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Engineering

Master Thesis:

**Investigation on the removal of selected organic micropollutants from
trickling filters and sand filters**

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Declaration of authorship

I hereby declare that this is my own work and the application of other material from other sources has been thoroughly acknowledged.

Signature:

Date:

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Abstract

Recently several different types of organic micropollutants are detected in the aquatic environment as a result of inadequate wastewater treatment. The adverse effects of the various micropollutants such as pharmaceuticals, personal care products, pesticides, herbicides and industrial chemicals with concentrations less than $1 \mu\text{gL}^{-1}$ on the ecosystem are challenging to be assessed. Thus, sufficient approaches are indispensable to curtail the negative impacts that these substances may have on the environment and human health. Much research was done especially in the recent years on the fate and removal of these emerging contaminants from wastewater by different measures.

In this work, a systematic literature review (SLR) is conducted to determine the current state of research in micropollutant removal around the globe which discovers the existing approaches for micropollutant treatment and enables applying an unbiased evaluation. Then one of the identified approaches (sand filter and trickling filter) which is the objective of this study was investigated, and the removal behavior of micropollutants by this method was experimented.

The influent and effluent of the trickling filters and sand filters in LFKW wastewater treatment plant were taken and the effect of biodegradation and sorption on the removal of the compounds was investigated. Micropollutant analysis regarding non-polar substances was performed by gas chromatography-mass spectrometry (GCMS) while high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MSMS) was applied instead for polar compounds. Furthermore, the molecular orbital energies of the substances were investigated. UV/Vis spectrophotometry and DOC analysis were other experimental approaches that have been used in order to shed some light on the behavior of these contaminants.

As a result of this study, micropollutants are classified in different groups based on their physical-chemical properties, providing it as an essential factor affecting micropollutant removal behavior. Moreover, different correlations between the physical-chemical properties and the micropollutants elimination are assessed.

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List of abbreviations

AOP	Advanced Oxidation Process
DOC	Dissolved Organic Carbon
GCMS	Gas Chromatography-Mass Spectrometry
HOMO	Highest Occupied Molecular Orbital
HPLC-MSMS	High Performance Liquide Chromatography coupled with tandem Mass Spectrometry
Koc	Organic-Carbon Partition Coefficient
Kow	Octanol-Water Partition Coefficient
LUMO	Lowest Unoccupied Molecular Orbital
MPs	Micropollutants
PCP	Personal Care Products
PPCP	Pharmaceuticals and Personal Care Products
RSF	Rapid Sand Filter
SAC	Spectral Absorption Coefficient
SF	Sand Filter
SLR	Systematic Literature Review
SPE	Solid Phase Extraction
SSF	Slow Sand Filter
TF	Trickling Filter
WWT	Wastewater Treatment

1. Introduction

Increasing chemical contamination of ground and surface waters due to the ascending global consumptions of chemical products causes unknown effects on aquatic life and human health. Pollution of natural water by many different classes of chemical compounds, although most of which have deficient concentrations, leads to significant concern in the world [1]. Moreover, low concentration and great diversity of micropollutants cause complications in associated detection and analysis procedures of these emerging contaminants. This creates challenges for water and wastewater treatment processes [2].

As current wastewater treatment plants are not specifically designed to remove micropollutants, many of these contaminants cross over the wastewater treatment processes and arrives in the aquatic environment. They may become a threat to wildlife and spell trouble to the drinking water industry. For instance, the feminization of the fish and mussels, as well as reproductive disruption in fish in many rivers downstream of the wastewater treatment plants, were observed which is probably corresponding to the release of endocrine disrupting estrogens. Other negative impacts of the micropollutants in water explicitly observed in case of low dilution of effluents such as neuroendocrine alterations and oxidative stress in freshwater mussels, histopathological effects in the fish, alteration of macroinvertebrate communities and gammarid health (fecundity, sex ratio, stress) which may affect the whole aquatic food web and thus the ecosystem. Besides the known negative impacts of micropollutants, there is a great number of micropollutants whose effects on living organisms are still unknown [1]. Therefore, removing these compounds is of great importance not only to preserve the environmental ecosystem but also to protect human health.

In this work, a systematic literature review (SLR) is conducted to discover the current focus of research around the world in the field of micropollutant removal from wastewater as well as determining the available approaches for the elimination of these substances. The SLR process makes it possible to evaluate these methods and researches in an unbiased pathway.

After performing the SLR and determining the available approaches as well as identifying the focus of this study, the theoretical background related to the mitigation of micropollutants by the sand and trickling filter is presented. This section provides an overview of the sorption and degradation mechanisms of micropollutants as well as comparing the components and operation of trickling filters and sand filters in wastewater treatment. During the experiment, samples taken from the influent and effluent of the sand and trickling filters in LFKW wastewater treatment plant were analyzed by different methods explained in the Experiments and Methodology section. Furthermore, the removal efficiencies of the micropollutants by each filter as well as correlations to the physical-chemical properties and conventional parameters are presented in the result section.

The objective of this work is to examine the efficiency of trickling filter and sand filter for the elimination of organic micropollutants from wastewater. Moreover, evaluating the effect of different physical-chemical properties on the removal behavior of the micropollutants as well as classifying the micropollutants according to their removal behavior and separation mechanism.

1.1. Systematic Literature Review

Systematic Literature Review (SLR) provides an unbiased means of identifying, evaluating and interpreting available research in the subject of interest [3]. The SLR process followed in this work is based on the Collaboration for Environmental Evidence (CEE) which is itself based on the existing guidelines by Cochrane and the health services sector (CRD). The SLR is composed of the following phases: planning, conducting and reporting [3]. The planning phase is the basis of the SLR. This phase is responsible for specifying the need for a review and defining a protocol which helps to avoid bias. The research questions are also defined in this phase. In conducting phase, the relevant research must be identified and the quality of the primary studies is assessed using an assessment of study design (to guarantee a minimum level of quality). Finally, the results of the review are reported (Reporting phase) [3].

The following diagram indicates the SLR process and its components.

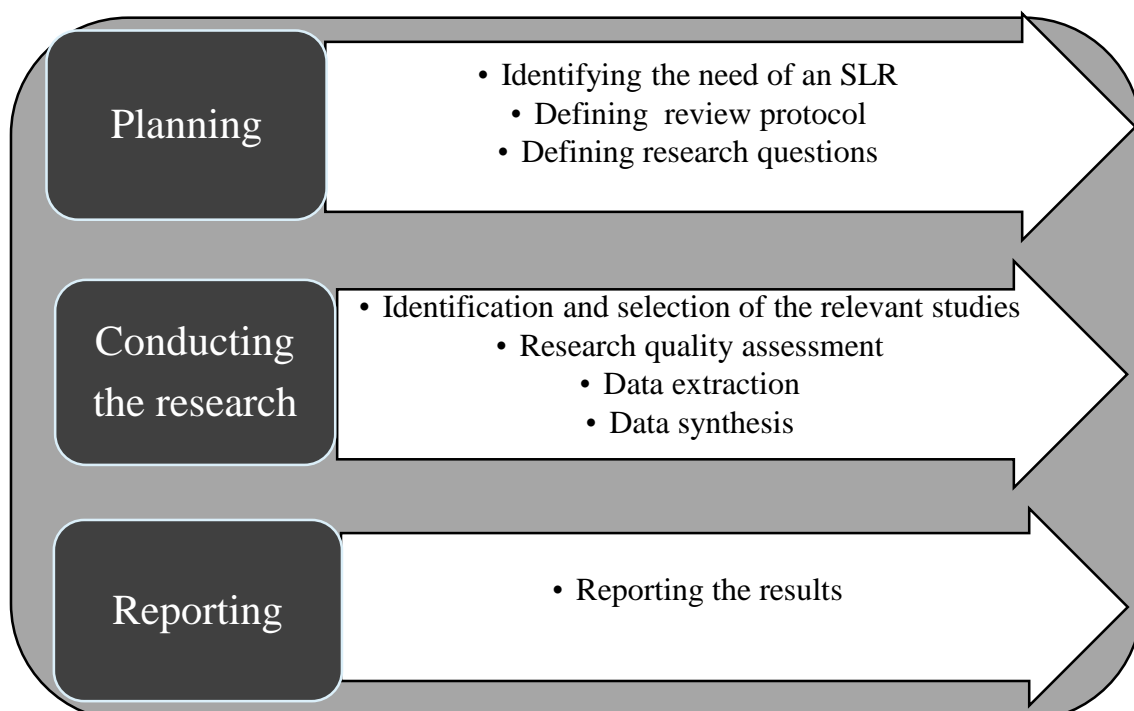


Figure 1.1. The steps of performing an SLR [3]

1.1.1. Planning phase

1.1.1.1. The need for SLR

Preventing environmental problems requires the translation of updated scientific research into accessible evidence that informs decision makers. However, the scientific literature is diverse, of varying quality, and often not easily accessible [4]. Therefore, an SLR in this field is required in order to provide this information and evidence in a transparent and reliable manner.

1.1.1.2. Research questions

Specifying research questions with respect to the topic of interest is the most critical part of SLR. As per the topic, the following research questions are defined:

- RQ1: How much activity has there been worldwide regarding the micropollutants in wastewater
- RQ2: Who (which countries) is active in this field?
- RQ3: What are the available approaches for micropollutant removal?
 - RQ3.1: Which one is the focus of this study?

RQ1 aims to obtain an overview of the number of current research. RQ2 is defined to recognize active researchers and organizations in the fields. RQ3 provides the existing methods and the focused approach of this research for removal.

1.1.1.3. Protocol review

Protocol review is another component of the SLR which is composed of the search strategy, in/exclusion criteria, the strategy of data extraction as well as synthesis strategy. A pre-defined protocol is required to not only reduce the amount of bias as much as possible but also to make the SLR replicable [3].

1.1.1.3.1. Search strategy

In this step, search phrases are formed with respect to research questions. The databases are also identified. The search phrases are composed of a combination of keywords of the research question as well as their synonyms and different spelling. These words are connected together with Boolean operands such as AND, OR and NOT. The keywords concerning the research questions are:

Micropollutants, “persistent organic pollutants”, pharmaceuticals, PhACs, hormones, pesticides, removal, treatment, sorption, adsorption, degradation, “sand filter”, “trickling filter”, “municipal wastewater”, CSO, “wastewater”

The search strings are visualized in the following figures:

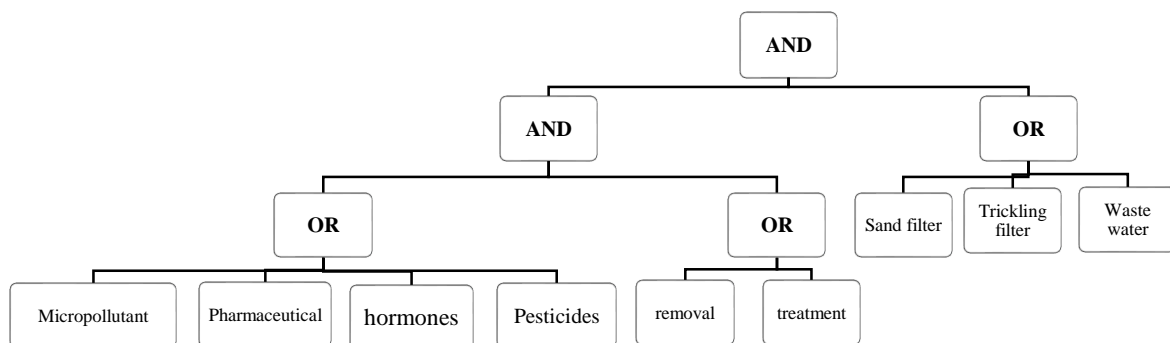


Figure 1.2. Derived search phrase 1

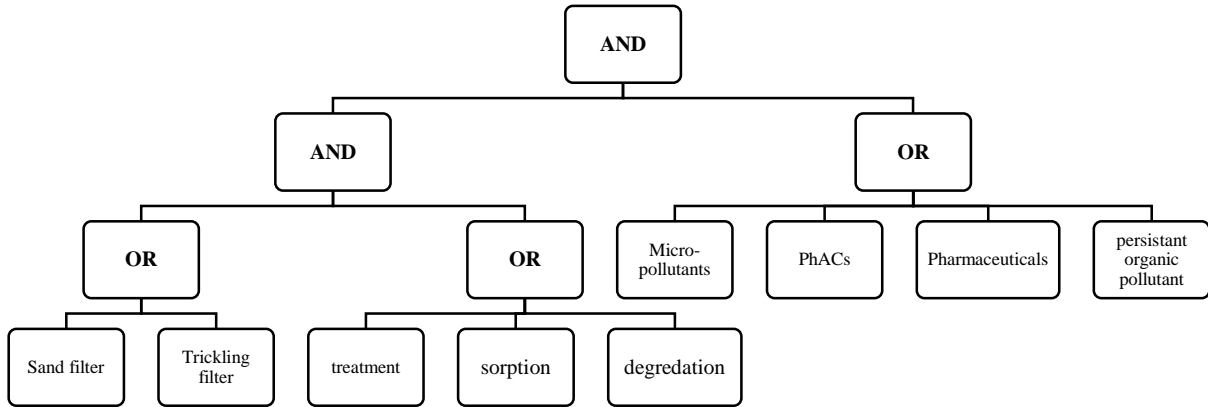


Figure 1.3. Derived search phrase 2

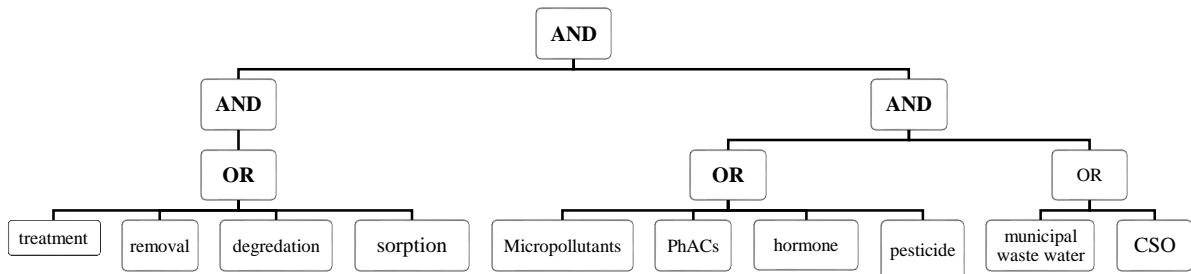


Figure 1.4. Derived search phrase 3

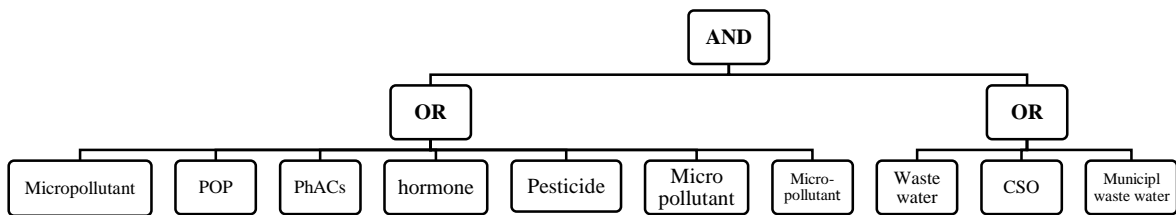


Figure 1.5. Derived search phrase 4

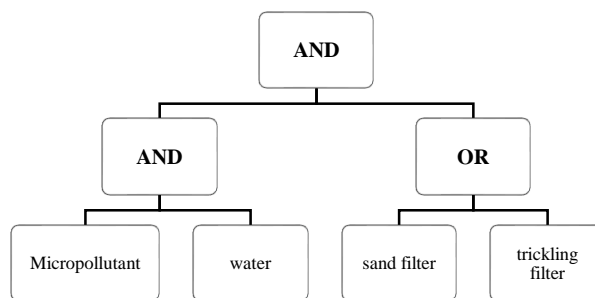


Figure 1.6. Derived search phrase 5

The database for the mentioned keyword algorithms are as below:

- Science Direct¹
- Google Scholar²

According to the graphs, the following search strings are to be queried in the database respectively.

- (((“Micropollutant” OR Pharmaceutical OR Hormone OR Pesticide) AND (removal OR treatment)) AND (“sand filter” OR “trickling filter” OR “wastewater”))
- ((“sand filter” OR “trickling filter”) AND (treatment OR sorption OR degradation))AND(pharmaceuticals OR micropollutant OR PhAC OR “persistent organic pollutant”)
- ((treatment OR removal, degradation OR sorption)AND(Micropollutant OR pharmaceuticals OR hormone OR pesticide))AND (“municipal waste water” OR CSO))
- (Micropollutant OR “micro pollutant” OR micro-pollutant OR pharmaceutical OR hormone OR pesticide OR “persistent organic pollutant”) AND (“waste water”OR “municipal waste water”)
- (Micropollutant AND water) AND (“sand filter” OR “trickling filter”)

1.1.1.3.2. Study selection criteria

A high number of unrelated studies returned by the databases introduces the need for having inclusion and exclusion criteria. Based on these criteria, the unrelated studies and related studies can be differentiated and further processing becomes more convenient.

Inclusion criteria:

- The study is about micropollutant removal from wastewater
- The study is about different methods to remove micropollutants from wastewater
- The study is about micropollutant removal by the sand filter and/or trickling filter

Exclusion criteria:

- In case that the search result provides a very high number of researches, the exclusion based on the date is performed and the researches which were published before 2012 are excluded.
- After the exclusion based on the date, if still a high number of the researches exist the exclusion can be performed based on the language, however, the exclusion based on the study language should be avoided as far as possible [3].
- When there is more than one study of the same data and information, only one of them which is more complete is included and the rest is excluded.

¹ www.sciencedirect.com

² www.scholar.google.com

1.1.1.3.3. Data extraction

In this section, the data extraction forms are designed to extract the data from the selected studies in a systematic manner. The table is formed concerning the research questions. RQ1 requires the attributes title and year attributes, RQ2 requires Title, Author(s), Organization and Country attributes. RQ3 requires the attributes of different methods for micropollutant removal.

