishing early warning systems that use climate and water/soil properties data to predict potential hotspots of ECs accumulation in the natural environment, allowing for proactive mitigation measures. Furthermore, the findings of Chapter 5 could be incorporated into the design of wastewater treatment processes to target ECs effectively under varying environmental conditions. For instance, utilize technologies that optimize photolytic degradation at elevated temperatures, design processes to counteract the inhibitory effects of high organic matter concentrations, such as advanced oxidation techniques, exploit the catalytic properties of silver sulphide nanoparticles (Ag₂SNPs) in treatment systems while managing their potential to influence the persistence and toxicity of ECs, and develop filtration or remediation techniques to remove microplastics from aquatic systems, reducing their role as carriers for hydrophobic ECs.

7.5. Interwoven Impact of ECs and PP-MPs on Soil Biota

The ecological impacts of ECs on soil microbiota and plant systems were examined in Chapter 6. The combined presence of microplastics and ECs elevated microbial and plant stress, emphasizing the importance of studying contaminant mixtures. These findings highlight the ecological risks posed by ECs, with implications for soil health, plant productivity, and broader ecosystem services.

7.5.1. The Soil Microbial Community

The results in Chapter 6 highlight the complex and dynamic effects of ECs and PP-MPs on soil microbial communities and their metabolic activity. The addition of the ECs mixture (Mix) alone at environmentally relevant concentrations did not significantly alter microbial activity (as indicated by soil respiration rate), or changed the microbial community composition. This finding is consistent with previous studies showing that low EC concentrations often have limited effects on soil microbial communities due to their relatively high biodegradability and minimal contribution to the soil carbon pool. Notably, significant impacts on microbial composition and respiration have typically been reported only at higher contaminant concentrations (10–150 mg/kg), underlining the dose-dependent nature of ECs effects on soil health.

Similarly, PP-MPs alone did not induce detectable changes in microbial composition or respiration compared to the control. This suggests that, at the concentrations tested, PP-MPs neither provide a substantial carbon or energy source nor impose sufficient abiotic stress to affect microbial activity. In contrast, the combination of ECs and PP-MPs (Mix+PP-MPs) produced synergistic effects, significantly shifting microbial community composition and increasing soil respiration rates compared to either contaminant alone. This stimulatory effect on respiration was most pronounced during the initial phase of incubation (days 1–3), diminishing by day 15, while changes in bacterial community composition and diversity persisted throughout the experiment.

The biodegradation results further support this interpretation. In sterile soils, no significant degradation of ECs was observed, confirming that microbial activity was the main driver of contaminant breakdown. In non-sterile soils, ciprofloxacin, diclofenac, diuron, and EE2 showed substantial microbial degradation, with reductions of 50–90% by day 15, while terbutryn remained comparatively stable, reflecting its

low biodegradability and stronger sorption affinity. Importantly, the presence of PP-MPs often reduced microbial degradation of ECs, except for EE2, where degradation proceeded similarly in Mix and Mix+PP treatments. These findings demonstrate that PP-MPs can modulate the persistence of contaminants in soils, either by altering adsorption-desorption dynamics or by affecting microbial accessibility to ECs.

The synergistic effects of Mix+PP-MPs on microbial respiration and community structure can be explained by several mechanisms: (i) increased bioavailability, where PP-MPs interact with soil particles and desorb certain ECs, enhancing microbial access; (ii) abiotic stress adaptation, where combined contaminant stressors stimulate microbial metabolic activity; and (iii) a priming effect, in which microbial degradation of ECs associated with PP-MPs accelerates the breakdown of native soil organic matter, thereby amplifying respiration rates.

Moreover, the findings from Chapters 3 and 6 demonstrate the strong interconnection between contaminant adsorption dynamics and microbial biodegradation. For instance, ciprofloxacin exhibited reduced adsorption in the presence of PP-MPs, enhancing its mobility and biodegradability, while EE2 displayed increased adsorption, limiting its availability for microbial utilization. These contrasting behaviors emphasize how the physicochemical interactions between ECs and PP-MPs directly govern their environmental fate, persistence, and microbial accessibility.

In conclusion, the results from Chapter 6 and Chapter 3 provide evidence that co-contaminants such as microplastics significantly influence the environmental behavior of emerging contaminants in soils. By modulating adsorption, mobility, and bioavailability, PP-MPs alter both the biodegradation of ECs and the structure and function of soil microbial communities. This work highlights the importance of considering contaminant mixtures in risk assessments, as their combined effects can diverge substantially from those of single contaminants. Ultimately, these findings contribute to a deeper understanding of the ecological impacts of ECs and microplastics in terrestrial ecosystems and highlight the need for integrated approaches to evaluate their long-term effects on soil health and microbial functioning.

7.5.2. Plants Growth and Biomass

Chapter 6 discussed the complex interactions between ECs and PP-MPs and their combined effects on maize plant growth and biomass. The findings demonstrate that the combination of Mix (ECs) and PP-MPs significantly influences plant health, particularly through its impact on soil, rhizosphere microbial communities, and contaminant bioavailability. The addition of Mix alone did not significantly reduce dried leaves biomass, indicating that low concentrations of ECs may not exert a pronounced toxic effect on plant growth. However, the combination of Mix and PP-MPs significantly decreased the dried biomass of maize leaves and shoots ($P = 0.032$). This highlights a synergistic toxic effect arising from the interaction between ECs and PP-MPs in the soil. The strongest toxic effect was observed in maize roots, where the Mix+PP-MPs treatment caused a significant reduction in root biomass. The reduction in plant biomass, particularly in the Mix+PP-MPs treatment, can be attributed to adverse effects on the soil and rhizosphere microbial communities. The observed alterations in the soil microbial activity (Section 7.5.1) due to the combination of ECs and PP-MPs, suggest that changes in the functional activity of soil microbial community may indirectly influence plant growth. Moreover, the beneficial root-associated microorganisms, such as nitrogen-fixing bacteria and mycorrhizal fungi, are essential for plant growth and health. The observed microbial disruptions may have impaired these functions, reducing nutrient availability and uptake by the plants. As observed in Chapter 3, PP-MPs were shown to increase the adsorption of some ECs by soil, potentially causing ECs to persist longer in the soil. The prolonged presence of ECs in the soil can amplify their toxic effects on the soil microbial community, creating a feedback loop that negatively impacts plant health. The results emphasize the need to consider the presence of microplastic particles with a comprehensive examination of their interactions with soil matrix, chemical contaminants and soil microbial community when assessing the impact of soil pollution on agricultural productivity and ecosystem health.

7.5.3. The Rhizosphere Volatile Organic Compounds.

The effect of ECs and PP-MPs on the rhizosphere microbial community secondary metabolites, particularly volatile organic compounds (VOCs) was highlighted in

Chapter 6. VOCs is known to have an essential role in shaping plant-microbe interactions and plant health. The results demonstrated how ECs and plastic residues, significantly alter the chemical composition of volatiles in the rhizosphere. These changes, in turn, impact plant growth and development. Heneicosane, a long-chain hydrocarbon naturally occurring in plants, was found to be significantly suppressed in treatments involving ECs and plastic residues. This compound is known to enhance plant growth, protect against environmental stresses, and form part of the cuticular wax layer critical for maintaining water retention and pathogen defense. Its reduced intensity in ECs+PP-MPs treatments correlates with the lower biomass of maize roots and shoots. This further highlights the detrimental effects of ECs and PP-MPs combination on the generation of beneficial volatiles in the rhizosphere.

γ -Palmitolactone, a lactone compound with known bioactive properties, was identified in PP-MPs treatments. Although its positive impacts on plants have been documented, the presence of this compound in elevated concentrations may have unknown adverse effects. The observed decline in plant biomass in PP-MPs treatments suggests the need for further investigation into the role of γ -Palmitolactone in contaminated rhizospheres. Treatments containing mixed contaminants (ECs+PP-MPs) recorded higher intensities of phenolic compounds 2-Methoxyphenol and 2,4-DTBP. 2-Methoxyphenol is a concentration-dependent effect compound. While it can provide antioxidant protection at low concentrations, higher intensities as detected in this study, are toxic to plants. This toxicity inhibits seed germination, root elongation, and overall growth. While 2,4-DTBP is strongly phytotoxic, suppressing seed germination, causing chlorosis and necrosis, and weakening plant immune systems, making them more vulnerable to diseases. The presence of these two VOCs in the rhizosphere likely contributed significantly to the observed reductions in plant biomass with ECs+PP-MPs treatment.

Therefore, the contaminants not only altered the release of VOCs but also introduced specific volatile profiles associated with reduced plant performance. These changes included the production of phytotoxic volatiles and the suppression of beneficial compounds, highlighting the complex interplay between contaminants, rhizosphere chemistry, and plant health. Thus, it is recommended to investigate the long-term effects of altered volatile profiles on soil microbial communities and plant-microbe interactions, exploring the specific mechanisms through which high concentrations of

γ -palmitolactone impact plant health, and assessing the cumulative effects of mixed contaminants on rhizosphere chemistry and plant growth under different environmental conditions.

7.5.4. Complex Interplay between Adsorption, Microbial Dynamics, Biodegradation, VOCs Emissions, and Plant Biomass

Chapter 3 demonstrated that the presence of PP-MPs altered the adsorption of several ECs in soil. For some compounds, PP-MPs can reduce retention and increase mobility, elevating their bioavailability to soil microorganisms. While for others, PP-MPs can promote their aggregation on its surface, creating concentrated zones of ECs in the soil matrix. Both outcomes highlight the ability of PP-MPs to modify contaminant fate, and thereby indirectly shape microbial processes in soils.

These findings align with the results of Chapter 6, where the combination of ECs and PP-MPs (Mix+PP-MPs) significantly altered microbial community composition and functional activity, whereas ECs or PP-MPs alone caused no major changes. In particular, microbial biodegradation patterns were strongly influenced by PP-MPs. Ciprofloxacin, diclofenac, diuron, and EE2 showed substantial microbial degradation in non-sterile soils, while terbutryn remained comparatively stable due to its low biodegradability and strong sorption affinity. Importantly, PP-MPs reduced the microbial degradation of several ECs by altering their adsorption–desorption dynamics, except for EE2, which exhibited comparable biodegradation in Mix and Mix+PP treatments. These observations demonstrate that adsorption behavior in the presence of PP-MPs is closely tied to contaminant bioavailability and microbial utilization. This stimulated microbial metabolism also shifted the synthesis and release of VOCs in the maize plants rhizosphere. Beneficial volatiles such as heneicosane, which contribute to plant growth, water retention, and pathogen resistance, were suppressed, while phytotoxic compounds such as 2-methoxyphenol and 2,4-DTBP were enriched. These changes correlate with the reduction in maize root and shoot biomass under Mix+PP-MPs treatments. While microbial respiration stabilized after day 7, reflecting adaptation to contaminant stress, the altered microbial community structure and VOCs profile persisted throughout the experiment. This indicates a legacy effect in the rhizosphere, where microbial adaptation to stressors does not necessarily reverse their indirect negative impacts on plants.

Collectively, the results of Chapter 3 and Chapter 6 show that the presence of PP-MPs disrupts contaminant adsorption, increases microbial exposure to ECs, alters biodegradation efficiency, and modifies microbial community composition. These microbial shifts, in turn, affect VOCs emissions and plant biomass, creating a series of linked ecological effects.

7.6. Environmental Implications

The findings from Chapter 6 underscore the complex ecological impacts of combined ECs and PP-MPs on soil microbiota and plant systems, with important implications for soil health, agricultural productivity, and ecosystem services. While ECs alone at environmentally relevant concentrations did not significantly affect microbial communities or respiration, their combination with PP-MPs produced synergistic effects, substantially altering microbial composition, biodegradation patterns, and rhizosphere functioning.

The interplay between adsorption dynamics (Chapter 3), microbial community shifts, and biodegradation outcomes (Chapter 6) illustrates how PP-MPs can act as long-term carriers and modulators of contaminant bioavailability. Reduced adsorption of compounds such as ciprofloxacin enhanced their biodegradation, while enhanced adsorption of EE2 restricted microbial utilization. These contrasting behaviors demonstrate that PP-MPs may either accelerate or inhibit microbial degradation depending on contaminant properties, thereby reshaping soil carbon cycling. The initial rise in microbial respiration under Mix+PP-MPs treatments suggests a priming effect, where contaminant degradation accelerates the breakdown of native organic matter. Over time, this could deplete soil carbon reserves, impair soil fertility, and reduce carbon sequestration capacity.