Table 1.1. Data extraction form

Title	Year	Author(s)	Organization	Country	Sorption on activated carbon	Ozonation	Sand filter	Trickling filter
-------	------	-----------	--------------	---------	------------------------------	-----------	-------------	------------------

1.1.1.3.4. Data synthesis

After systematically extracting the data, the gathered information is synthesized and summarized. The data extraction forms for each research questions are presented in a tabular form.

RQ1 provides the number of studies categorized by year. Hence, the following table is formed:

Table 1.2. Distribution of studies per year

Year	Number of Studies
------	-------------------

RQ2 aims to have an overview of the activity in the field. The goal of this question is to gain information on the type of organizations, countries and also authors that are active in the field. As a result, the following attributes are defined:

Table 1.3. Activities in the related field

Study	Author	Institution	Country
-------	--------	-------------	---------

RQ3 is respecting the different approaches of MPs removal and the specific approach of this study. The following tables aim to provide the data for this step:

Table 1.4. Available approaches for micropollutant removal from wastewater

Available approaches	Number of Supporting Studies
----------------------	------------------------------

Table 1.5. Sand filter and trickling filter for micropollutant removal

Trickling filter + Sand filter	Number of Supporting Studies
--------------------------------	------------------------------

1.1.2. Conducting phase

In this phase, the SLR is practically performed through a literature review. This stage is in charge for searching for the relevant studies based on the planned search approach, excluding

the irrelevant data, according to the predefined criteria, and assessing the quality of the data by extraction and synthesizing the information.

1.1.2.1. Search based on the strategy

In this step, the specified search strings are queried in the defined databases providing the following results.

Table 1.6. Search result 1

Database	Number of the articles
Google scholar	58310
Science Direct	666

1.1.2.2. Filtering the data

In this step, the search results are filtered according to the inclusion and exclusion criteria, which has been previously defined in order to limit the number of the articles to be reviewed. As can be seen from the previous table there are a high number of articles relevant to the topic in google scholar, that is to be limited. Firstly, the filtering is performed by activating the “sort by date” option in google scholar which significantly reduces the number of the relevant articles. Second, the articles which are in a language other than English are also excluded from the search study. Finally, only PDF-file types are considered as another filter. In addition, the “open access” filtration for Science Direct database is performed providing a lower number of articles.

After performing this step, the remaining documents are as below:

Table 1.7. Search result 2

Database	Number of the articles
Google scholar	40
Science Direct	21

The final filtration is performed by reading the titles and abstracts of the selected papers in order to exclude those that are less relevant in addition to keeping the ones that are more complete among the similar articles and excluding the same papers.

1.1.3. Reporting phase

In this step, reporting on the conduct and outcome of the study is performed. The defined research questions are answered and the synthesized data is reported. In this phase, the result and evidence shall be presented rather than offering advice. In addition, recommendations that depend on assumptions about resources and values should be avoided [6].

1.1.3.1. Report and interpretation

RQ1: How much activity has there been with regard to micropollutants?

Table 1.8. Distribution of the studies by year

Year	Number of Studies
2010	1
2012	1
2013	2
2016	2
2017	8
2018	30
Total	44

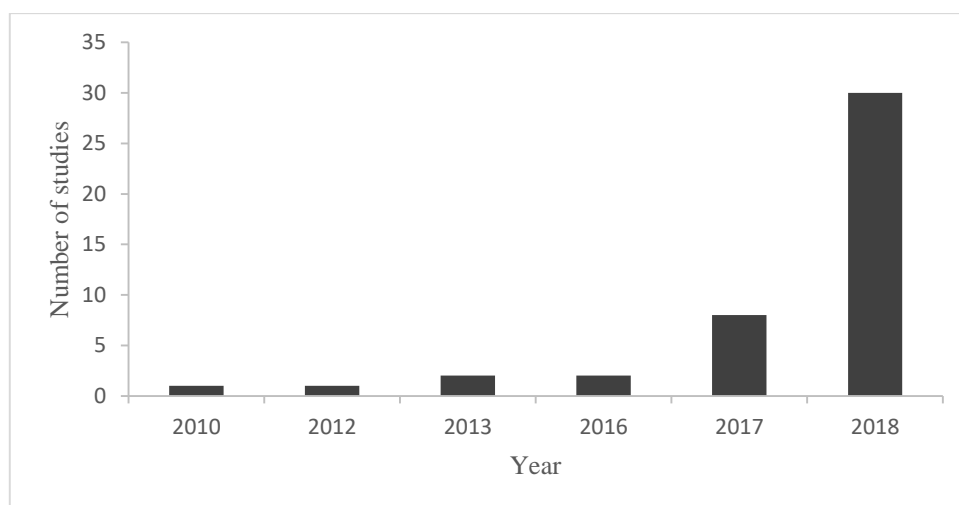


Figure 1.7. Distribution of studies by year

As per the graph, there is an increasing number of studies relevant to micropollutants per year.

RQ2: Who (which countries) is active in this field?

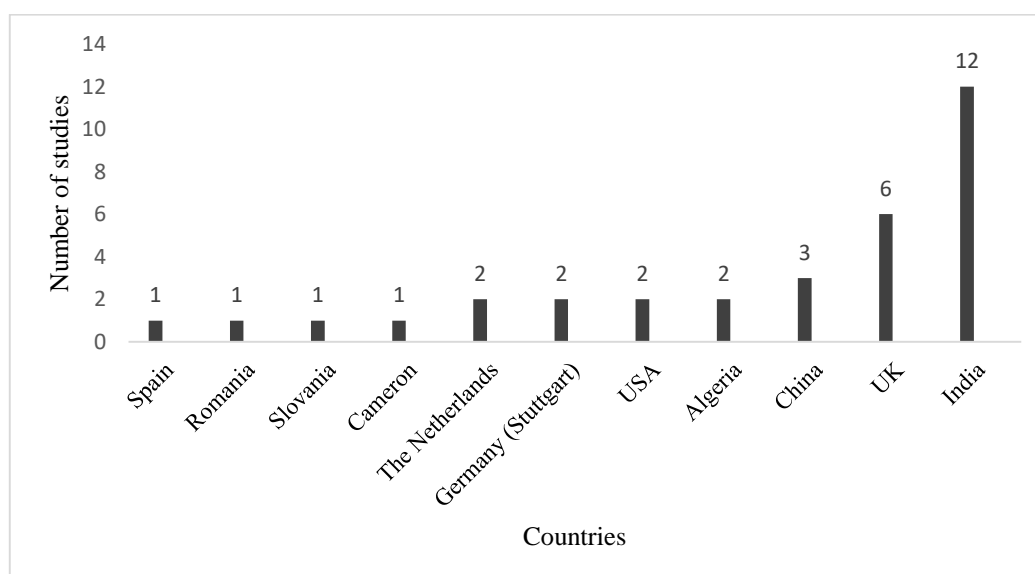


Figure 1.8. Distribution of studies by country

RQ3: What are the available approaches for micropollutant removal?

Table 1.9. Available approaches for micropollutant removal from wastewater (filled form)

Available approaches for MP removal	Objective	Supporting studies
Graphene-based material	Pharmaceutical WWT	[7], [8], [9]
Activated carbon	MP removal, Pharmaceutical WWT	[10], [11]
Electrochemical method	pesticide removal	[12]
Photocatalytic degradation	Pharmaceutical WWT	[13], [14], [15]
Catalysis	Pharmaceutical WWT	[16]
AOP (advanced oxidation process)	Pharmaceutical WWT	[17], [18], [19], [20]
Marine algae biomass	Detergent removal	[21]
TF (Trickling filter)	Herbicide removal	[22]
Redox (Ferrate (VI))	Pharmaceutical WWT	[23]
GAC sandwich slow sand filtration	Pharmaceutical WWT	[24]
VFCW (vertical flow constructed wetland)	PPCP removal	[25]
Sand filter	PPCP removal	[25]
Adsorption by cereal byproducts	Industrial WWT	[26]
Bioremediation	Hormone removal	[27]
Hydrothermal treatment	Pharmaceutical WWT	[28]

According to the table, four studies are supporting “AOP” methods for MP removal, three studies are supporting the “Photocatalytic degradation” and “Graphene-based material” and two of them are involved with “removal by AC”. On the other hand, other studies suggest different methods designed for specific treatment objectives.

RQ3.1: Which one is the focus of this research?

In this study, combinations of trickling filter, slow sand filter and rapid sand filter for biological degradation and sorption of different micropollutants from municipal wastewater is proposed and the efficiency of removal is investigated.

2. Theoretical background

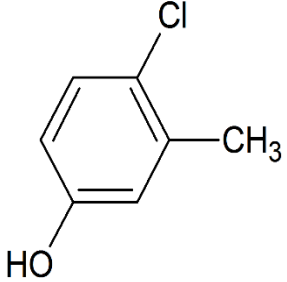
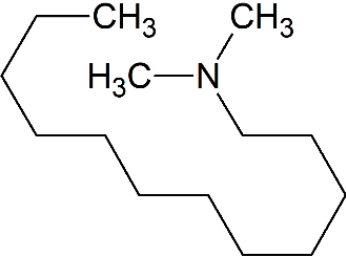
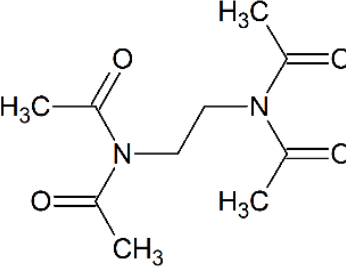
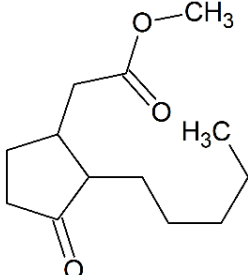
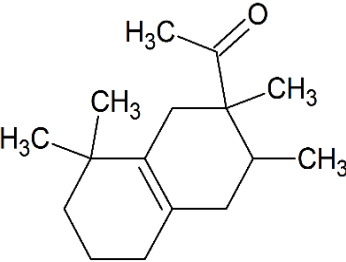
2.1. Definition and classification of micropollutants

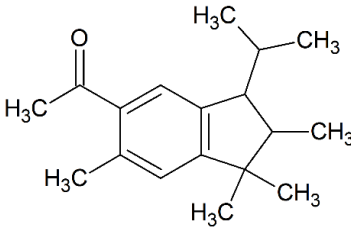
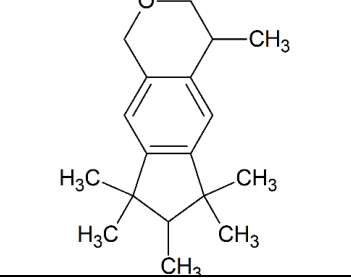
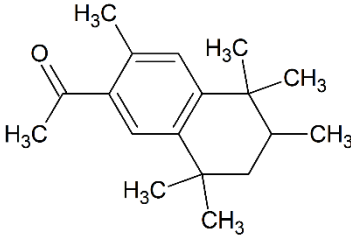
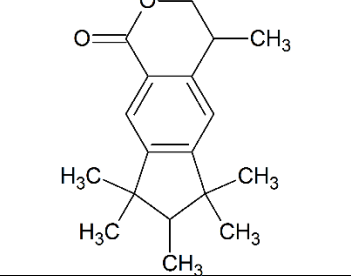
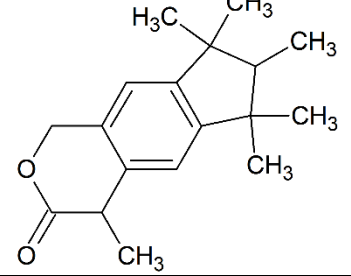
Micropollutants are defined as persistent and bioactive substances in trace concentration of ngL^{-1} to μgL^{-1} with possible hazards to the ecosystem and human health [1]. Although they consist of a variety of compounds, they can be categorized by their application and origin into leading groups of pharmaceuticals, personal care products (PCP), pesticides and herbicides, industrial chemicals and others.

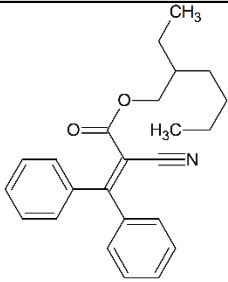
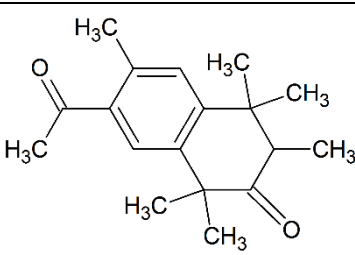
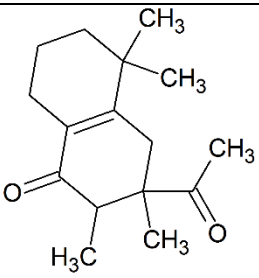
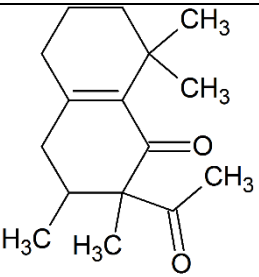
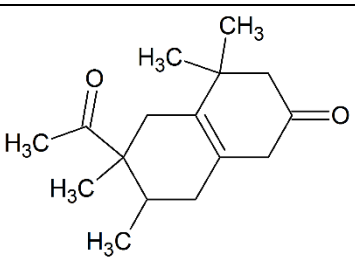
Table 2.1 summarizes the list of selected categories of the emerging pollutants which are subjected in this study.

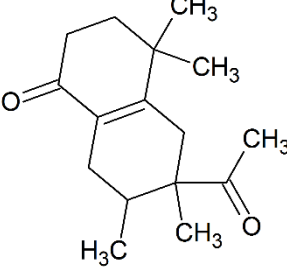
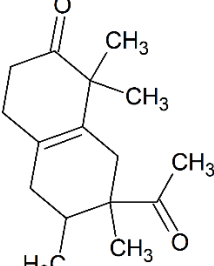
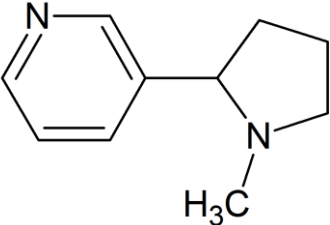
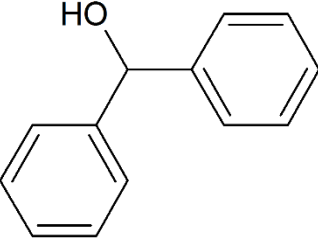
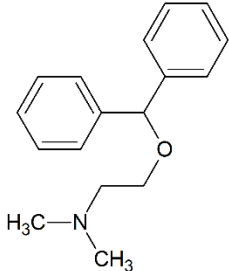
Table 2.1. Selected micropollutants characteristics and their application

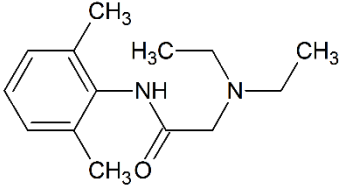
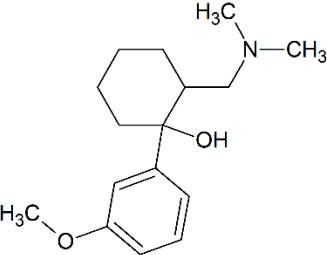
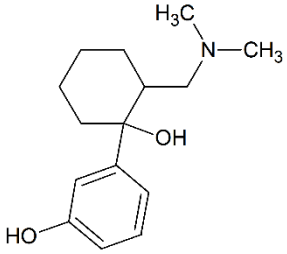
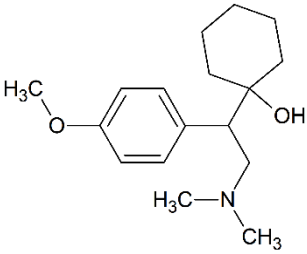
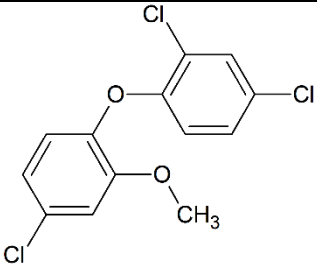
Compound name	Chemical formula	Structure	<u>Class</u> • Application
Octamethyl- cyclopenta- siloxane D4	C ₈ H ₂₄ O ₄ Si ₄		<u>Personal care product</u> • Cosmetics • Shampoo
Decamethyl- cyclopenta- siloxane D5	C ₁₀ H ₃₀ O ₅ Si ₅		<u>Personal care product</u> • Cosmetics • Hair conditioner
Phenoxyethanol	C ₈ H ₁₀ O ₂		<u>Personal care product</u> • Perfume fixative

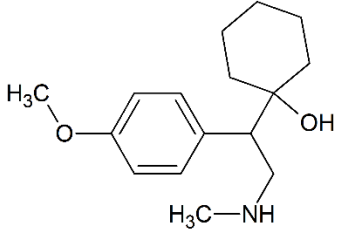
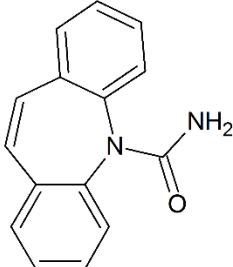
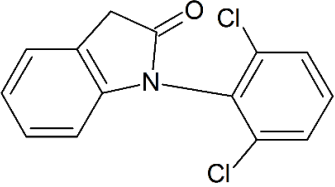
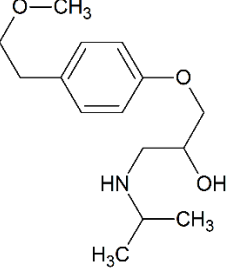
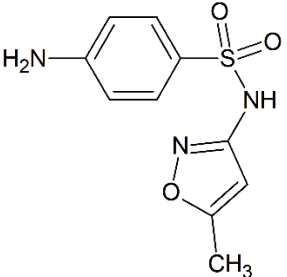
Compound name	Chemical formula	Structure	<u>Class</u> <ul style="list-style-type: none"> Application
P-Chlorocresol PCMC	C ₇ H ₇ ClO		<u>Personal care product</u> <ul style="list-style-type: none"> Antiseptic and disinfectant
Dimethyldodecylamine DMDA	C ₁₄ H ₃₁ N		<u>Personal care product</u>
Tetraacetylene-diamine TAED	C ₁₀ H ₁₆ N ₂ O ₄		<u>Personal care product</u> <ul style="list-style-type: none"> Bleaching activator Detergents
Methyldehydrojasmonate Methyl-DHJ	C ₁₃ H ₂₂ O ₃		<u>Personal care product</u> <ul style="list-style-type: none"> Aroma fragrance
Iso-E Super OTNE	C ₁₆ H ₂₆ O		<u>Personal care product</u> <ul style="list-style-type: none"> Woody, floral fragrance