Furthermore, the persistence of altered microbial communities and VOCs emissions has downstream consequences for plant health. Suppression of growth-promoting volatiles and enrichment of phytotoxic compounds contributed to the observed reduction in maize biomass. This points to indirect mechanisms by which PP-MPs and ECs jointly impair soil-plant interactions. While microbial respiration stabilized over time, the VOCs and biomass effects did not recover, highlighting the potential for irreversible consequences on terrestrial ecosystems.

In environmental terms, these findings emphasize that microplastics are not inert particles but active modulators of contaminant fate, microbial metabolism, and soil-plant interactions. Their strong affinity for organic contaminants, persistence in soils, and ability to alter microbial accessibility to ECs suggest long-term risks for soil ecosystem services, including nutrient cycling, organic matter decomposition, and pollutant attenuation. If persistent, these effects may undermine soil fertility, reduce crop productivity, and destabilize terrestrial carbon budgets.

In conclusion, while ECs alone may have limited short-term effects at low concentrations, their interaction with PP-MPs significantly amplifies their environmental impacts, leading to altered biodegradation, microbial dynamics, VOCs emissions, and plant biomass reduction. These results underscore the importance of accounting for co-contaminant interactions in environmental risk assessments. Future studies should focus on long-term and field-scale validation, mechanistic understanding of ECs-microplastic-microbe interactions, and the development of mitigation strategies to reduce risks posed by ECs and microplastics in terrestrial ecosystems.

8. CONCLUSION AND RECOMMENDATION FOR FURTHER STUDIES

This thesis demonstrates the complex interplay of environmental factors, co-contaminants, and the intrinsic chemical nature of emerging contaminants (ECs) in shaping their environmental fate and impacts. By integrating climate variables (temperature and organic matter), co-contaminants such as microplastics (PP-MPs) and silver nanoparticles (Ag-NPs), and different environmental matrices, this research provides a comprehensive view of ECs' photolysis by sunlight, adsorption to the natural soil, biodegradation, and their terrestrial ecological risks. Findings clearly reveal that both climate change and co-contaminants significantly alter ECs' environmental behavior, highlighting the need for multifactorial studies to accurately predict their persistence, mobility, and ecological risks. Importantly, the results also emphasize the necessity of accounting for contaminant mixtures and interactions with physical stressors (e.g., microplastics), as single-contaminant studies underestimate the real-world complexity.

The results obtained in this thesis contribute directly to multiple Sustainable Development Goals (SDGs). For SDG 6 (Clean Water and Sanitation), the photodegradation experiments provide critical insights into natural attenuation processes in aquatic systems. These data show how temperature, organic matter, and co-contaminants influence photolysis rates, affecting contaminant persistence and transport in natural surface water. Such knowledge supports the design of targeted water treatment technologies (e.g., advanced oxidation, adsorption-based filtration) adapted to local environmental conditions. Similarly, for SDG 14 (Life Below Water), insights into reduced photodegradation of some ECs in organic matter rich environments demonstrate how these compounds may accumulate in marine systems, increasing bioavailability and toxicity to aquatic organisms. These findings can inform stricter discharge limits and improved wastewater treatment to mitigate marine pollution.

This thesis also addresses SDG 13 (Climate Action) by showing how climate variables shape the fate of ECs. Rising temperatures were shown to either accelerate or inhibit photolysis, depending on organic matter content, while changes in dissolved or soil

organic matter influenced adsorption-desorption dynamics. This demonstrates how climate change induced shifts will directly affect ECs behavior in both terrestrial and aquatic systems, with additional implications for persistence and exposure.

For SDG 15 (Life on Land), the adsorption results from Chapter 3 and the toxicity results from Chapter 6 highlight the direct and indirect risks of ECs and co-contaminants to soil ecosystems. Adsorption experiments revealed that PP-MPs and Ag-NPs altered ECs retention in soils, reducing adsorption of some contaminants (e.g., ciprofloxacin) while enhancing adsorption of others (e.g., EE2). These changes strongly influenced microbial degradation outcomes in Chapter 6, where ciprofloxacin, diclofenac, diuron, and EE2 exhibited significant biodegradation in non-sterile soils. Crucially, the presence of PP-MPs reduced the microbial degradation efficiency of most ECs, except for EE2, by disrupting their adsorption-desorption balance. These findings demonstrate that microbial accessibility, and therefore contaminant persistence is not only chemically determined but is also mediated by physical co-contaminants such as microplastics.

Shifts in microbial community composition and activity further reinforced these biodegradation results. The Mix+PP-MPs treatment caused a distinct restructuring of bacterial communities, increased respiration during the early incubation phase, and altered VOCs emissions in the rhizosphere. While microbial respiration rates stabilized over time due to adaptation, microbial community composition and VOCs profiles remained altered throughout the experiment, leaving a persistent legacy effect. Beneficial VOCs such as heneicosane, which promote plant growth and stress tolerance, were suppressed, while phytotoxic volatiles such as 2-methoxyphenol and 2,4-DTBP increased. These changes directly correlated with the observed reduction in maize biomass under Mix+PP-MPs conditions. Together, these results demonstrate that co-contaminants like PP-MPs not only reshape contaminant bioavailability and microbial degradation efficiency but also indirectly impair plant growth via changes in microbial community structure and rhizosphere chemistry.

These integrated findings have profound environmental implications. Reduced adsorption under certain conditions increases contaminant mobility and risk of groundwater contamination, while increased adsorption may cause long-term soil contamination. Altered microbial degradation patterns and VOCs emissions demonstrate how soil health, fertility, and plant-microbe interactions can be disrupted,

potentially accelerating land degradation and desertification in vulnerable ecosystems. This undermines biodiversity and ecosystem stability, key targets of SDG 15.

Future research should build on these insights by extending laboratory findings to field-scale studies under natural environmental variability. Predictive models must integrate multifactorial influences, including climate change scenarios, co-contaminants, and biological feedback to accurately forecast ECs fate and ecological risks. Particular emphasis should be placed on developing mitigation strategies targeting microplastic pollution, investigating the chronic impacts of ECs and co-contaminants on soil microbial networks and plant health, and expanding the scope to include other ubiquitous contaminants and stressors. Finally, this thesis highlights the urgent need to update Life Cycle Assessment (LCA) datasets to include the effects of co-contaminants and climate change. Current LCAs often treat stressors in isolation, overlooking synergistic interactions that drastically alter contaminant fate, persistence, and ecological impact. By accounting for these complexities, LCAs will provide more accurate evaluations of environmental burdens, particularly for industries contributing to chemical emissions and plastic waste.