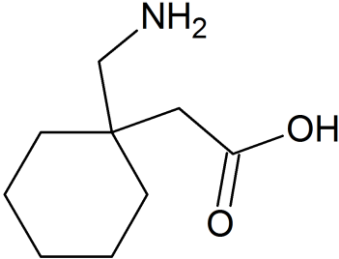
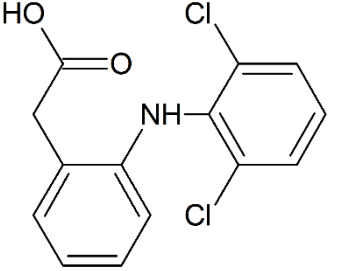
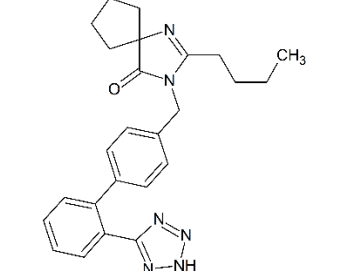
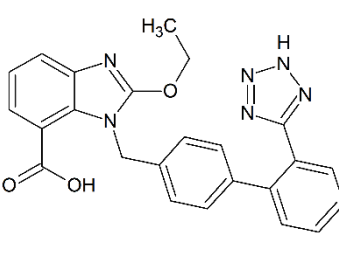
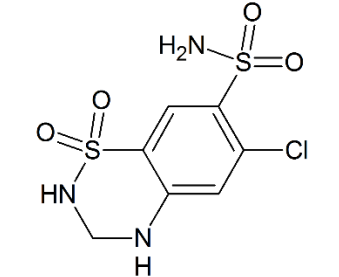
Compound name	Chemical formula	Structure	<u>Class</u> • Application
Traseolide	C ₁₈ H ₂₆ O		<u>Personal care product</u> • Polycyclic musk
Galaxolide HHCB	C ₁₈ H ₂₆ O		<u>Personal care product</u> • Polycyclic musk
Tonalide AHTN	C ₁₈ H ₂₆ O		<u>Personal care product</u> • Polycyclic musk
Galaxolidone HHCB-lactone I	C ₁₈ H ₂₄ O ₂		<u>Personal care product</u>
Galaxolidone II HHCB-lactone II	C ₁₈ H ₂₄ O ₂		<u>Personal care product</u>

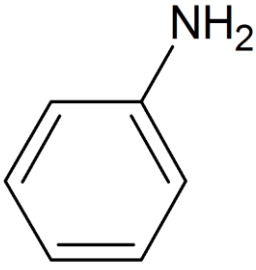
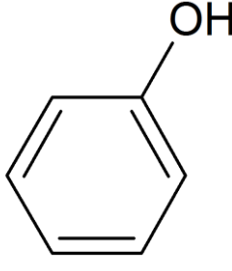
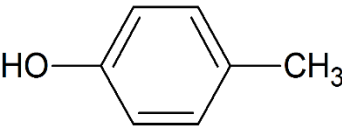
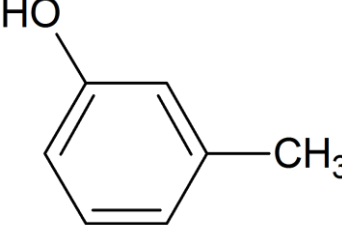
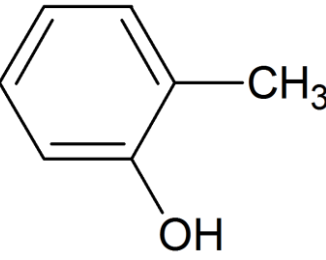
Compound name	Chemical formula	Structure	<u>Class</u> • Application
Octocrylene	C ₂₄ H ₂₇ NO ₂		<u>Personal care product</u> • Cosmetics
AHTN-OX	C ₁₈ H ₂₄ O ₂		<u>Personal care product</u>
OTNE-OX	C ₁₆ H ₂₄ O ₂		<u>Personal care product</u>
OTNE-OX	C ₁₆ H ₂₄ O ₂		<u>Personal care product</u>
OTNE-OX	C ₁₆ H ₂₄ O ₂		<u>Personal care product</u>

Compound name	Chemical formula	Structure	<u>Class</u> • Application
OTNE-OX	C ₁₆ H ₂₄ O ₂		<u>Personal care product</u>
OTNE-OX	C ₁₆ H ₂₄ O ₂		<u>Personal care product</u>
Nicotine	C ₁₀ H ₁₄ N ₂		<u>Pharmaceutical</u> • Nicotine replacement products
Diphenylmethanol	C ₁₃ H ₁₂ O		<u>Pharmaceutical</u> • Synthesis of antihistamines and antihypertensive
Diphenhydramine	C ₁₇ H ₂₁ NO		<u>Pharmaceutical</u> • Antihistamine

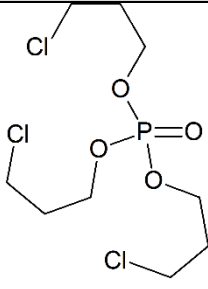
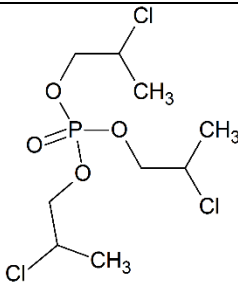
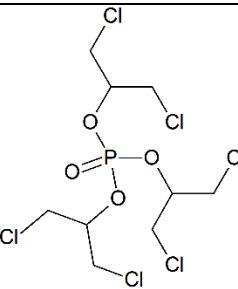
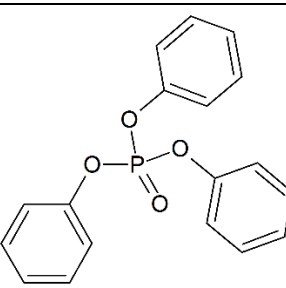
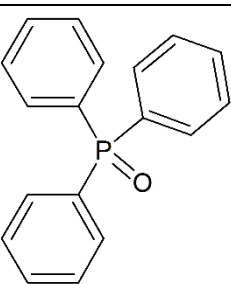
Compound name	Chemical formula	Structure	<u>Class</u> • Application
Lidocaine	C ₁₄ H ₂₂ N ₂ O		<u>Pharmaceutical</u> • Local anesthetic
Tramadol	C ₁₆ H ₂₅ NO ₂		<u>Pharmaceutical</u> • Analgesic
O-Desmethyl-tramadol	C ₁₅ H ₂₃ NO ₂		<u>Pharmaceutical</u> • Opioid analgesic
Venlafaxine	C ₁₇ H ₂₇ NO ₂		<u>Pharmaceutical</u> • Anti-depression
Methyltriclosan	C ₁₃ H ₉ Cl ₃ O ₂		<u>Pharmaceutical</u>

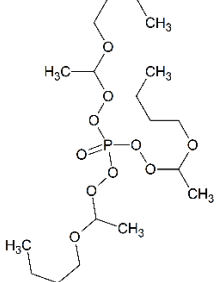
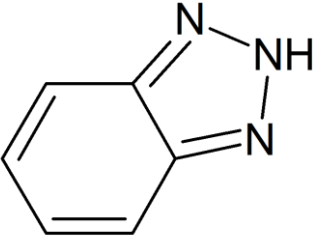
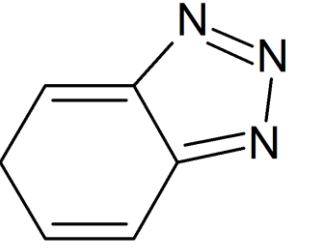
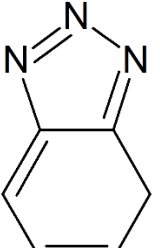
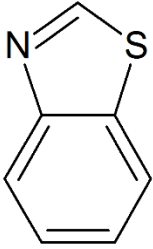
Compound name	Chemical formula	Structure	<u>Class</u> • Application
Norvenlafaxine	C ₁₆ H ₂₅ NO ₂		<u>Pharmaceutical</u> • Anti-depression
Carbamazepine	C ₁₅ H ₁₂ N ₂ O		<u>Pharmaceutical</u> • Analgesic, • Anticonvulsant
Diclofenac (ring closure)	C ₁₄ H ₉ Cl ₂ NO		<u>Pharmaceutical</u> • Anti-inflammatory
Metoprolol	C ₁₅ H ₂₅ NO ₃		<u>Pharmaceutical</u> • β-Blocker
Sulfamethoxazole	C ₁₀ H ₁₁ N ₃ O ₃ S		<u>Pharmaceutical</u> • Antibacterial

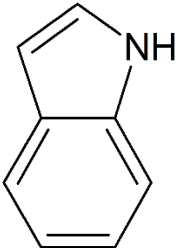
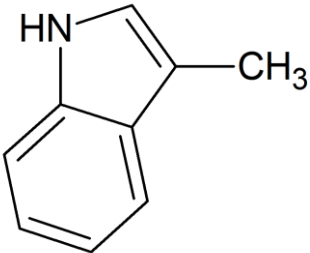
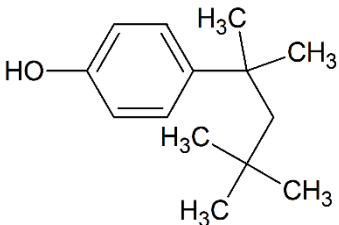
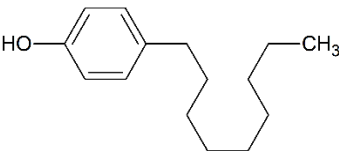
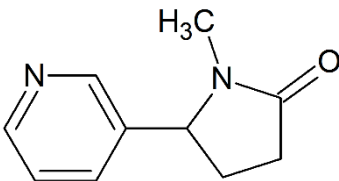
Compound name	Chemical formula	Structure	<u>Class</u> • Application
Gabapentin	C ₉ H ₁₇ NO ₂		<u>Pharmaceutical</u> • Anti-epilepsy
Diclofenac	C ₁₄ H ₁₁ Cl ₂ NO ₂		<u>Pharmaceutical</u>
Irbesartan	C ₂₅ H ₂₈ N ₆ O		<u>Pharmaceutical</u> • Angiotensin receptor blocker • Hypertension treatment
Candesartan	C ₂₄ H ₂₀ N ₆ O ₃		<u>Pharmaceutical</u> • Angiotensin receptor blocker • Hypertension treatment
Hydrochlorothiazide	C ₇ H ₈ ClN ₃ O ₄ S ₂		<u>Pharmaceutical</u> • Diuretic medication • Hypertension treatment

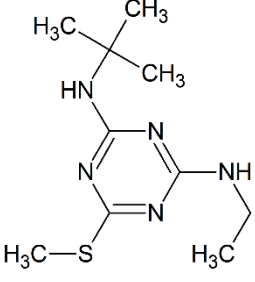
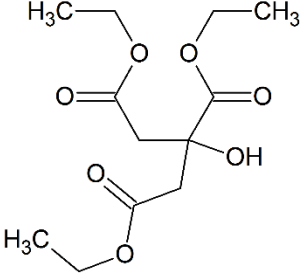
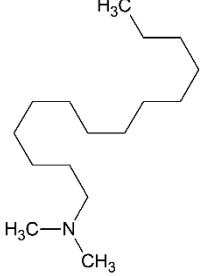
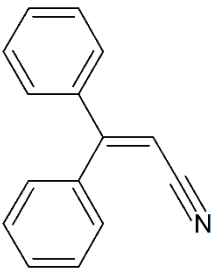
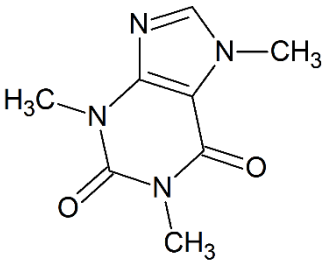
Compound name	Chemical formula	Structure	<u>Class</u> • Application
Aniline	C ₆ H ₅ NH ₂		<u>Industrial Chemical</u> • Polyurethane production • Precursors
Phenol	C ₆ H ₆ O		<u>Industrial Chemical</u> • Precursors for plastics
4-Methylphenol	C ₇ H ₈ O		<u>Industrial Chemical</u> • Precursors for plastics
3-Methylphenol	C ₇ H ₈ O		<u>Industrial Chemical</u> • Precursors for plastics
2-Methylphenol	C ₇ H ₈ O		<u>Industrial Chemical</u> • Precursors for plastics

Compound name	Chemical formula	Structure	<u>Class</u> • Application
Triethylphosphate	C ₆ H ₁₅ O ₄ P		<u>Industrial Chemical</u> • Plasticizer • Catalyst
Phenoxypropanol	C ₉ H ₁₂ O ₂		<u>Industrial Chemical</u>
Methylthio- benzothiazole MTBT	C ₈ H ₇ NS ₂		<u>Industrial Chemical</u>
Benzophenone	C ₁₃ H ₁₀ O		<u>Industrial Chemical</u> • Coatings
Tris-(2- chloroethyl)- phosphate TCEP	C ₆ H ₁₂ Cl ₃ O ₄ P		<u>Industrial Chemical</u> • Flame-retardant • Plasticizer

Compound name	Chemical formula	Structure	<u>Class</u> • Application
Tris-(3-chloropropyl)-phosphate TCPP	C ₉ H ₁₈ Cl ₃ O ₄ P		<u>Industrial Chemical</u> • Flame-retardant
Tris(2-chloropropyl) phosphate TCPP	C ₉ H ₁₈ Cl ₃ O ₄ P		<u>Industrial Chemical</u> • Flame-retardant
Tris(1,3-dichloro-2-propyl) phosphate TDCPP	C ₉ H ₁₅ Cl ₆ O ₄ P		<u>Industrial Chemical</u> • Flame-retardant
Triphenyl phosphate TPP	C ₁₈ H ₁₅ O ₄ P		<u>Industrial Chemical</u> • Flame-retardant • Plasticizer
Triphenyl phosphine-oxide TPPO	C ₁₈ H ₁₅ O ₁ P		<u>Industrial Chemical</u> • Flame-retardant • Catalyst

Compound name	Chemical formula	Structure	<u>Class</u> • Application
Tris-(butoxyethoxy)-phosphate TBEP	C ₁₈ H ₃₉ O ₁₀ P		<u>Industrial Chemical</u> • Flame-retardant • Plasticizer
1H-Benzotriazol	C ₆ H ₅ N ₃		<u>Industrial Chemical</u> • Corrosion inhibitor
5H-Benzotriazole	C ₆ H ₅ N ₃		<u>Industrial Chemical</u> • Corrosion inhibitor
4H-Benzotriazole	C ₆ H ₅ N ₃		<u>Industrial Chemical</u> • Corrosion inhibitor
1,3-Benzothiazole	C ₇ H ₅ NS		<u>Pesticide/Herbicide</u>

Compound name	Chemical formula	Structure	<u>Class</u> • Application
Indole	C ₈ H ₇ N		<u>Pesticide/Herbicide</u> • Plant growth
Skatol (3-Methylindole)	C ₉ H ₉ N		<u>Pesticide/Herbicide</u>
4-Tert-octylphenol	C ₁₄ H ₂₂ O		<u>Pesticide/Herbicide</u>
4-Nonylphenol	C ₁₅ H ₂₄ O		<u>Pesticide/Herbicide</u>
Cotinine	C ₁₀ H ₁₂ N ₂ O		<u>Pesticide/Herbicide</u>

Compound name	Chemical formula	Structure	<u>Class</u> • Application
Terbutryn	C ₁₀ H ₁₉ N ₅ S		<u>Pesticide/Herbicide</u> • Inhibitor of photosynthesis
Triethylcitrate	C ₁₂ H ₂₀ O ₇		<u>Others</u> • Food additive
Dimethyl-tetradecylamine	C ₁₆ H ₃₅ N		<u>Others</u> • Production of chemicals
3,3-Diphenylacrylonitrile	C ₁₅ H ₁₁ N		<u>Others</u> • Synthetic rubbers
Caffeine	C ₈ H ₁₀ N ₄ O ₂		<u>Others</u> • Food • Medical therapies

2.2. Mitigation of aqueous micropollutants

Because of the ascending demand for clean water due to the urbanization and also increasing industrialization, it is essential to investigate powerful strategies to mitigate water contamination. These strategies not only should focus on the limitation of some critical substances into the environment, but also have to concentrate on suggesting more efficient and economic approaches. Hence, strategies regarding microbial or abiotic degradation of the micropollutants have to be quantified and taken into account.

Removal of micropollutants during the treatment lies its foundation on the mechanism of mineralization into stable and nontoxic products, biological degradation, transformation, and sorption. Among these approaches, sorption and biological degradation were reported to play significant roles [29].

2.2.1. Sorption mechanism of micropollutants

Adsorption is the attachment of a substance (adsorbate) on the surface of another molecule of a different state (adsorbent). Adsorption should not be confused with absorption. During absorption, adsorbate diffuses into the adsorbent.

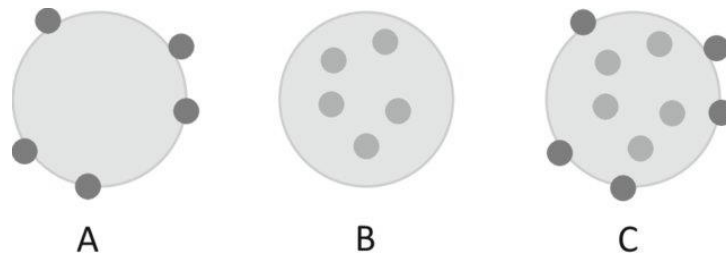


Figure 2.1. Illustration of the difference between adsorption (a) and absorption (b) the sorption may also be a combination of ab-and adsorption [30]

Equilibrium of adsorption is reached when the adsorbed and desorbed amount of substances are equal. This is in fact due to the dynamic behavior of the adsorption process on which the solute (wastewater) simultaneously adsorbs to and desorbs from the medium. The equilibrium corresponds to the solute concentration and water temperature. This equilibrium, between the solute concentration (C_e) and the adsorbed solute quantity at a certain temperature, is often reflected via the equilibrium isotherms such as Freundlich and Langmuir that can be linearized as it is demonstrated in the following table [31].

Table 2.2. Adsorption isotherms [32]

Adsorption isotherm	Equation	Linear isotherm model	Parameters
Langmuir	$C_s = \frac{C_{max} K_l C_w}{1 + K_l C_w}$	$\frac{C_w}{C_s} = \frac{1}{C_{max}} C_w + \frac{1}{K_l C_{max}}$	<p>C_s: adsorbed concentration at equilibrium in $\mu\text{g kg}^{-1}$</p> <p>C_w: Solution concentration at equilibrium in $\mu\text{g L}^{-1}$</p> <p>K_l: Langmuir constant</p> <p>C_{max}: Max adsorbed concentration in $\mu\text{g kg}^{-1}$</p>
Freundlich	$C_s = K_f C_w^{\frac{1}{n}}$	$\log C_s = \log K_f + \frac{1}{n} \log C_w$	<p>C_s: adsorbed concentration at equilibrium in $\mu\text{g kg}^{-1}$</p> <p>C_w: Solution concentration at equilibrium in $\mu\text{g L}^{-1}$</p> <p>K_f: Langmuir constant</p> <p>n: Freundlich exponent</p>

The Langmuir constant K_L can be related to the Gibbs free energy of adsorption (ΔG) [32].

$$\Delta G = RT \ln K_l$$

The Langmuir sorption isotherm assumptions are as follow:

- Adsorption layer is assumed to be a monolayer.
- All species have equal access to different sites of the adsorption monolayer.
- The energy of adsorption is evenly distributed over the surface.
- No interaction occurs between adsorbed substances.

On the other hand, heterogeneity of the adsorption surface is taken into account in Freundlich formula by the Freundlich exponent (n). This model is often suitable to be applied at low to moderate solute concentration, as it lacks the maximum adsorption capacity (C_{max}) [32].

2.2.2. Biodegradation mechanism of micropollutants

Micropollutants are grazed during the wastewater treatment processes via main pathways of metabolism or co-metabolism. Metabolism can be described as a mechanism in which the required energy for growth of the microorganisms is provided predominantly by the micropollutants. However, in co-metabolism micropollutants are toxic to be consumed by the microbes, thus making it necessary for them to utilize other compounds as the primary substrates in order to support their growth. Indeed, the organisms use a compound for growth and simultaneously oxidize the second substrate (micropollutant) in order to be consumed as a nutrient and energy source [33].

Table 2.3. Biodegradation pathway of micropollutants [33]

Biodegradation pathway	Main involving microorganisms	Micropollutants (Pharmaceuticals)
Metabolism	Heterotrophs (e.g., <i>Delfia tsuruhatensis</i> , <i>Pseudomonas aeruginosa</i> , and <i>Sphingomonas</i>)	e.g., Ketoprofen, acetaminophen, 17 β -estradiol, and ibuprofen
Co-metabolism	Ammonia oxidizing bacteria (AOB) (e.g. <i>Nitrosomonas europaea</i>)	e.g. triclosan, bisphenol, EE2

Co-metabolic mechanism of micropollutants consists of the biodegradation of the pharmaceuticals by ammonia-oxidizing bacteria (AOB). In this case, Ammonium is utilized as the primary substrate. Hence, Nitrification process is accomplished by AOB converting NH_4^+ to NO_2^- with the help of the ammonia monooxygenase (AMO) enzyme.

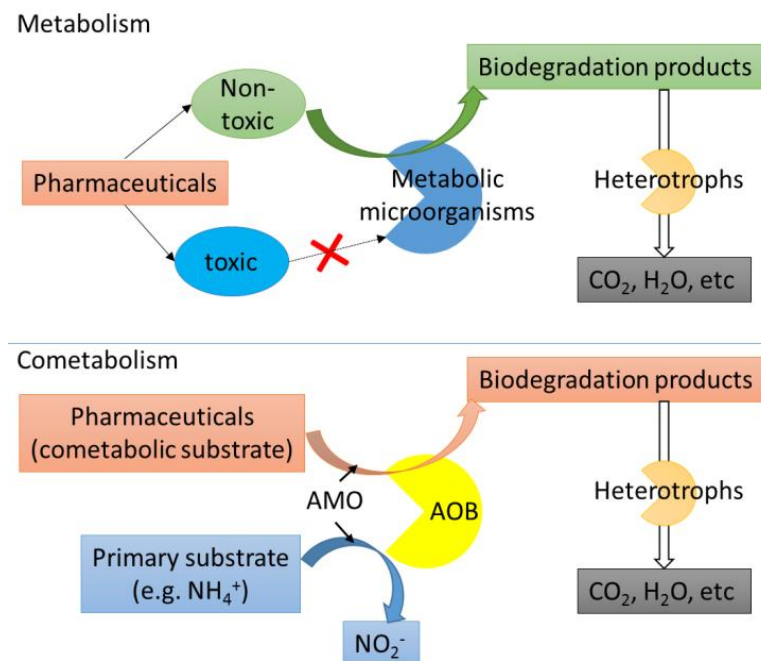


Figure 2.2. Metabolic and cometabolic pathways of pharmaceuticals biodegradation [33]

This process is able to degrade a wide range of aromatic pharmaceutical compounds through co-metabolic pathways such as hydrocarbons and phenol [33].

2.3. Trickling filters

Trickling filters (TF) are relatively simple wastewater treatment approaches consisting of a tank with a fixed bed of high permeable material such as stones, coke, wooden chips, and plastic material. On top of this material, wastewater flow is applied downward and dropwise or in the form of jets, allowing the bacteria to grow on the surface of the packing medium and

form a biofilm. Hence, as wastewater passes through the fixed film, organic matter is absorbed by microorganisms while the wastewater drains out with the help of the support bed [34].

TFs consist of autotrophic and heterotrophic bacteria. On the top layers of the TF, heterotrophic bacteria consume BOD as a substrate while the nitrifying bacteria have a slower growth rate and are not able to compete. As the depth of the TF further increases, BOD concentration diminishes to an amount in which heterotrophic microorganisms growth rate is low enough that allows the nitrifying organisms to grow and contribute to the nitrification process [35].

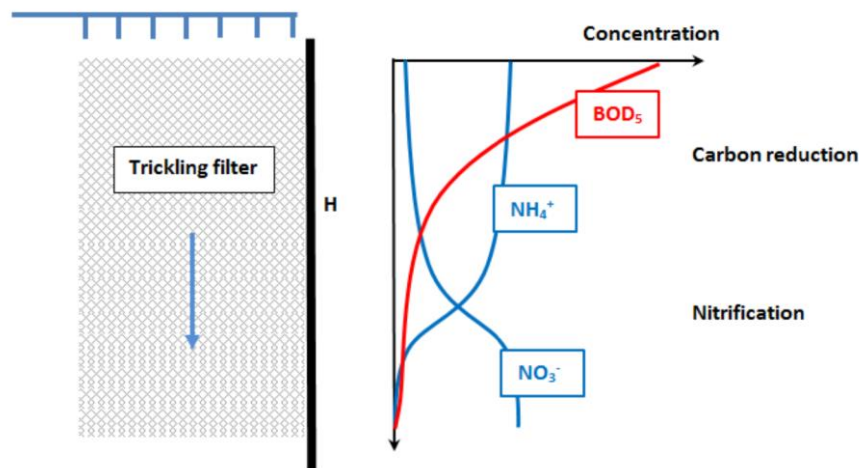


Figure 2.3. TF depth versus BOD₅ removal and nitrification process [35]

The application of wastewater through the filter bed is made by rotating distributors which are moved by the hydraulic head of the liquid. Natural ventilation is usually applied through the packing medium via the ventilation holes at the bottom of the tanks, making the trickling filters aerobic systems [34].

2.3.1. Trickling filter components

TFs are biological reactors comprising a media such as rocks, gravel, coke or plastic material providing a proper structure for microorganisms to attach. They may also consist of a fixed or rotary distributor system to disperse the wastewater over the medium uniformly. Moreover, a container tank for holding the medium respecting the free draining of water from the bottom of the tank and ventilation holes at the base of the tank for allowing the system to be aerated and promoting the aerobic reactions are involved (Figure 2.4).

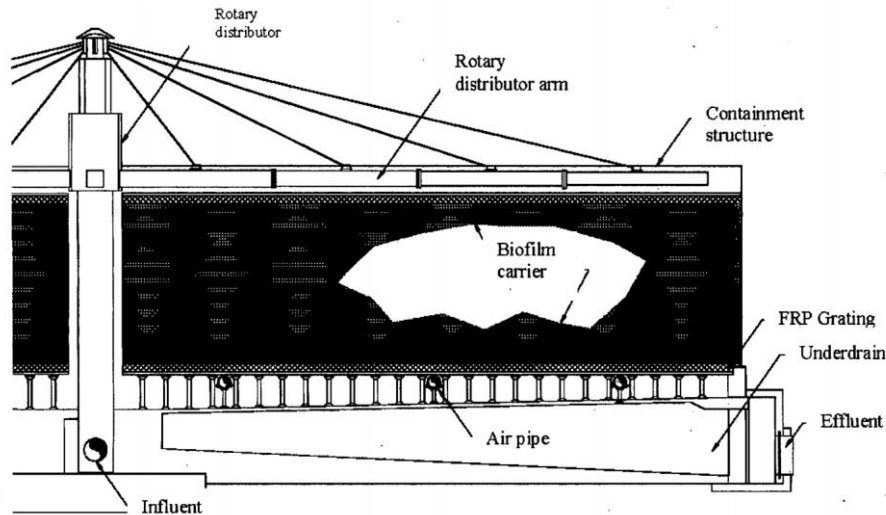


Figure 2.4. TF cross-section and biological reactor component [36]

2.3.2. Advantages and limitations of trickling filters

Trickling filters are rather simple and reliable processes which are effective in treating high concentrations of organic matter and very efficient in removing the ammonia from wastewater. By the application of the plastic filter media to substitute the conventional media, rotary distributor and the speed control, the performance of TFs can be substantially enhanced.

Additionally, TFs require much lower energy compared to the equivalent activated sludge processes due to the passive aeration mechanism which makes them independent of the energy-intensive blowers. TFs which are attached growth processes produce less sludge than comparable activated sludge systems which are suspended growth processes, and the sludge tends to settle well as it is compact and dense.

On the other hand, sludge production in this process operation should be considered and respectfully treated. Besides, there is also odor and macrofauna problems that can be controlled by some practical considerations [37].

2.3.3. Practical considerations to control trickling filters

- Sludge removal

In order to control the microbial population on the support medium, the removal of dislodged sludge in the settling tank should be taken into account in order to decrease the level of suspended solids in the effluent. The reason is that, by ongoing biomass growth on the surface of the packing bed, the empty spaces tend to decrease, resulting in elevating the velocity of water flowing down through the pores; thus, shear stress is generated that discharges some of the attached substances [34].

- Flushing rate

Based on the studies, the flushing rate (SK value) is critical for obtaining a good efficiency in TFs by controlling the biofilm thickness, increasing wetting ratio and macrofauna and odor prevention. Flushing rate or Spülkraft (SK value) is indirectly

proportional to the distributor arm rotational speed (n). Hence, in order to have a higher organic load, greater flushing intensity or lower distributor rotational speed is required [38].

$$\circ \text{SK}(\text{mm/pass of arm}) \propto \frac{1}{n \left(\frac{\text{rev}}{\text{min}}\right)}$$

- **Recirculation**

Recirculating the wastewater flow contributes to the enhanced wetting of the medium and better aeration. Furthermore, it maintains the consistency of the flow through TF during diurnal flow fluctuation. Recirculation prevents the generation of snails and flies by keeping the wetting rate at a proper level [38].

- **Macrofauna controlling**

Macrofauna is not necessarily nuisance animals; however, the pollution may cause overgrazing of nitrifying biofilm, damaging pumps and belts. Organic snails remaining in the effluent stream may exert BOD5 and the shells remaining in the effluent stream may prevent the bacteria from disinfection processes.

Macrofauna and the associated problems can be controlled by increasing the flushing intensity mentioned above. Other control mechanisms involving this problem include the addition of dosing chemicals such as ammonia (toxic for snails) or sodium hydroxide (to raise the PH) [38].

2.4. Slow sand filters

Slow sand filtration is a relatively simple operation that has been used for many years as a suitable filtration process which can be done without the addition of any chemicals to aid the filtration process. Slow sand filtration is applied to filter water in a flow rate of at least fifty times lower than rapid sand filtration. Hence, more filtration columns and a larger space would be required for the slow sand filtration basins. Consequently, small communities or rural areas are usually the right choices for this treatment option [39].

Particle elimination by biological activity in slow sand filters is mainly done in the top biofilm layer of the filter known as “Schmutzdecke” which has a reddish brown color and takes at least 2-3 weeks to form naturally. This layer provides the initial zone for biological activity as well as some degradation of soluble organics in wastewater in order to reduce color and odor. By passing water slowly through a sand filter, particles are trapped by the bacteria existing on the Schmutzdecke layer, and as the deeper water passes through the sand layers, impurities are left behind, making the removal more efficient [40].

2.4.1. Slow sand filter components

Slow sand filters usually consist of a tank, a bed of fine sand, a layer of gravel to support the sand, a system of underdrains for collecting the filtered water and a flow regulator in order to control the filtration rate [41] (Figure 2.5).

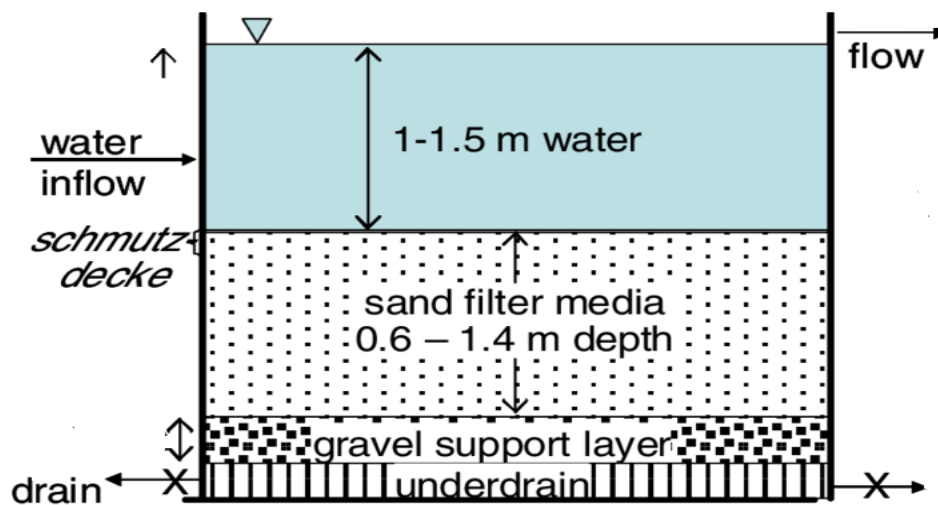


Figure 2.5. Sketch of a typical slow sand filter [42]

2.4.2. Advantages and limitations of the slow sand filtration process

The simplicity of design and operation, introduce this method as a process with limited technical supervision, special pipework, equipment or instrumentation. In addition, no chemicals are required making the slow sand filter an appropriate technique for wastewater removal. Power is not needed if a gravity head is available making it a slightly cheap approach. These filters are good options for removing suspended organic and inorganic matters as well as reducing bacteria, turbidity, and organic level. Hence, reducing the need for disinfection and as a result, the existence of disinfection byproducts in the effluents [41].

On the other hand, large land area is required for the slow sand filtration units which are to treat the high amount of wastewater (about five times that of rapid sand filtration plants). Clogging may occur if the influent is excessively turbid or if certain types of algae are present in the wastewater. In case of occurring such clogging frequently, pretreatment with settling tanks or other filters is prerequisite (Usually water is applied without any pretreatment when the turbidity level is lower than 10 NTU) [41].

2.5. Rapid sand filters

Rapid sand filters are commonly part of a multi-stage treatment system used by large municipalities or industrialized countries. They usually consist of coarse sand and granular media compared to the slow sand filters. Rapid sand filtration is a rather sophisticated and automated system often requiring power-operated pumps for backwashing the filter beds and flow control of the filter effluent. Operation of these filters requires regular backwashing (reversing the direction of the water and adding compressed air) of the filter bed. Backwashing is aimed to remove suspended material that has been deposited in the filter bed during the filtration cycle, and the intervals between the frequent backwash depend on the quality of the influent to be filtered. While a continuous operation of the rapid sand filters, with low turbidity influent, backwashing of the filter beds in every two days will be essential to avoid possible

clogging. In case of a high turbid water source, pretreatment of the wastewater using chemical flocculation agents in combination with a settling tank is applied [43].

2.5.1. Rapid sand filter components

The filter chamber can be constructed as open tanks (rapid gravity filters) or closed tanks (pressure filters). The main components of these systems are a filter box (open rapid sand filter) or a filter tank (closed rapid sand filter), a bed of sand particles as the filter media, gravel layer as the support section, underdrain system and wash line (Figure 2.6 and Figure 2.7).