In conclusion, this thesis shows that the environmental fate and ecological impacts of ECs are not fixed properties, but context-dependent outcomes shaped by climate, co-contaminants, soil processes, and microbial community responses. By linking photolysis, adsorption, microbial biodegradation, VOCs emissions, and plant biomass, it provides a holistic framework to understand and predict the cascading effects of ECs and microplastics on terrestrial and aquatic ecosystems.

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BIOGRAPHY

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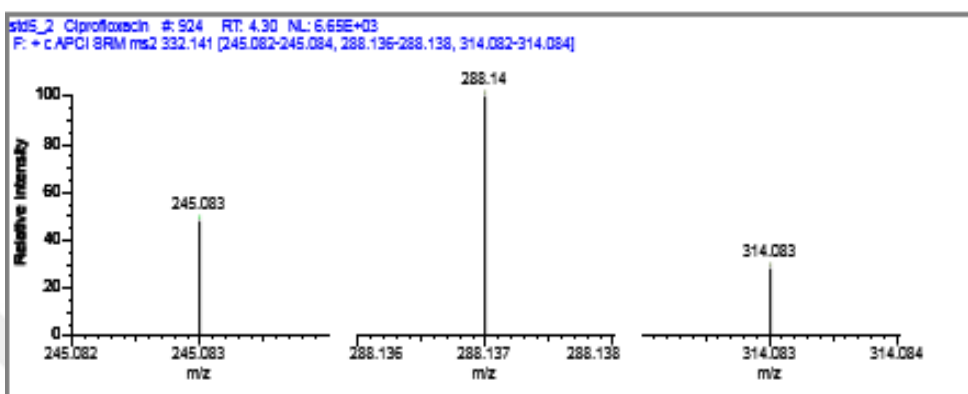
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APPENDICES

APPENDIX-A: Instrumental Conditions, Peak Shapes, And Calibration Curves Of Emerging Contaminants

MS-Data

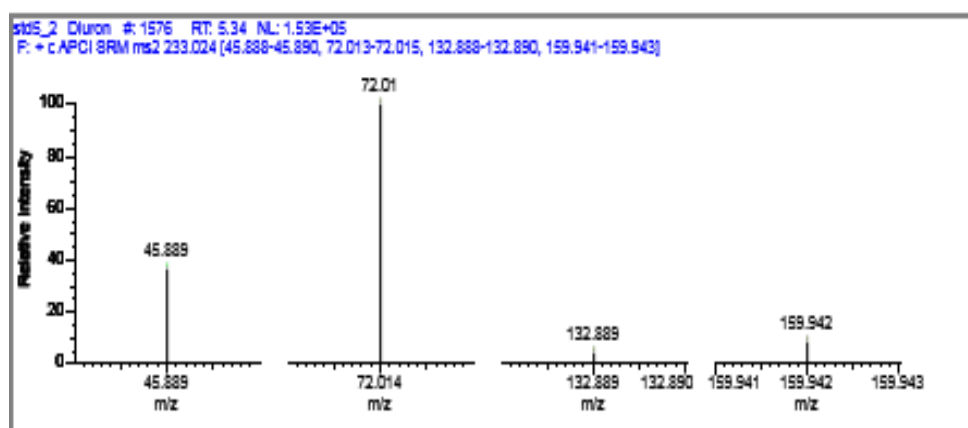


MS-Reference

std250ppb5.raw

Figure A.1: MS spectrum for ionization products of ciprofloxacin.

MS-Data

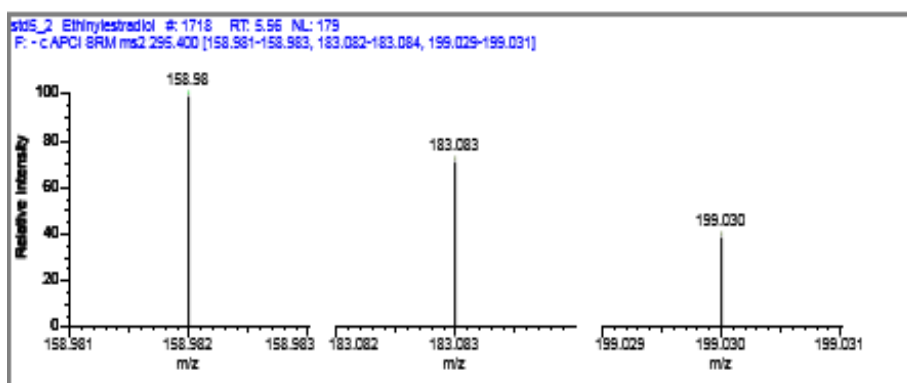


MS-Reference

std250ppb5.raw

Figure A.2: MS spectrum for ionization products of diuron.

MS-Data

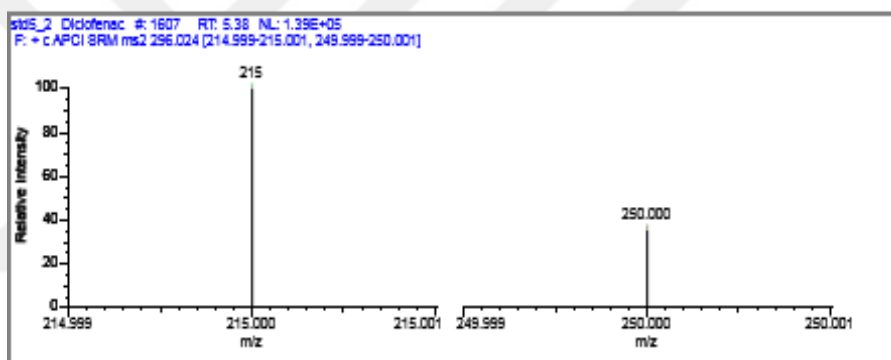


MS-Reference

std250ppb5.raw

Figure A.3: MS spectrum for ionization products of EE2.