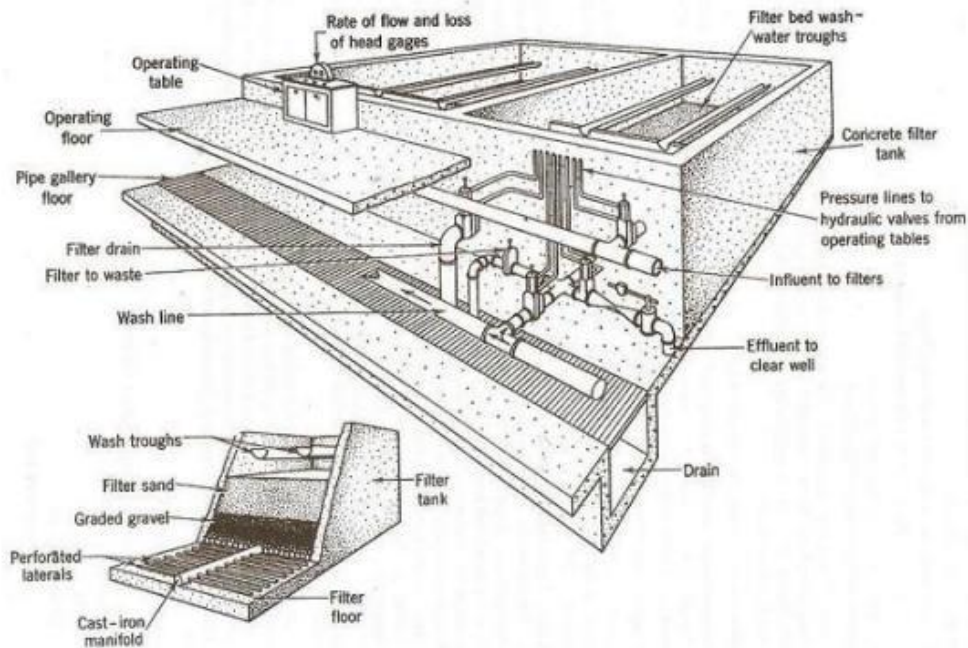


Figure 2.6. Components of an open (gravity) rapid sand filter [44]

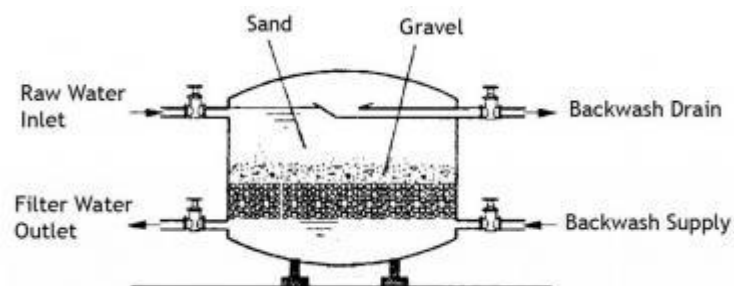


Figure 2.7. Closed rapid sand filter (pressure filter) [45]

2.5.2. Advantages and limitations of rapid sand filtration

Rapid sand filtration can be a very efficient approach regarding turbidity removal if it is appropriately operated. Indeed, it can contribute to the reduction of turbidity to less than 1 NTU and often less than 0.1 NTU. These filters are operated in high filter rates, in contrary to the

slow sand filters they require a small area for the filtration. Initial turbidity level does not have any specific limitation, and the filtration is less sensitive to the water source quality. Also, despite the necessity of the frequent backwashing, it takes only a few minutes, and the filters can be put back into operations immediately.

On the other hand, rapid sand filtration is not a reliable process for removing bacteria, viruses, protozoa, arsenic, salts, and odor. Moreover, the removal of organic matter by this method cannot be attained unless by the combination of pre- and post-treatment. Treatment of backwashed water and sludge should also be considered as another aspect during the operation by rapid sand filters. Other limiting factors consist of frequent cleaning of the filter bed, high energy demand and relatively high investment and operational costs [45].

3. Experiments and methodology

In general, four experiments in two units containing sand and trickling filters were performed, and the effect of the mentioned filters for the treatment of micropollutants was investigated. The first unit of the filters consists of two trickling filters one of which treats the micropollutants from the raw wastewater and leads further to the sand filter for more separation. The other trickling filter in this unit is responsible for proceeding the pre-treated wastewater. The second unit consists of high retention time sand filters. The influent to this unit is the pre-treated wastewater from the treatment plant. Figure 3.1 indicates the focus of each experiment regarding the unit and investigated filters. The properties of the mentioned sand and trickling filters in the mentioned units are different which is explained in the following subchapter.

Experiment 1	• TF1, RSF, SSF + TF2 (Unit 1)
Experiment 2	• TF1, RSF, SSF + TF2 (Unit 1)
Experiment 3	• TF1, RSF, SSF + TF2 (Unit 1) • Coarse SF, SSF2 (Unit 2)
Experiment 4	• TF1, RSF, SSF + TF2 (Unit 1) • and Coarse SF, SSF2 (Unit 2)

Figure 3.1. Investigated filters in each experiment

3.1. Site description

The study was conducted in the facilities of LFKW (Lehr und Forschung Klärwerk) wastewater treatment plant which lies below the district of Bösingen and on the edge of the nature reserve "Rot- und Schwarzwildpark" in the west of the city of Stuttgart, Germany. In this treatment plant, sewage from the areas of Lauchhau, Bösingen, the northern area of Vaihingen, as well as large parts of the university area Vaihingen-Paffenwald are processed that corresponds to about 10,000 inhabitants. The treated wastewater is discharged into the "Bandtälesbach" river and reaches the Rhine river via the rivers Glems, Enz and Neckar. Despite other wastewater treatment plants, the LFKW facilities treat the wastewater through a flexible arrangement due to their multi-pronged cleaning systems, meaning that there is more than one equipment of each type in the processing system. Figure 1 in Appendix demonstrates the schematic of the LFKW wastewater treatment plant.

3.1.1. Filtration equipment in the wastewater treatment plant

3.1.1.1. Unit 1

This unit (unit 1) of the wastewater treatment plant is composed of a storage tank with the influent of raw wastewater from the primary sedimentation tank, a trickling filter (TF1) with a sedimentation tank which is placed underneath the TF1, a rapid sand filter (RSF), three slow sand filters (SSF) in parallel. Figure 3.2 shows a schematic of this unit of the wastewater treatment plant containing TF1, RSF, and the three SSFs. Furthermore, another trickling filter

similar to TF1 but with the influent of the treated wastewater from micro-sieves is located in this unit (TF2).

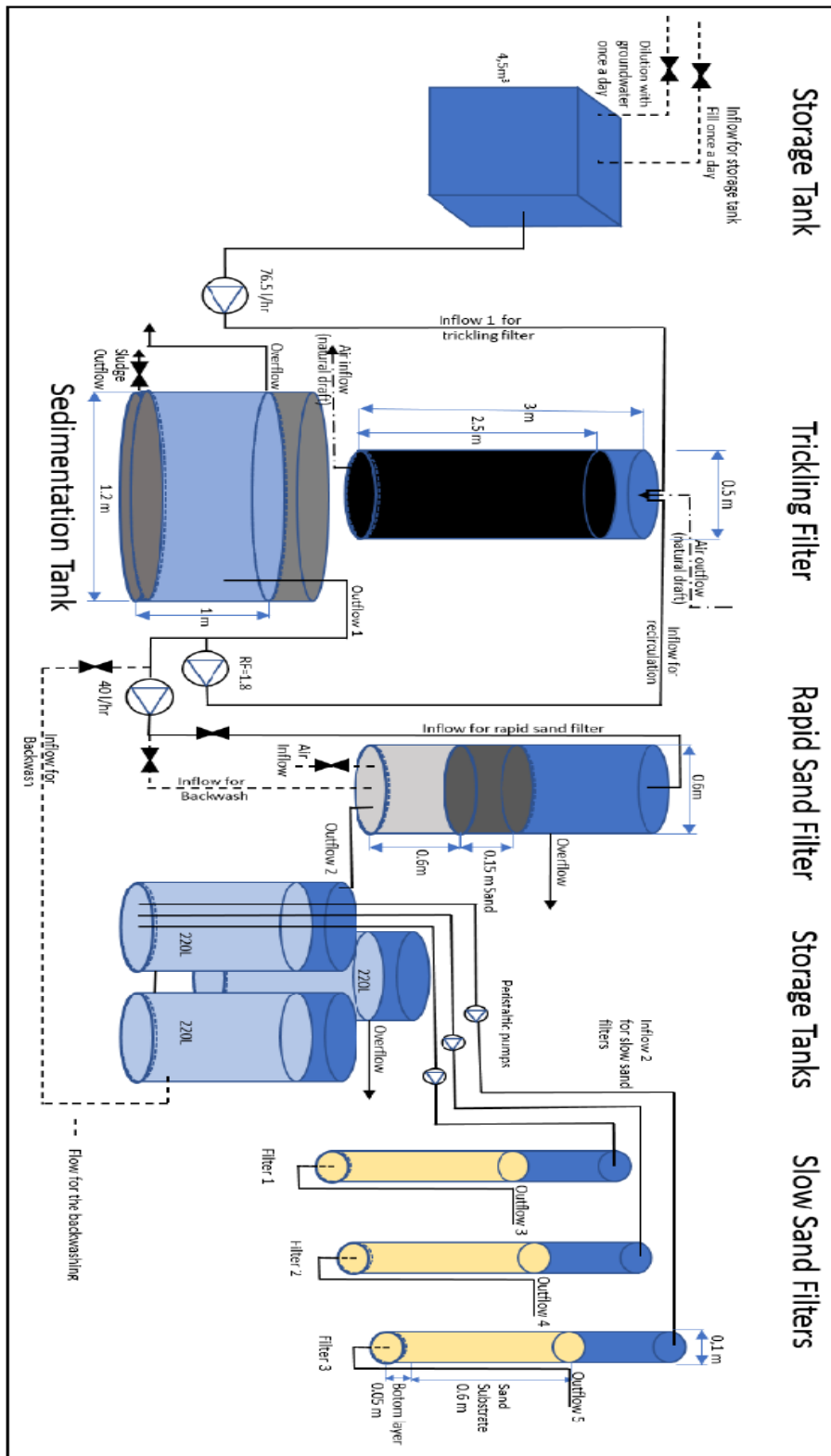


Figure 3.2. Schematic of Unit 1 of the wastewater treatment process [46]

The storage tank has a continuous recirculation in order to dilute the wastewater stream and prevent sedimentation. The fluid is transported through a pump to the rapid sand filter and through a peristaltic pump to the slow sand filters.

The flushing of the TF is usually once a week and when the sloughing of particles occurs. Regarding the RSF, the backwashing with treated effluent is performed when the filter is clogged which is between every day to two times per week. The data from the equipment of this unit is detailed in Table 3.1 [46].

Table 3.1. Equipment dimensions in treatment unit 1 [46]

Equipment	Parameter	amount	Unit
Storage tank	Volume	4.5	m ³
Trickling filter	Height of column	3	m
	Height of substrate	2.5	m
	Diameter	0.5	m
Rapid sand filter	Height of column	0.6	m
	Height of substrate	0.15	m
	Diameter	0.6	m
	Sand particle size	0.4-0.8	mm
Slow sand filter	Height of column	1	m
	Height of the sand layer	0.6	m
	Sand particle size	0.4-0.8	mm
	Porosity	44.1	%
	Weight of sand per column	6.84	kg

3.1.1.2. Unit 2

This unit is composed of a storage tank of nearly 1 m³ with the pre-treated water from the wastewater treatment plant as its influent. The water is led to the coarse sand filter for further treatment. The space between the coarse particles and gravel inside this filter provides an aerobic process besides making a thin biofilm on its top layer. Then water from the bottom of this column flows through a slow sand filter with fine particles which provide an anaerobic system. The latter filter has a rather high hydraulic retention time in order to provide better treatment. Both of these filters have removable covers in order to insulate them from extreme cold weather and minimize the maintenance.

Sampling from the influent of the coarse sand filter was done from the storage tank, the effluent sample of the coarse sand filter was taken through the hose on the top of the slow sand filter column, and the sample from the slow sand filter was taken from the bottom hose located on this filter. Figure 3.3 shows the treatment process in this unit as well as the dimensions of the equipment.

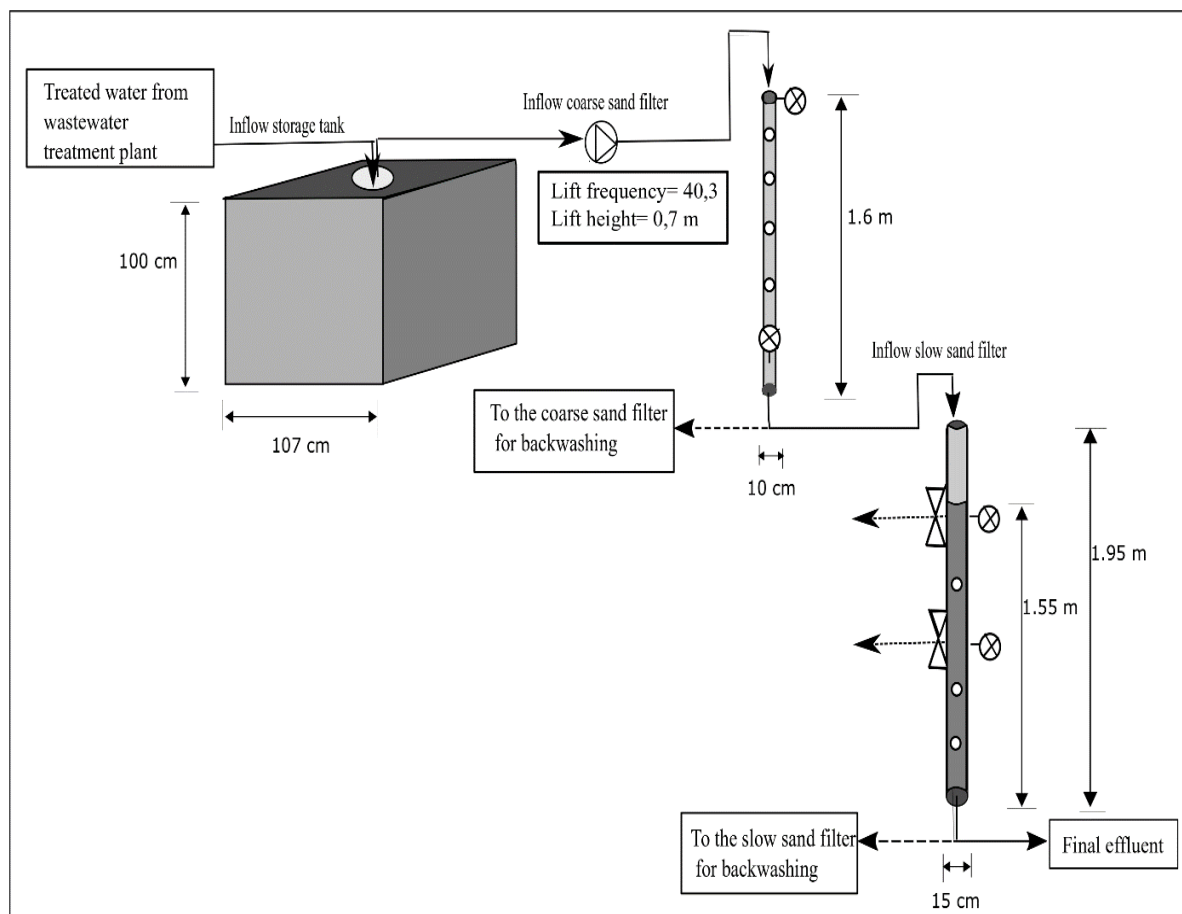


Figure 3.3. Schematic of unit 2 of the treatment process

3.2. Sample preparation

Sample preparation took place in the ISWA Laboratory, and it consisted of the solid phase extraction (SPE) method. SPE is a common approach in laboratories for the extraction of the compounds from a complex matrix to prepare and clean up the analytes for their quantification. SPE lies its foundation on the difference of affinity for a solid phase sorbent (cartridges) between an analyte and interferences, existing in a liquid matrix (wastewater).

In the first step for sample preparation, they were weighed on a scale in order to measure their exact volume considering the density of water. Afterward, specific volumes of the internal standards were added via a syringe. In the next step, SPE was applied. Usually, this technique contains five steps such as conditioning or equilibrating, loading, drying, elution and evaporation (Figure3.4 and Figure3.5).

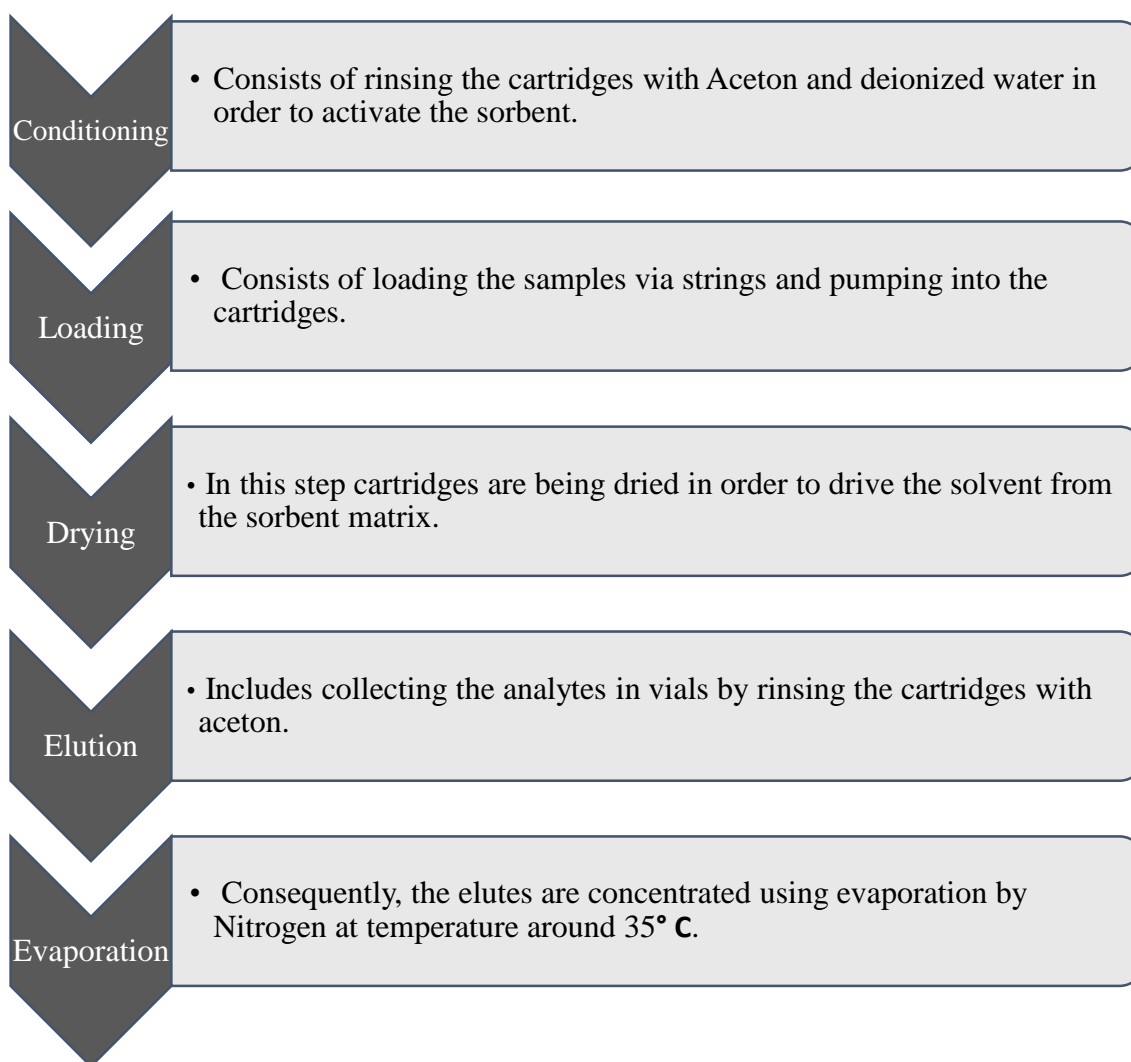


Figure3.4. Solid phase extraction procedure

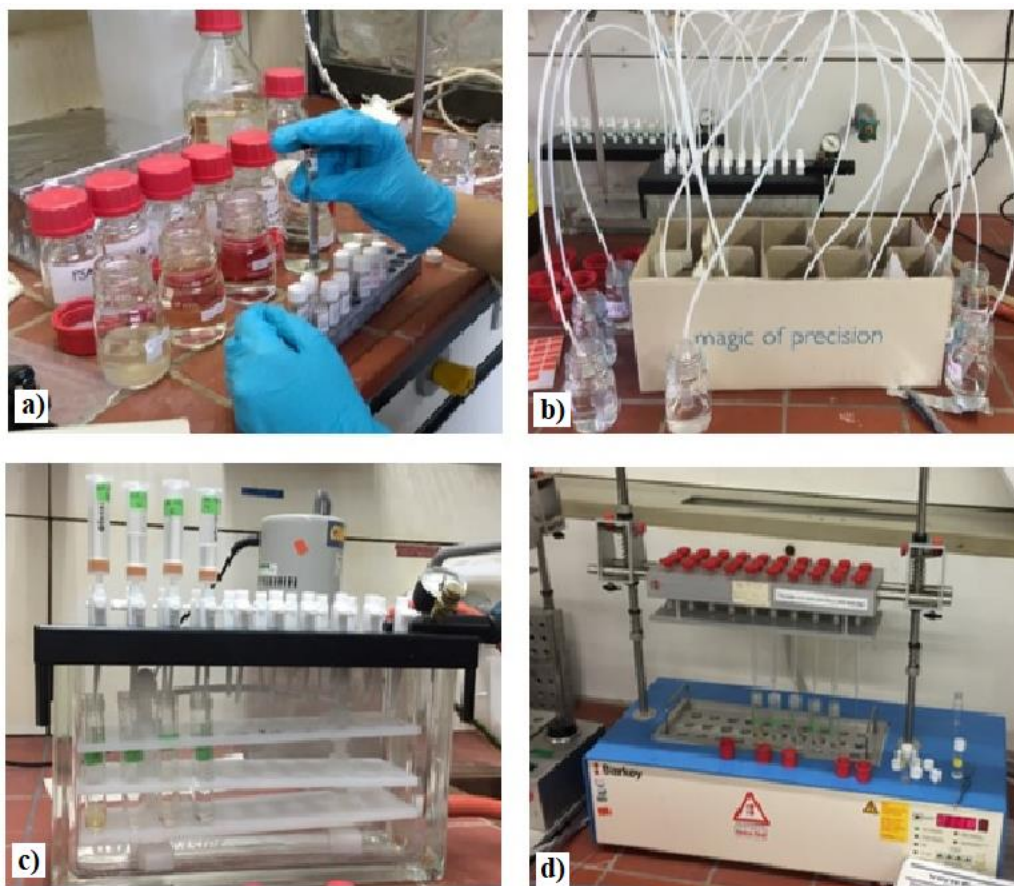


Figure 3.5. Sample preparation procedure: a) Adding the standards to the samples b) Loading c) Elution d) Evaporation

After evaporation, and when the elute volume reached to about 200 μL , it would be ready for the analysis by GCMS. Hence, 50 μL of the sample was injected to a small bottle in order to be placed inside the GCMS device.

3.3. Analysis methods

3.3.1. Micropollutant analysis

The samples were analyzed by gas chromatography-mass spectrometry (GCMS) and high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MSMS) for the determination of micropollutants concentration. GCMS is a common way of analyzing volatile and non-polar compounds while HPLC-MSMS is usually applied for analyzing less volatile and polar compounds. For the purpose of analyzing, the internal calibration method (Isotope dilution) was applied.

3.3.1.1. Internal standard calibration

In this method, the internal standard (the reference compound) has the same chemical and physical properties as the target compound. Hence, by adding the internal standard, the response of the target compound is normalized to the response of the reference standard. For each calibration standard, the ratio of the peak area/height of the target compound to the peak area/height of the internal standard has a similar ratio. The internal standard is a method for the calibration of low concentrates of the compounds and also accounts for the exact extract volume of the sample.

The main disadvantage to internal standard calibration is that the internal standards must be different compounds than those existing in the samples to be analyzed and they must produce a recognizable response on the chromatographic detector system.

Table 3.2 and 3.3 indicate the selected internal standards that have been applied for the GCMS and HPLC-MSMS analysis of the micropollutants.

Table 3.2. Selected internal standards for GCMS analysis

	Internal standard	Volume (μL)	Concentration (ng/μL)
Neutral samples	Carbamazepine-d ¹⁰	50	10.5 in DCM
	Lidocaine-d ¹⁰	50	9.9 in DCM
	AHTN-d ³	100	1.1 in Methanol
	Caffeine-13C ₃	100	2.154 in Methanol
	Terbutryne-d ⁵	50	4.2 in Methanol
	BBP-d ⁴ / DBP-d ⁴	100	2 in Methanol
Acidified samples	Triclosan-d ³	100	1 in DCM
	Mecorop-d ³	50	8.88 in Methanol
	Naproxen-d ³	50	6.32 in Methanol
	Bisphenol A-d ¹⁶	100	1.08 in Methanol

Table 3.3. Selected internal standards for HPLC-MSMS analysis

Internal standard	Concentration (μg/mL)
1 H Benzotriazole-d4	1.27
Gabapentine-d10	0.25
Carbamazepine-d10	0.2
Sulfamethoxazole-d4	0.5825
Metoprolol-d7	0.2022
Hydrochlorothiazide-d6	0.514
Irbesartan-d7	0.5
Candesartan-d5	0.5
Diclofenac-d4	0.5

3.3.1.2. Quantification

Figure 3.6 indicates Aniline peak obtained from MSD ChemStation software. Graph (a) demonstrates the quantity of Aniline on its retention time (min), graph (b) shows the quality of this micropollutant based on retention time and graph (c) provides information regarding the abundance of the internal standard depends on its retention time. By knowing the retention time of each compound, the peaks can be detected, and the area beneath them can be integrated for further calculating the concentration of the micropollutant.

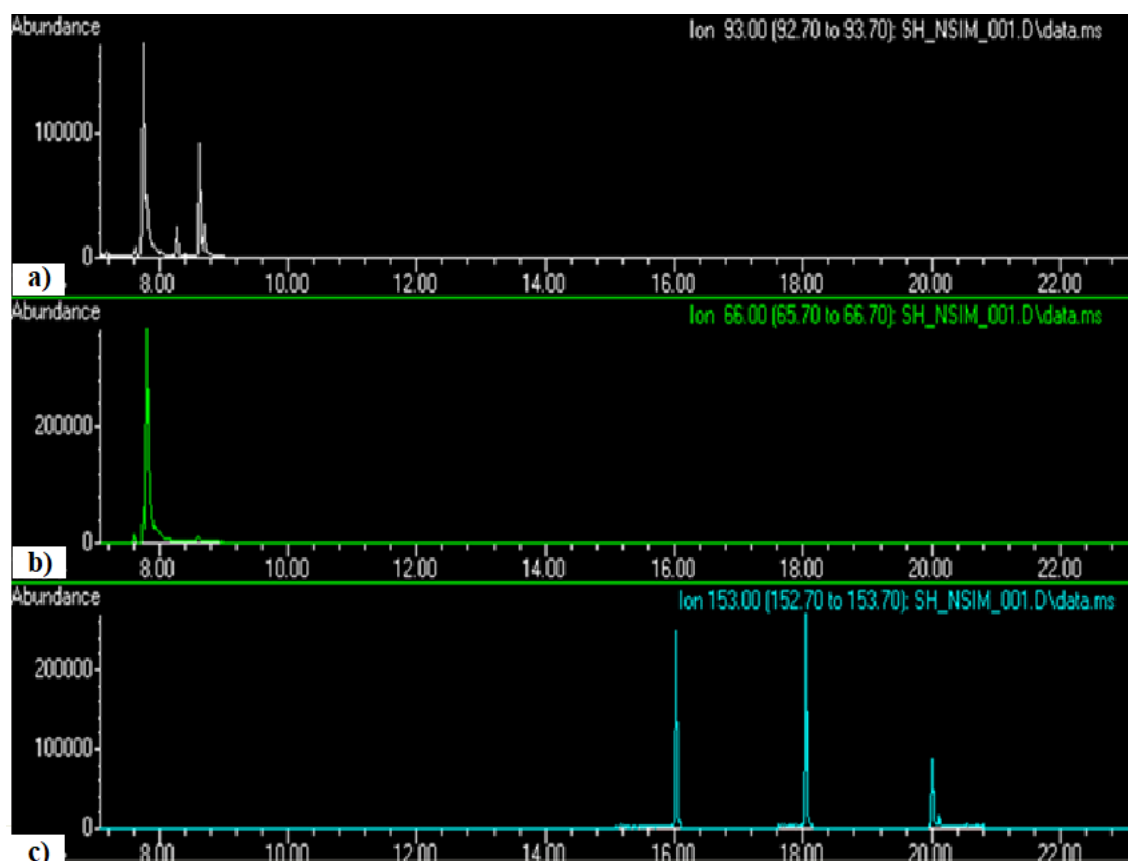


Figure 3.6. Target and internal standard peaks of Aniline detected in MSD ChemStation: a) Quantifier $m/z=93$, retention time=7.758. b) Qualifier $m/z=66$, retention time= 7.758. c) Internal standard quantifier $m/z=153$, retention time=18.028

The concentration of the target compound in the extracted sample can be derived using the following formula.

$$C = \frac{\frac{A_c}{A_s} * M_s}{V}$$

C: Micropollutant concentration ($\mu\text{g/L}$)

M_s : Mass of the internal standard (ng)

A_c : Peak area of the target compound

A_s : Peak area of the internal standard

V: Sample volume (mL)

Table 3.4 provides information regarding the retention time, quantifier and qualifier of the target compounds and the internal standards applied in this study.

Table 3.4. Properties of the selected target compound and the internal standards

Target compound				Internal standard			
RT (min)	Compound	Quantifier (m/z)	Qualifier (m/Z)	RT (Min)	Compound	Quantifier (m/z)	Qualifier (m/Z)
7,700	Siloxane-D4	281	265	18.028	Di-n-butyl-phthalate-d4	153	–
7,758	Aniline	93	66	18.028	Di-n-butyl-phthalate-d4	153	–
7,814	Phenol	94	66	18.028	Di-n-butyl-phthalate-d4	153	–
9,380	Methylphenol	107	108	18.028	Di-n-butyl-phthalate-d4	153	–
10,000	Triethylphosphate	155	99	18.028	Di-n-butyl-phthalate-d4	153	–
10,050	Siloxane-D5	355	267	18.028	Di-n-butyl-phthalate-d4	153	–
11,461	Phenoxyethanol	94	138	18.028	Di-n-butyl-phthalate-d4	153	–
11,633	Benzothiazole	135	108	18.028	Di-n-butyl-phthalate-d4	153	–
11,740	Phenoxypropanol	94	152	18.028	Di-n-butyl-phthalate-d4	153	–
12,433	Indole	117	90	18.028	Di-n-butyl-phthalate-d4	153	–
13,035	Nicotine	84	133	18.028	Di-n-butyl-phthalate-d4	153	–
13,450	Chlorocresol	156	158	18.028	Di-n-butyl-phthalate-d4	153	–
13,540	Methylindole	130	131	18.028	Di-n-butyl-phthalate-d4	153	–
14,605	Dimethyldodecylamine (DMDA)	58	213	18.028	Di-n-butyl-phthalate-d4	153	–
15,835	MTBT	181	148	18.028	Di-n-butyl-phthalate-d4	153	–
15,900	TAED	72	127	18.028	Di-n-butyl-phthalate-d4	153	–
15,996	Benzophenone	105	182	18.028	Di-n-butyl-phthalate-d4	153	–
16,000	Diphenylmethanol	105	184	18.028	Di-n-butyl-phthalate-d4	153	–

Target compound				Internal standard			
RT (min)	Compound	Quantifier (m/z)	Qualifier (m/Z)	RT (Min)	Compound	Quantifier (m/z)	Qualifier (m/Z)
16,000	Triethylcitrate	157	203	18.028	Di-n-butyl-phthalate-d4	153	–
16,027	Methyl-DHJ	83	153	18.028	Di-n-butyl-phthalate-d4	153	–
16,198	4t-Octylphenol	135	206	18.028	Di-n-butyl-phthalate-d4	153	–
16,205	OTNE	191	234	18.028	Di-n-butyl-phthalate-d4	153	–
16,363	Dimethyltetradecylamine (DMTDA)	58	241	18.028	Di-n-butyl-phthalate-d4	153	–
16,450	4-Nonylphenols	135	121	18.028	Di-n-butyl-phthalate-d4	153	–
16,557	Cotinine	98	176	18.028	Di-n-butyl-phthalate-d4	153	–
16,865	Tris-(chloroethyl)-phosphate (TCEP)	249	251	18.028	Di-n-butyl-phthalate-d4	153	–
17,058	Tris-(chloropropyl)-phosphate (TCPP)	277	279	18.028	Di-n-butyl-phthalate-d4	153	–
17,332	Traseolide	258	243	17.484	AHTN-d3	261	246
17,462	Galaxolide (HHCB)	258	243	17.484	AHTN-d3	261	246
17,497	Tonalide (AHTN)	258	243	17.484	AHTN-d3	261	246
17,500	3,3-Diphenylacrylonitrile	204	205	18.028	Di-n-butyl-phthalate-d4	153	–
17,520	Caffeine	194	109	17.520	Caffeine-13C3	197	111
17,689	Diphenhydramine	58	165	17.687	Lidocaine-d10	96	244
17,727	Lidocaine	86	234	17.687	Lidocaine-d10	96	244
18,020	Terbutryne	226	241	17.994	terbutryne-d5	231	246
18,206	Tramadol	58	263	17.687	Lidocaine-d10	96	244
18,293	OTNE-OX	121	248	18.028	Di-n-butyl-phthalate-d4	153	–
18,600	O-Desmethyl-tramadol	58	149	17.687	Lidocaine-d10	96	244
18,928	Venlafaxine	58	134	17.687	Lidocaine-d10	96	244
19,000	AHTN-OX	244	272	17.484	AHTN-d3	261	246
19,014	Methyltriclosan	302	304	18.028	Di-n-butyl-phthalate-d4	153	–

Target compound				Internal standard			
RT (min)	Compound	Quantifier (m/z)	Qualifier (m/Z)	RT (Min)	Compound	Quantifier (m/z)	Qualifier (m/Z)
19,251	Norvenlafaxine	58	120	17.687	Lidocaine-d10	96	244
19,298	Galaxolidone-I (HHCb-Lactone-I)	257	272	17.484	AHTN-d3	261	246
19,300	Diclofenac (ring closure)	214	242	18.028	Di-n-butyl-phthalate-d4	153	–
19,500	Galaxolidone-II (HHCb-Lactone-II)	257	272	17.484	AHTN-d3	261	246
19,900	Tris-(dichloropropyl)-phosphate (TDCPP)	381	383	18.028	Di-n-butyl-phthalate-d4	153	–
20,125	Tris-(butoxyethoxy)-phosphate (TBEP)	125	199	18.028	Di-n-butyl-phthalate-d4	153	–
20,182	Carbamazepine	193	236	20.160	Carbamazepine-d10	203	246
20,307	Triphenylphosphate (TPP)	325	326	18.028	Di-n-butyl-phthalate-d4	153	–
21,260	Octocrylene	249	360	18.028	Di-n-butyl-phthalate-d4	153	–
21,776	Triphenylphosphin-oxide (TPPO)	277	278	18.028	Di-n-butyl-phthalate-d4	153	–

3.3.2. DOC analysis

Dissolved organic carbon (DOC) in the water sample, is oxidized to CO₂ through two different approaches by a measurement system which make it detectable. These approaches are composed of:

- **High-temperature digestion HT:** In this method, the inorganic carbon (carbonate, lime) is separated by acidification, then thermal-catalytic oxidation is applied on the dissolved organic carbons of water with the help of supplied air in order to form CO₂ and water, finally, CO₂ is detected with a non-dispersive infrared sensor, NDIR device or an elementary cube.
- **Wet-chemical digestion:** First, the acidification of the samples is performed similarly to the HT approach. Subsequently, oxidation through UV light and Peroxydisulfate is applied to form CO₂ in order to be recognized by NDIR device [47].

For the measurement of DOC in wastewater, the samples were collected into 100 ml glass bottles; then they were filtered through a membrane prior to the analysis. Indeed, this is the main difference in measurement, between total organic carbon (TOC) and dissolved organic carbon (DOC). The DOC content of the samples was measured by the laboratory expert using the method High-temperature digestion according to DIN 38409-H3.

3.3.3. UV/Vis spectrophotometry

UV/Vis spectrophotometry is mainly a quantitative analytical technique dealing with the absorption of 180 to 390 nm (near UV) or 390 to 780 nm (visible) radiation. The amount of absorbed radiation is directly proportional to the concentration of the analyte in the solution. This relation is known as Beer's law:

$$A = \text{Log}(I_0/I) = \epsilon L C$$

A: Absorbance

I_0 : Light intensity of the sample entering

I: Light intensity of the sample leaving

ϵ : Molar extinction coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)

L: Path length of the cuvette containing the sample (cm)

C: Concentration ($\text{mol}\cdot\text{L}^{-1}$)

This absorption method relies on the transition of the substances to the excited state. The species which require high energy for accomplishing their excited states show low absorption wavelength whereas when less energy is needed, the absorption wavelength is higher [48].