MS-Data

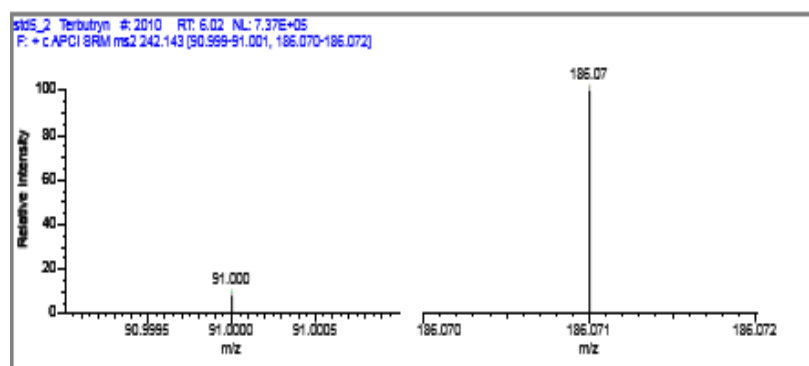


MS-Reference

std250ppb5.raw

Figure A.4: MS spectrum for ionization products of diclofenac.

MS-Data



MS-Reference

std250ppb5.raw

Figure A.5: MS spectrum for ionization products of terbutryn.

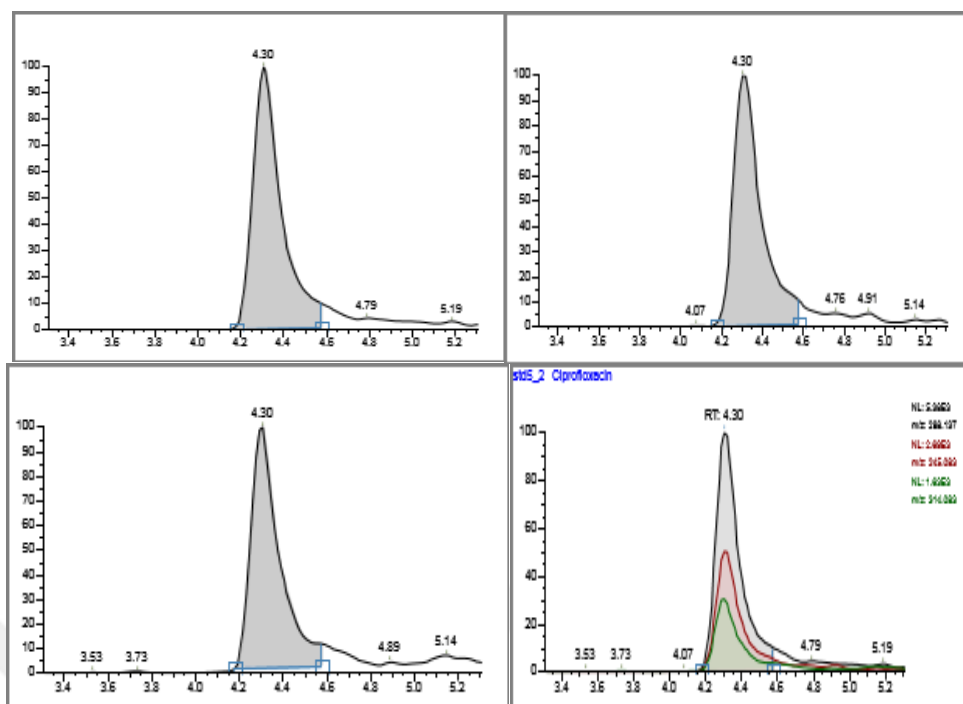


Figure A.6: Peaks of the optimized ionization products of ciprofloxacin in MS.

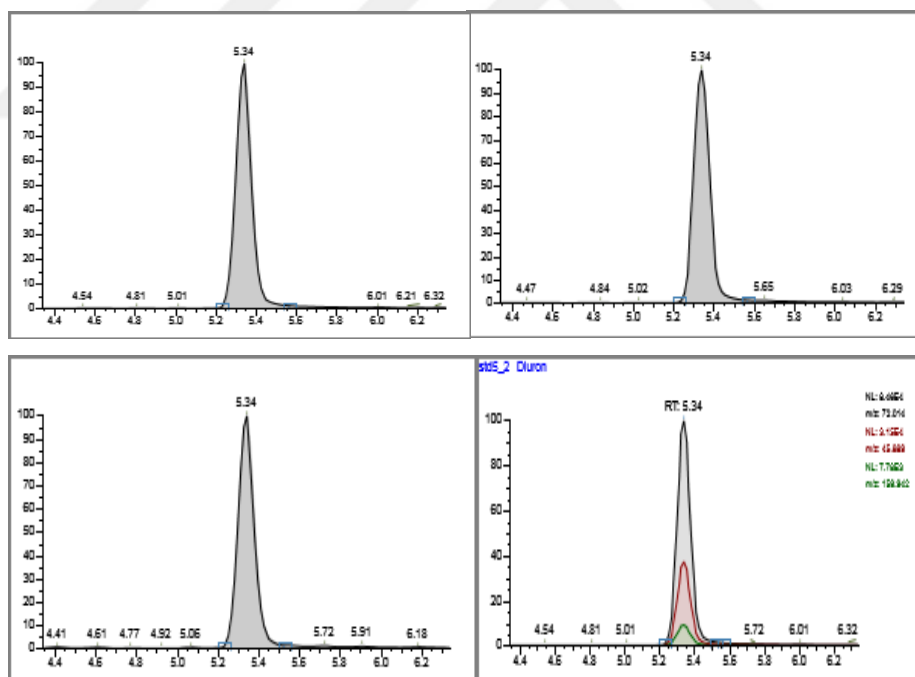


Figure A.7: Peaks of the optimized ionization products of diuron in MS.

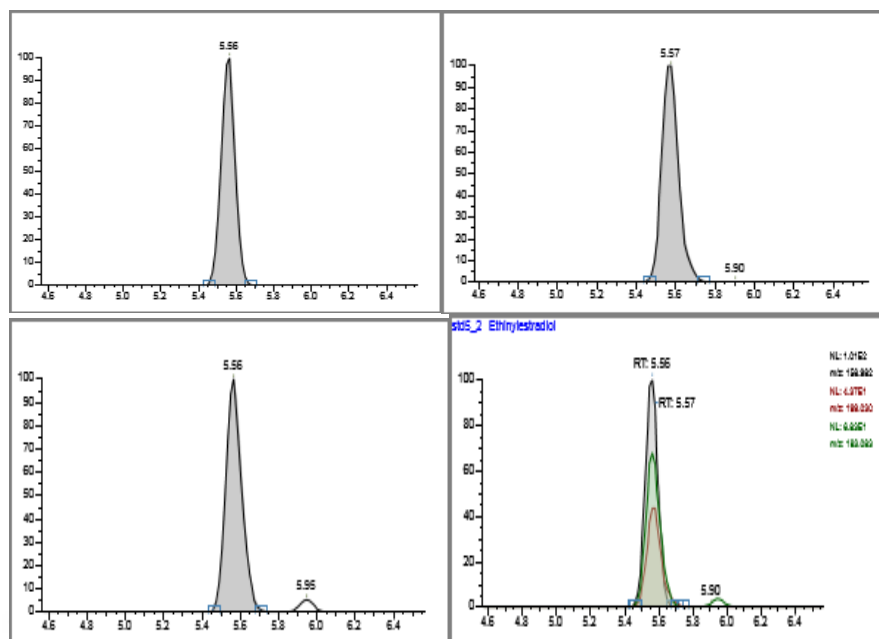


Figure A.8: Peaks of the optimized ionization products of EE2 in MS.