The spectrometry of the samples was performed via a Shimadzu UV-1800 measurement device with the following path lengths and wavelength ranges:

- The path length of 1 cm for 190-650 nm wavelengths.
- The path length of 5 cm for 240-650 nm wavelengths.

Spectral absorption coefficient SAC is a parameter commonly used in this method for demonstrating the absorption in visible regions of 436 nm (yellow region), 525 nm (red region) and 620 nm wavelength (blue region). SAC is calculated as follow:

$$\text{SAC} = (\text{Abs.} / L) * 100$$

SAC: Spectral absorption coefficient (m^{-1})

Abs: Absorption at a certain wavelength

L: Path length of the cuvette (cm)

3.3.4. Conductivity measurement

The conductivity of all samples was measured using a measurement apparatus called Inolab Cond Level 2 in $\mu\text{s}/\text{cm}$ for each sample at its specific temperature.

3.3.5. Molecular orbital energy

The reactivity and structure of the molecules can be explained using the ideas of “Frontier molecular orbital” theory. The most critical orbitals in molecules regarding the reactivity are the two frontier orbitals such as:

- Highest occupied molecular orbital (HOMO)
- Lowest unoccupied molecular orbital (LUMO)

HOMO is considered as a nucleophile or electron donor, whereas LUMO is electrophile and an electron acceptor. In addition, chemical reactions and resonance can also be explained by interactions between a filled HOMO and an empty LUMO [48]. Concerning the energy, the HOMO-LUMO energy gap is where the excitation can occur. Hence, the excitation becomes easier as the energy gap decreases for instance in the case of large aromatic compounds.

The orbital energies of the selected micropollutants were calculated by HyperChem Professional 8.05. The calculation has been performed in a semi-empirical approach and by three methods of PM3, AM1 and Extended Hückel. Furthermore, the dipole moment and Log P has been calculated for further investigation (Table 4 in Appendix). Figure 3.7 from Hyperchem, indicates the HOMO and LUMO as well as the energies of the orbitals for Aniline molecule. The corresponding energies for HOMO and LUMO in this molecule through the semi-empirical PM3 approach correspond to -8.068 eV and 0.615 eV respectively.

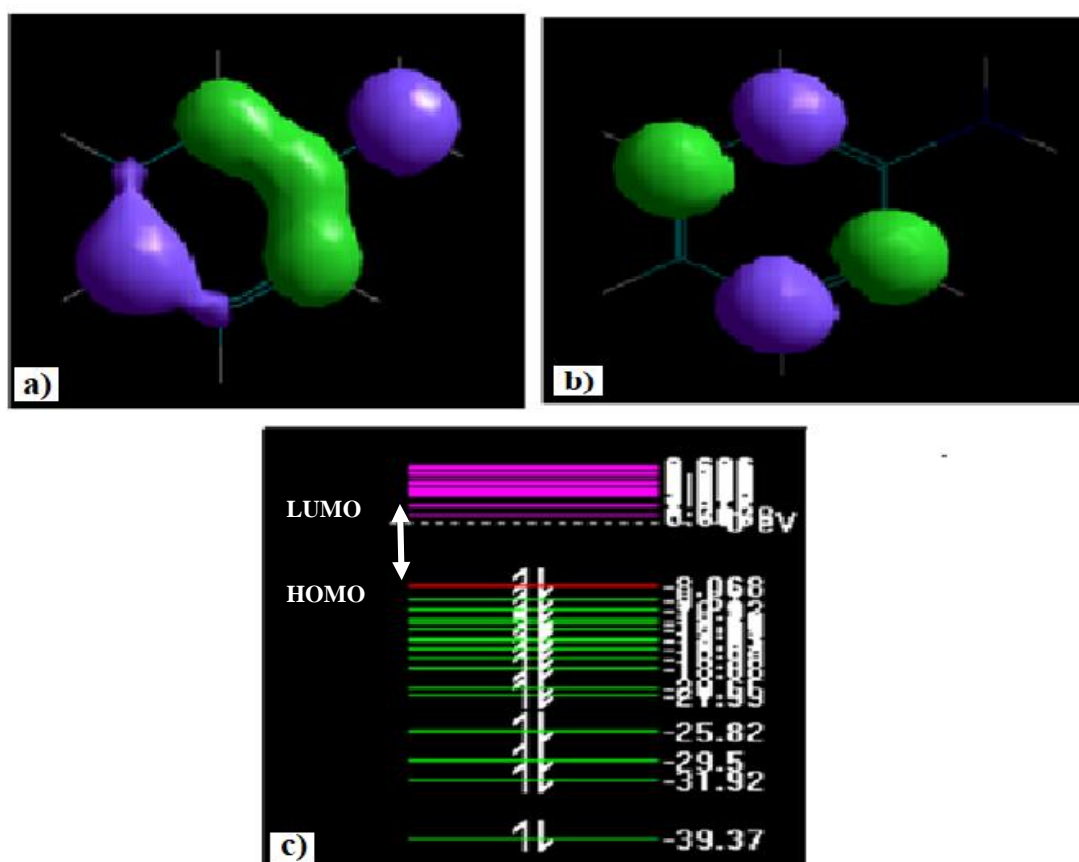


Figure 3.7. a) HOMO in Aniline b) LUMO in Aniline c) Orbital energies HOMO=-8.068 eV, LUMO=0.616 eV

4. Results and discussion

4.1. Removal of Micropollutants by sand filters and trickling filters

In this section, elimination of the analyzed micropollutants of the wastewater by sand filters and trickling filters are plotted respecting their physical-chemical properties and molecular orbital energies in order to compare the filter type in addition to classifying the micropollutants.

4.1.1. Influence of physical-chemical properties on the removal of Micropollutants by Trickling Filters and Sand Filters

4.1.1.1. Influence of Hydrophobicity

Octanol-water coefficient (Log Kow) is one of the properties of the compounds, applied as a measure to indicate the hydrophobicity. It is the main reason for adsorbing the compounds to the solid. Indeed, it is an estimate of partitioning the organic solute between the organic phase, octanol and the water phase. Hence, high Kow (Log Kow>4) is characteristic for hydrophobic compounds and poor hydro-solubility, which can be an indicator of high sorption [29].

Elimination of Micropollutants through Trickling Filters TF1 and TF2

Figure 4.1 indicates the elimination of the Micropollutants with Log Kow>4 by Trickling Filter 1 and Trickling Filter 2 which are located in Unit 1 of the treatment plant. TF1 is to proceed with the raw wastewater and TF2 proceeds the pre-treated wastewater. It is implied from the graph that TF1 has better performance rather than TF2 due to its higher influent concentration. An exception can be seen for Nonylphenol with significantly higher removal by TF2 than TF1 and Triphenyl phosphine oxide (TPPO) with slightly higher degradation by TF2 than TF1.

Micropollutants including Galaxolidone I and II, Traseolide, AHTN-Oxide and Candesartan show nearly no degradation in trickling filters. Galaxolidone I and II plus AHTN-Oxide are metabolites of Galaxolide and AHTN which are applied as polycyclic musks. Candesartan is a pharmaceutical with a complex structure and a high number of aromatic rings.

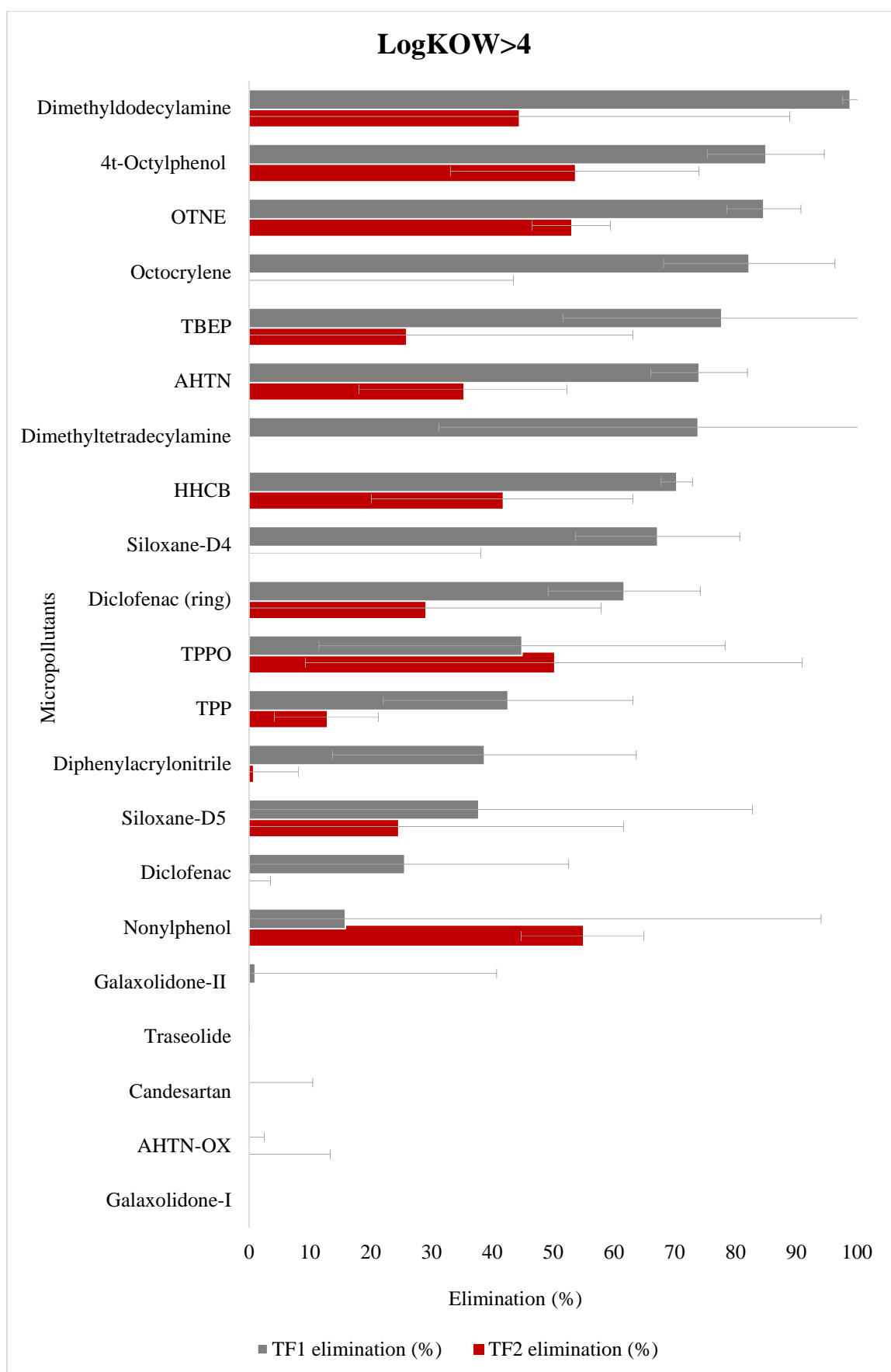


Figure 4.1 Removal of MPs with Log Kow>4 from wastewater by TF1 and TF2

Figure 4.2 provides information on the removal of organic compounds with moderate sorption ($2.5 < \text{Log Kow} < 4$) by TF1 and TF2. The higher performance of TF1 with dirty influent of the wastewater can be observed except for MTBT and Norvenlafaxine. MTBT and Norvenlafaxine (derivative of Venlafaxine) are both transformation products in TF1.

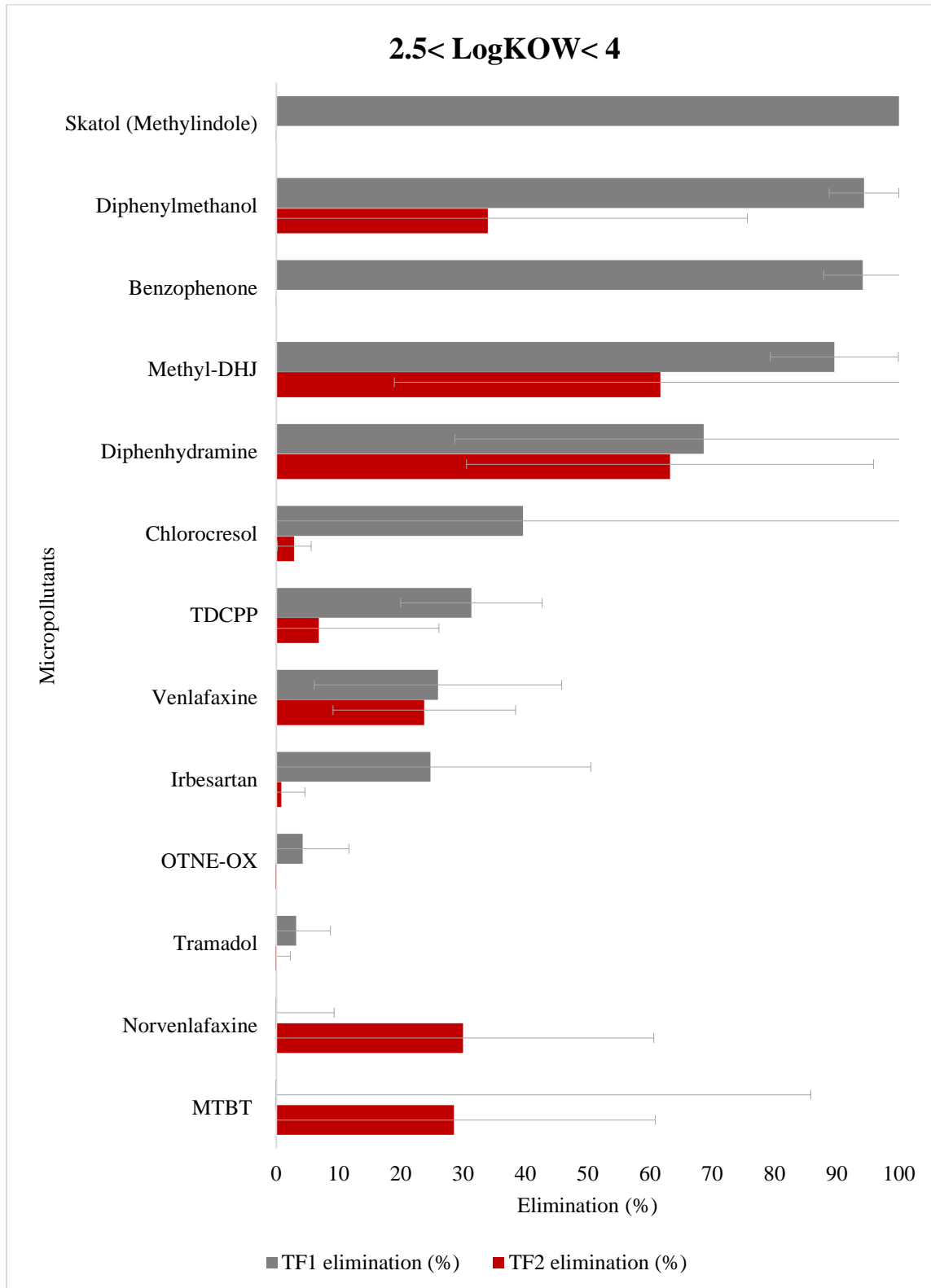


Figure 4.2. Removal of MPs with $2.5 < \text{Log Kow} < 4$ from wastewater by TF1 and TF2

Figure 4.3 demonstrates the treatment of micropollutants with low sorption capability ($\text{Log Kow} < 2.5$) by TF1 and TF2 showing more than 99% elimination of TAED, Phenol, Indole, Cotinine, Methylphenol and Phenoxyethanol by TF1 making it an efficient method for treatment of these compounds. It can also be concluded that trickling filter (TF2) can be an excellent approach for the treatment of Indole even with very low concentration, as it has removed more than 90% of this micropollutant from pre-treated wastewater.

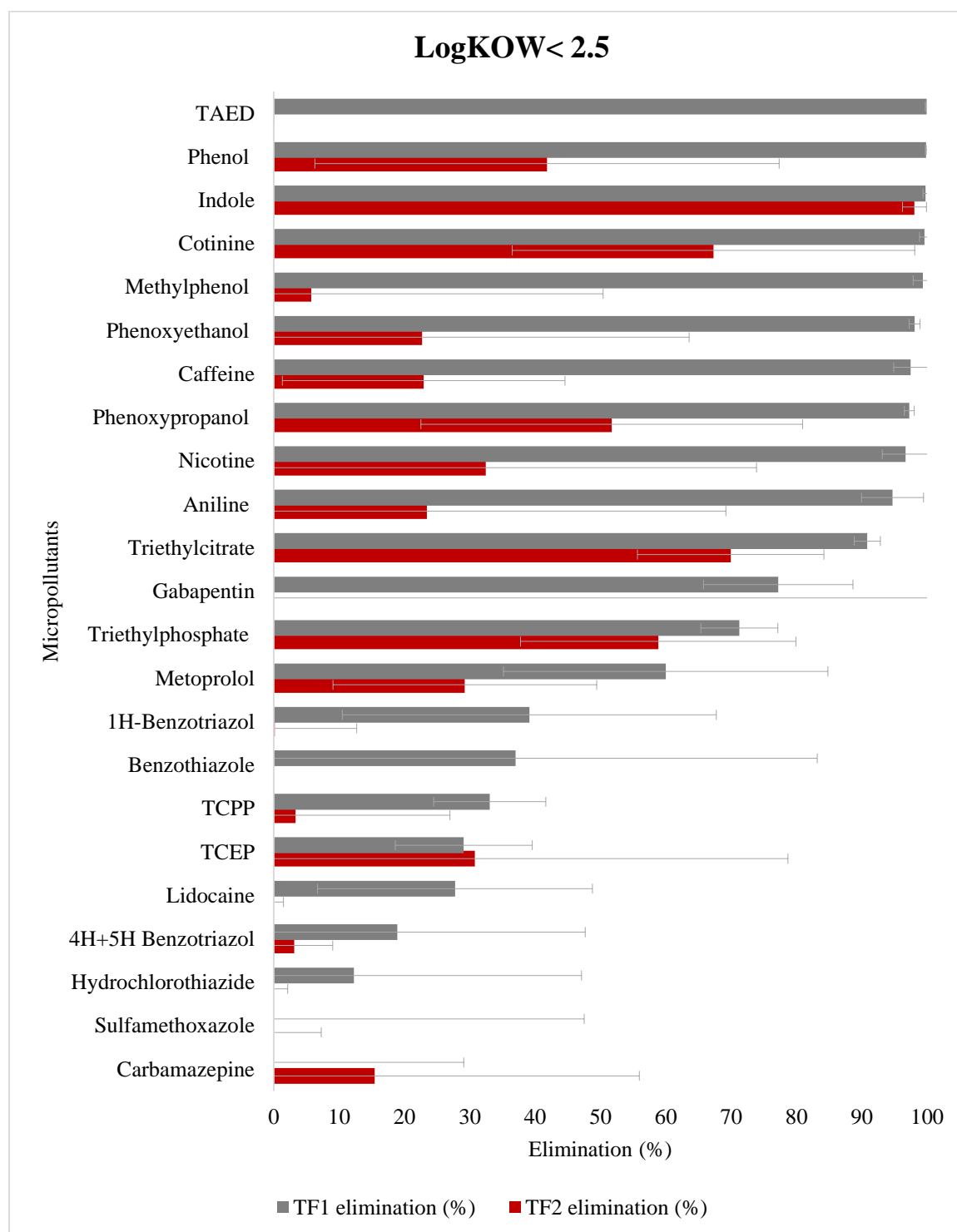


Figure 4.3. Removal of MPs with Log Kow < 2.5 from wastewater by TF1 and TF2

Elimination of Micropollutants through Sand Filters in Unit 1 and Unit 2

Figure 4.4 to Figure 4.6 provides information on the removal of organic compounds through the rapid sand filter (RSF) and slow sand filter (SSF) which are located in unit 1 of the treatment plant following each other. The compounds are categorized based on their hydrophobicity or sorption characteristic into three different groups.