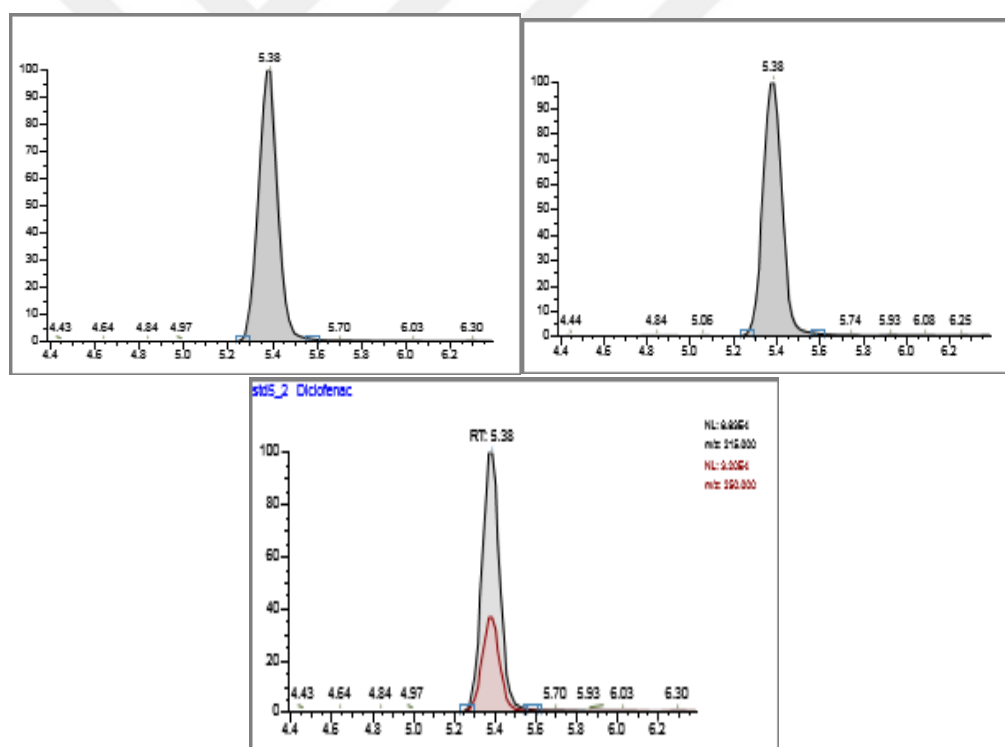


Figure A.9: Peaks of the optimized ionization products of diclofenac in MS.

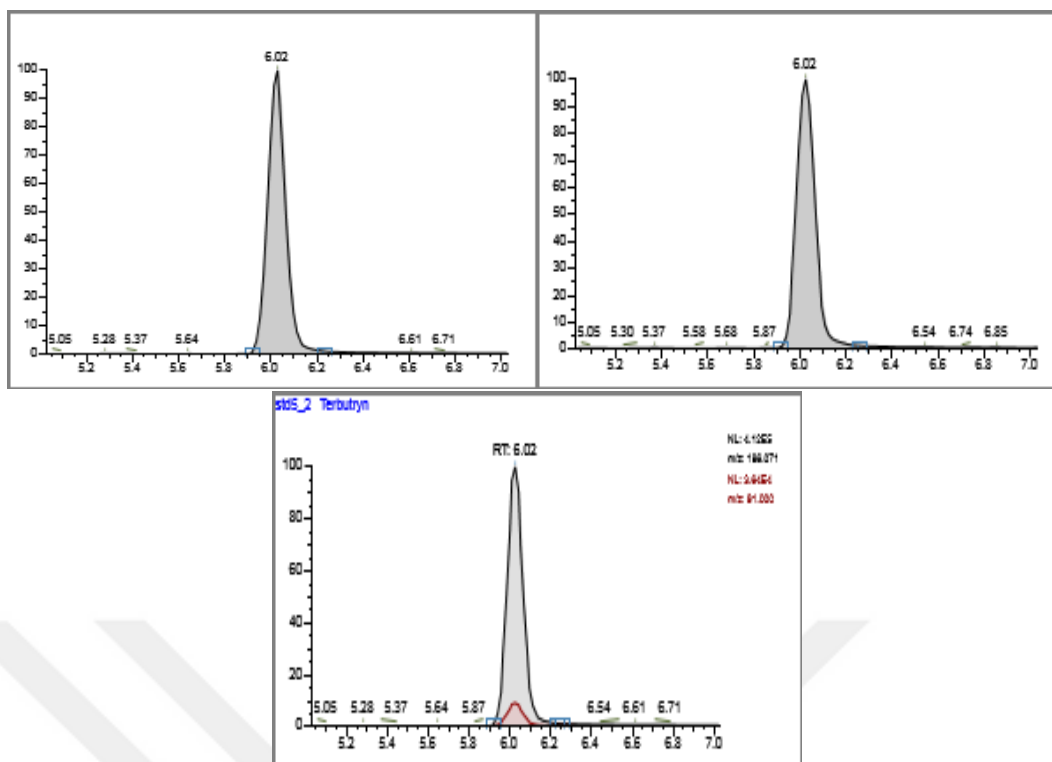


Figure A.10: Peaks of the optimized ionization products of terbutryn in MS.

General Settings | Inject Mode | User Defined Program | Temperature Control

☒ Use Temperature Control ⓘ

Temperature ⓘ [4.0...45.0 °C]

Max. Deviation ⓘ [None...10.0 °C]

Safety Limits

Lower Limit ⓘ [4.0...45.0 °C]

Upper Limit ⓘ [4.0...45.0 °C]

Figure A.11: Autosampler conditions for LC in the optimized measurement method.

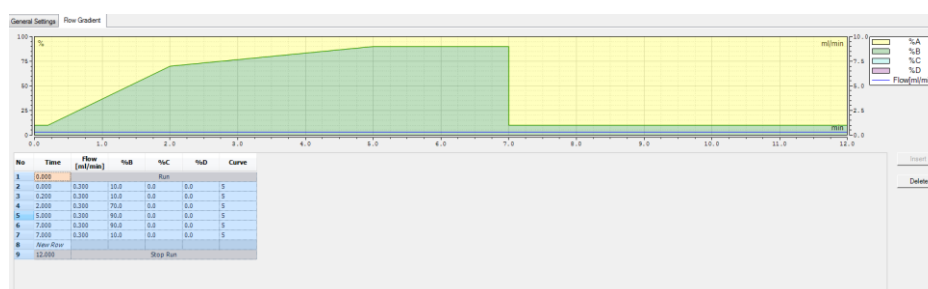


Figure A.12: Carrier phase current gradient for LC in the optimized measurement method.

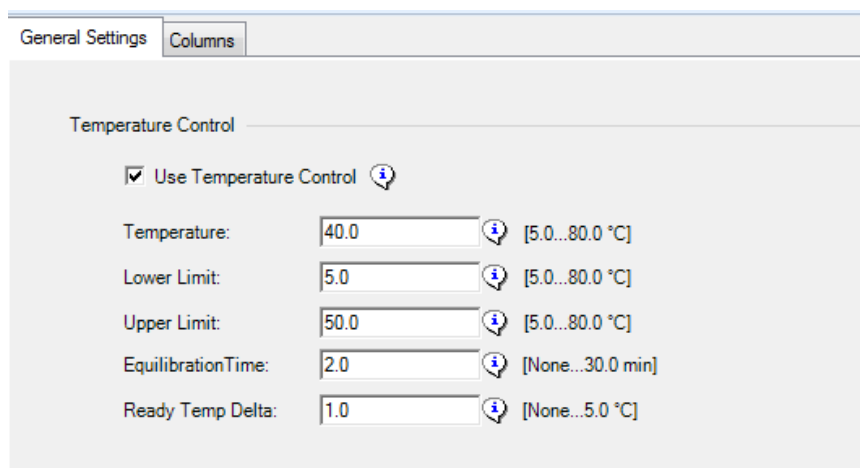


Figure A.13: Column temperature for LC in the optimized measurement method.

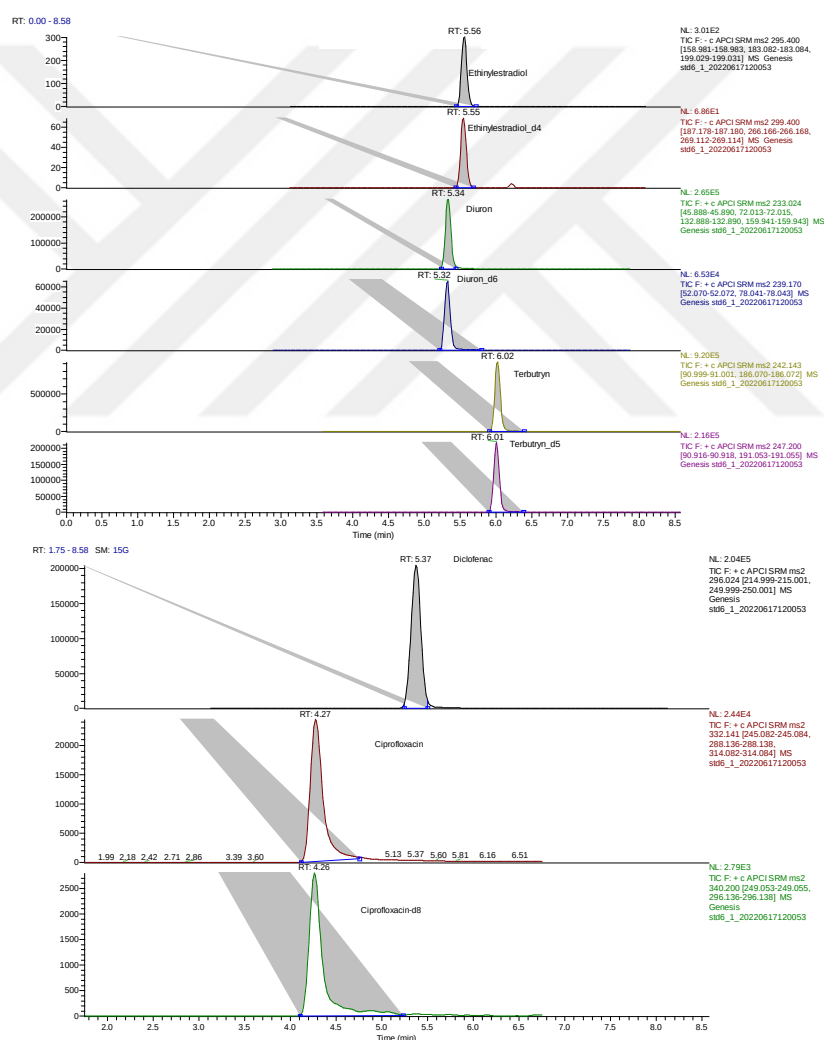


Figure A.14: Chromatogram obtained when injection was made from the column in LC-MS-MS with the developed method.

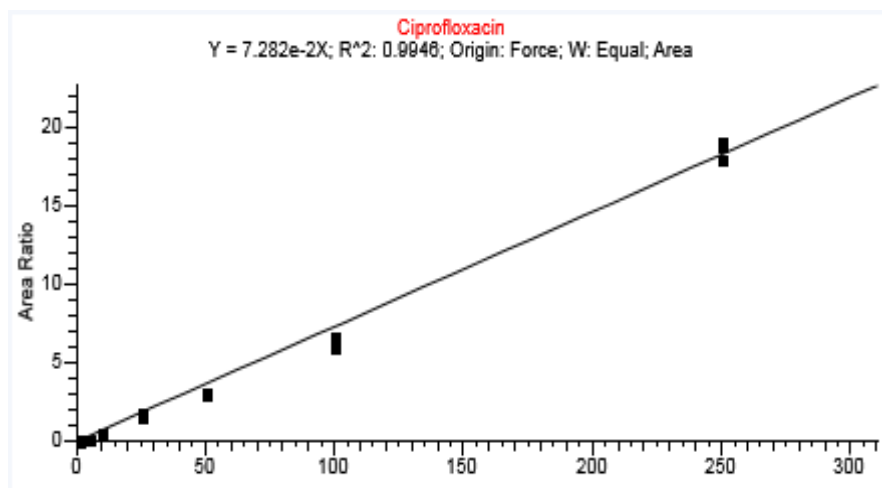


Figure A.15: Ciprofloxacin calibration curve generated by LC-MS/MS.

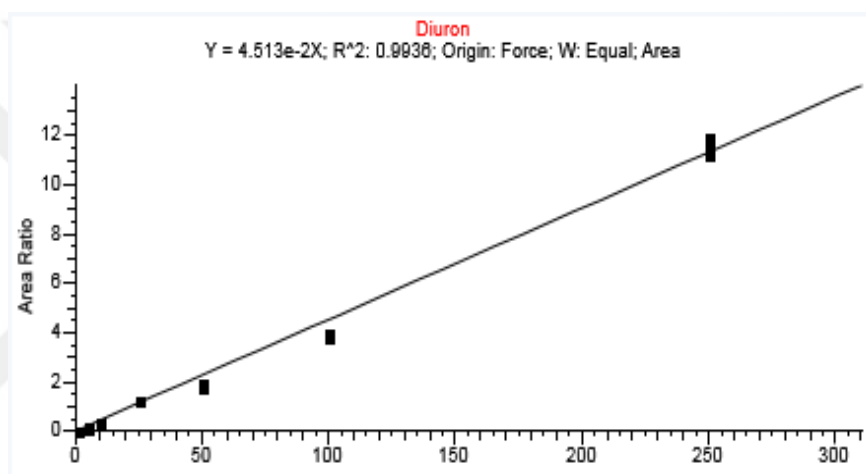


Figure A.16: Diuron calibration curve generated by LC-MS/MS.

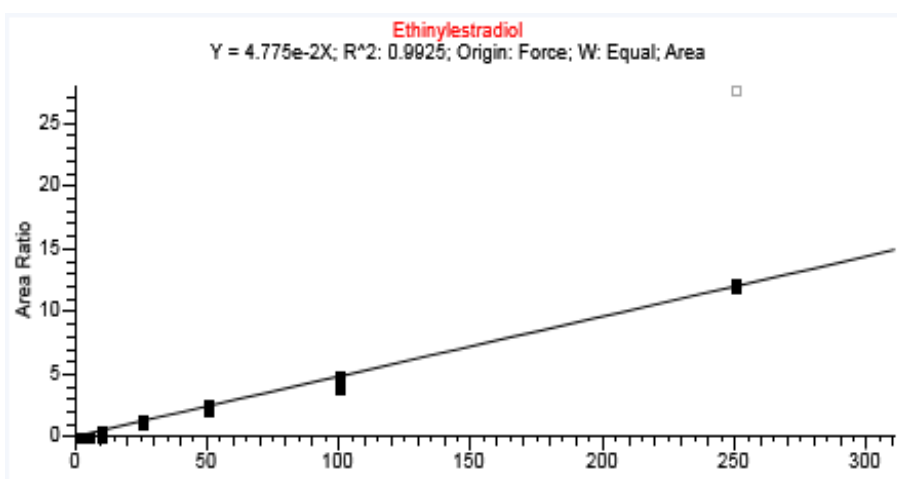


Figure A.17: EE2 calibration curve generated by LC-MS/MS.

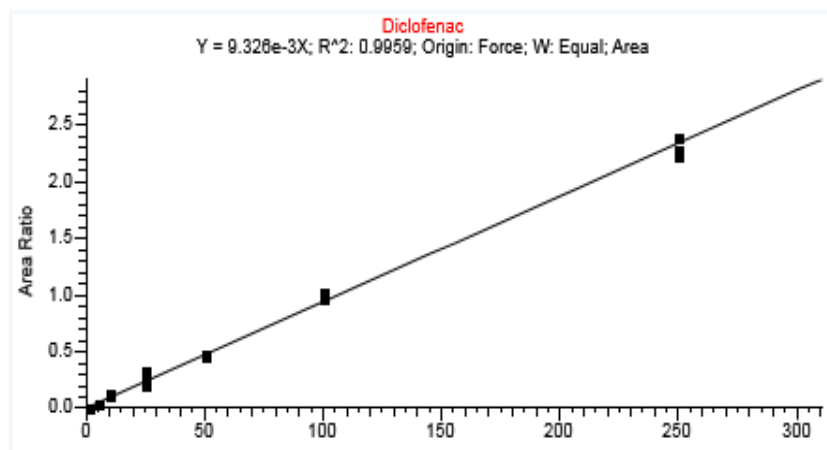


Figure A.18: Diclofenac calibration curve generated by LC-MS/MS.

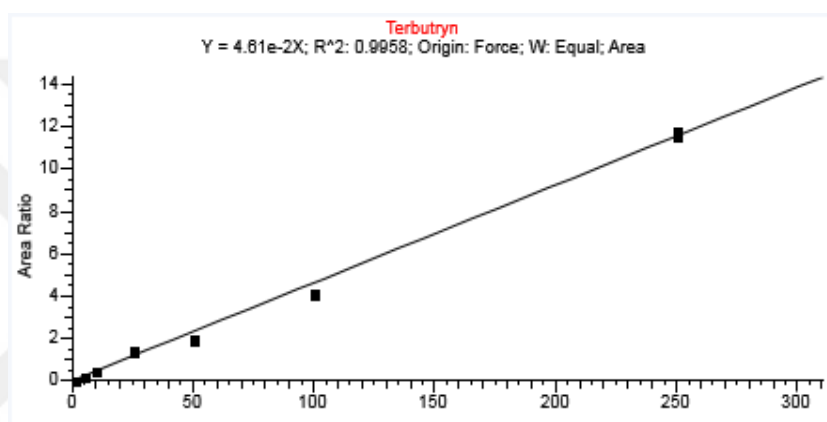


Figure A.19: Terbutryn calibration curve generated by LC-MS/MS.