SSF is followed by RSF and many of the compounds have better removal through RSF comparing to those eliminated by SSF. For instance, Dimethyldodecylamine (DMDA) has 74% elimination by RSF and 37 % further removal by SSF. On the other hand, compounds such as TBEP, Octocrylene, HHCB, Triphenyl phosphate (TPP), Triphenyl phosphine oxide (TPPO) and Siloxane-D4 have higher elimination by SSF (Figure 4.4).

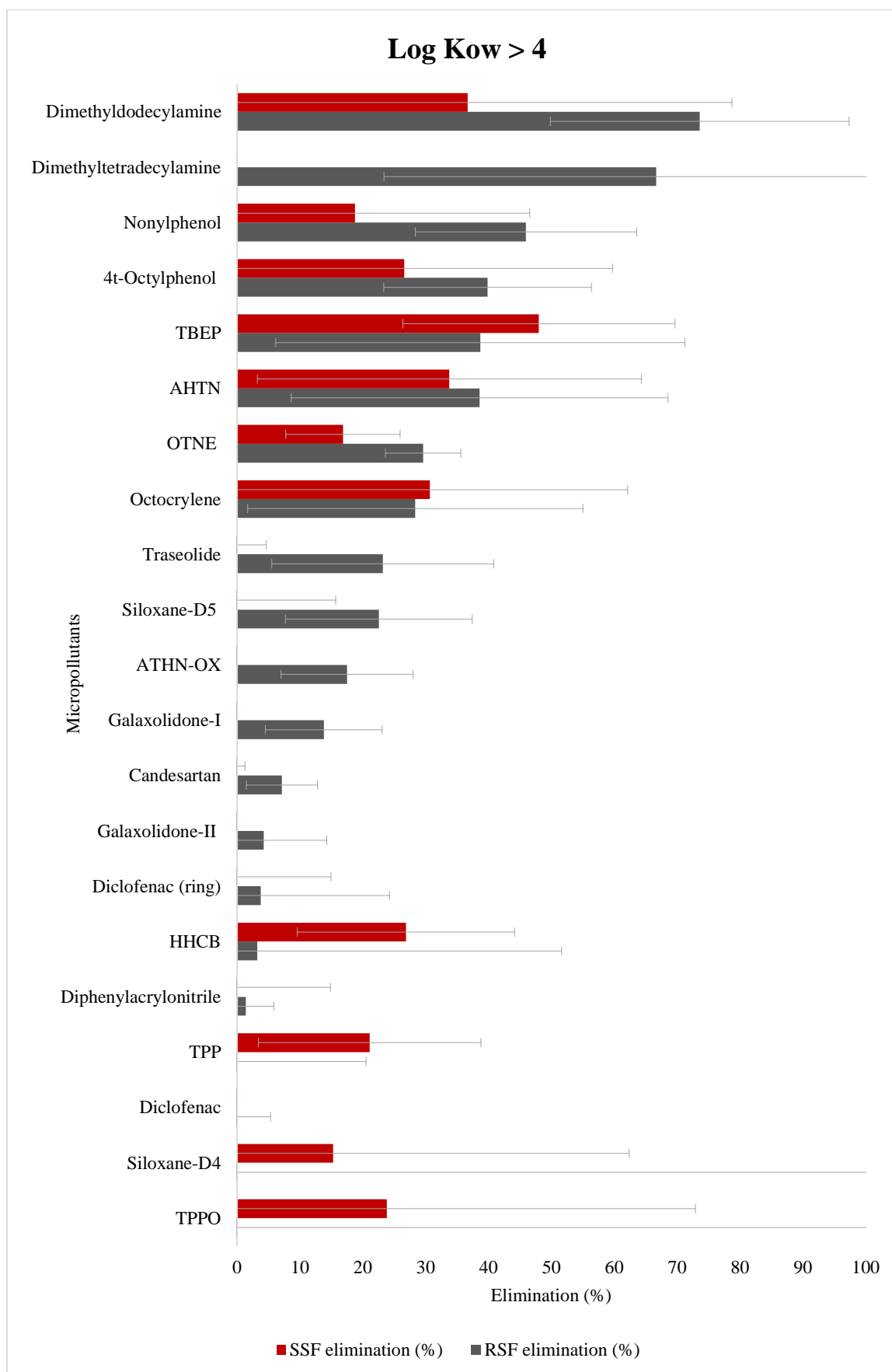


Figure 4.4. Removal of MPs with Log Kow>4 from wastewater by RSF and SSF

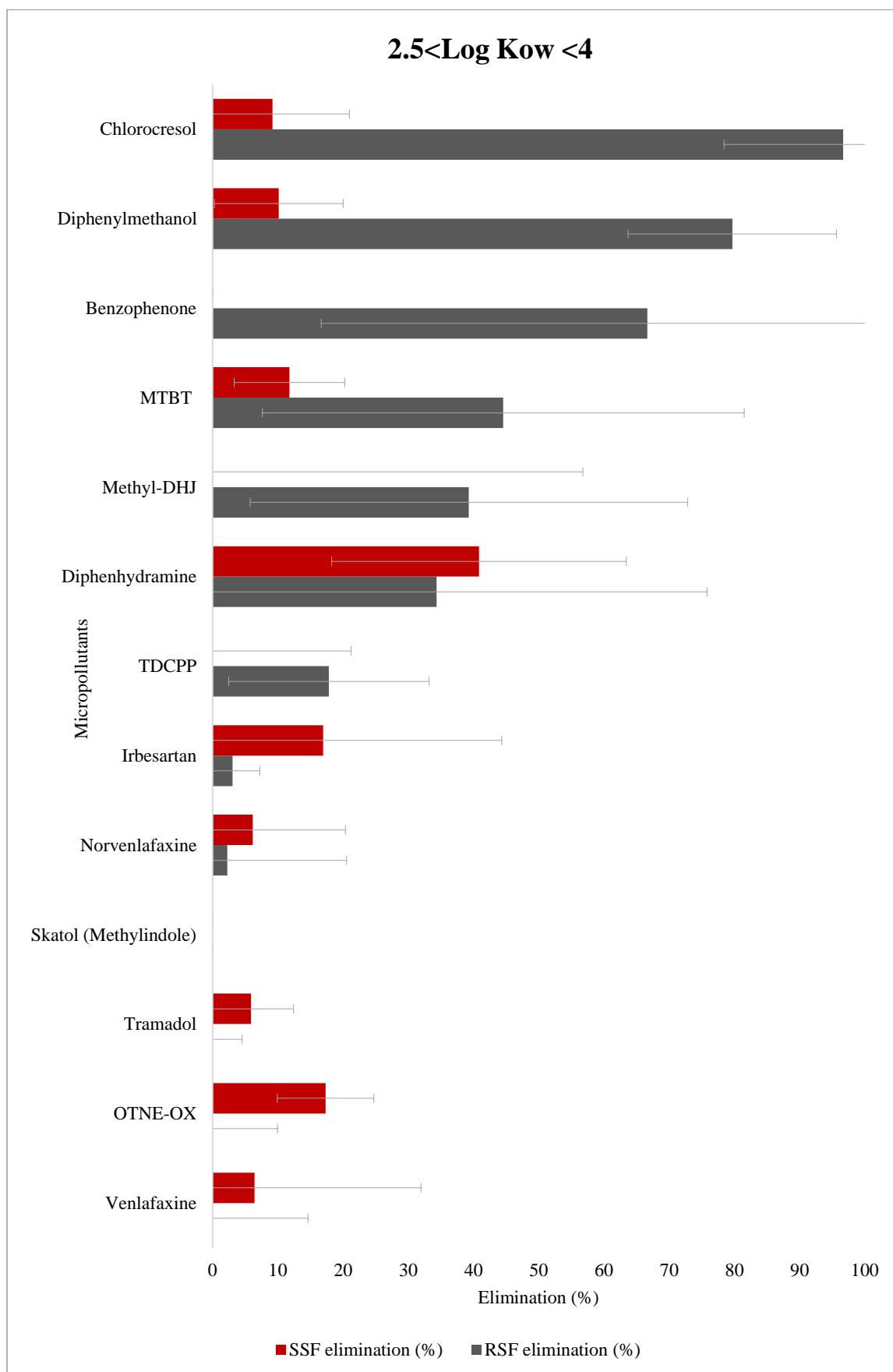


Figure 4.5. Removal of MPs with $2.5 < \text{Log K}_{ow} < 4$ from wastewater by RSF and SSF

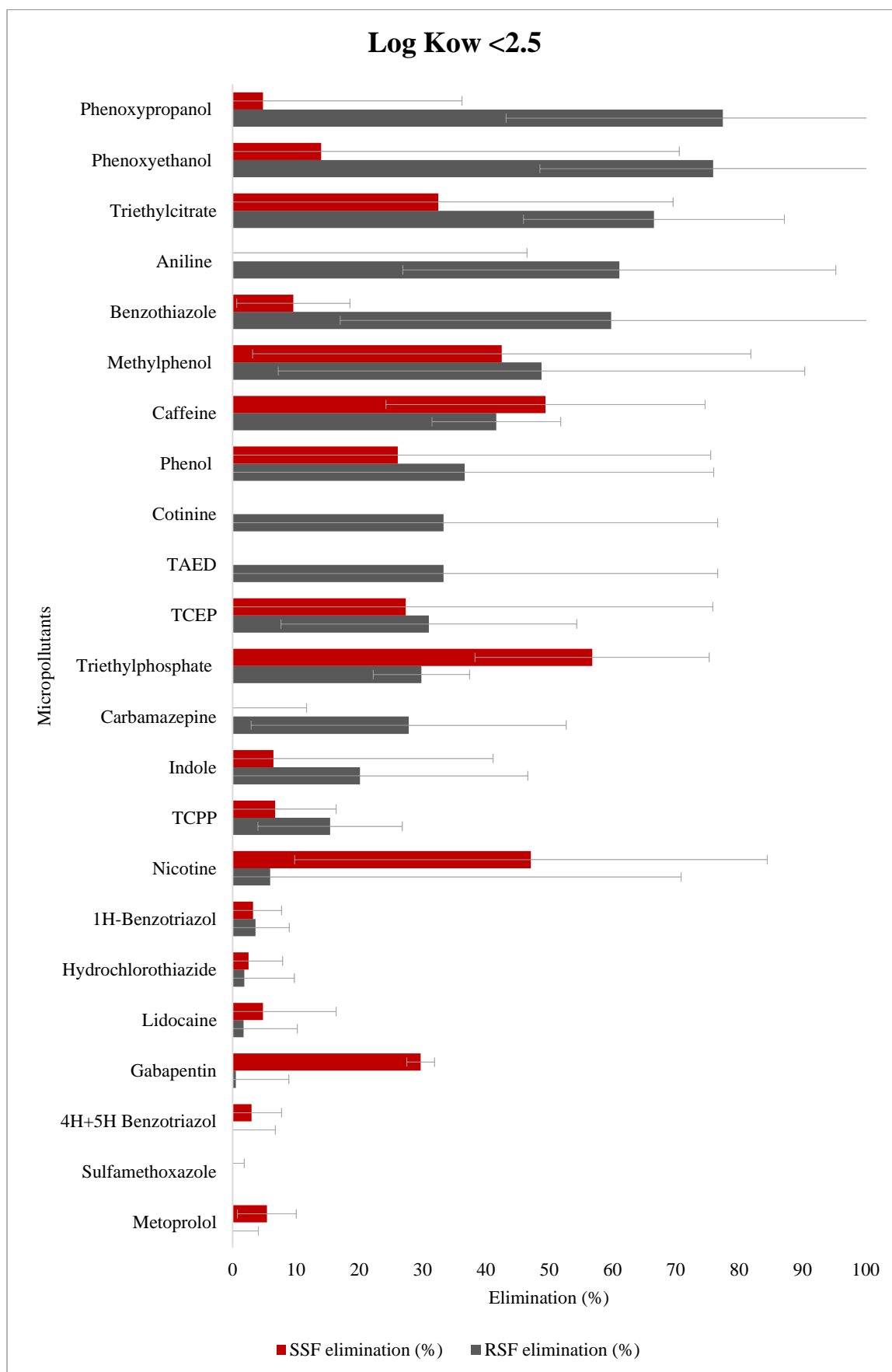


Figure 4.6. Removal of MPs with Log Kow<2.5 from wastewater by RSF and SSF

Figure 4.7 to Figure 4.9 shows micropollutant removal by sand filters with high retention time locating in unit 2 for three different categories of the micropollutants based on hydrophobicity.

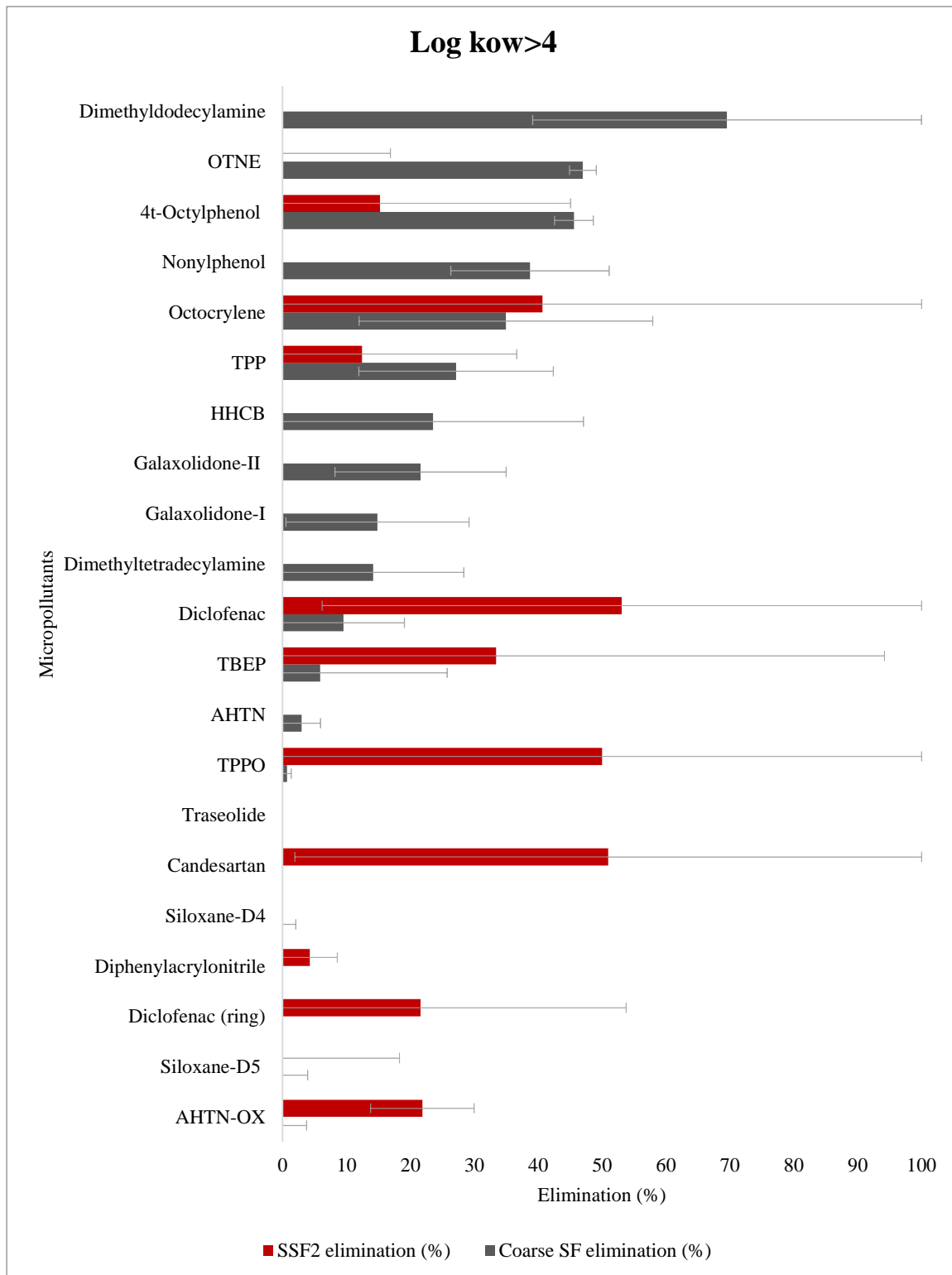


Figure 4.7. Removal of MPs with Log Kow > 4 from wastewater by Coarse SF and SSF2

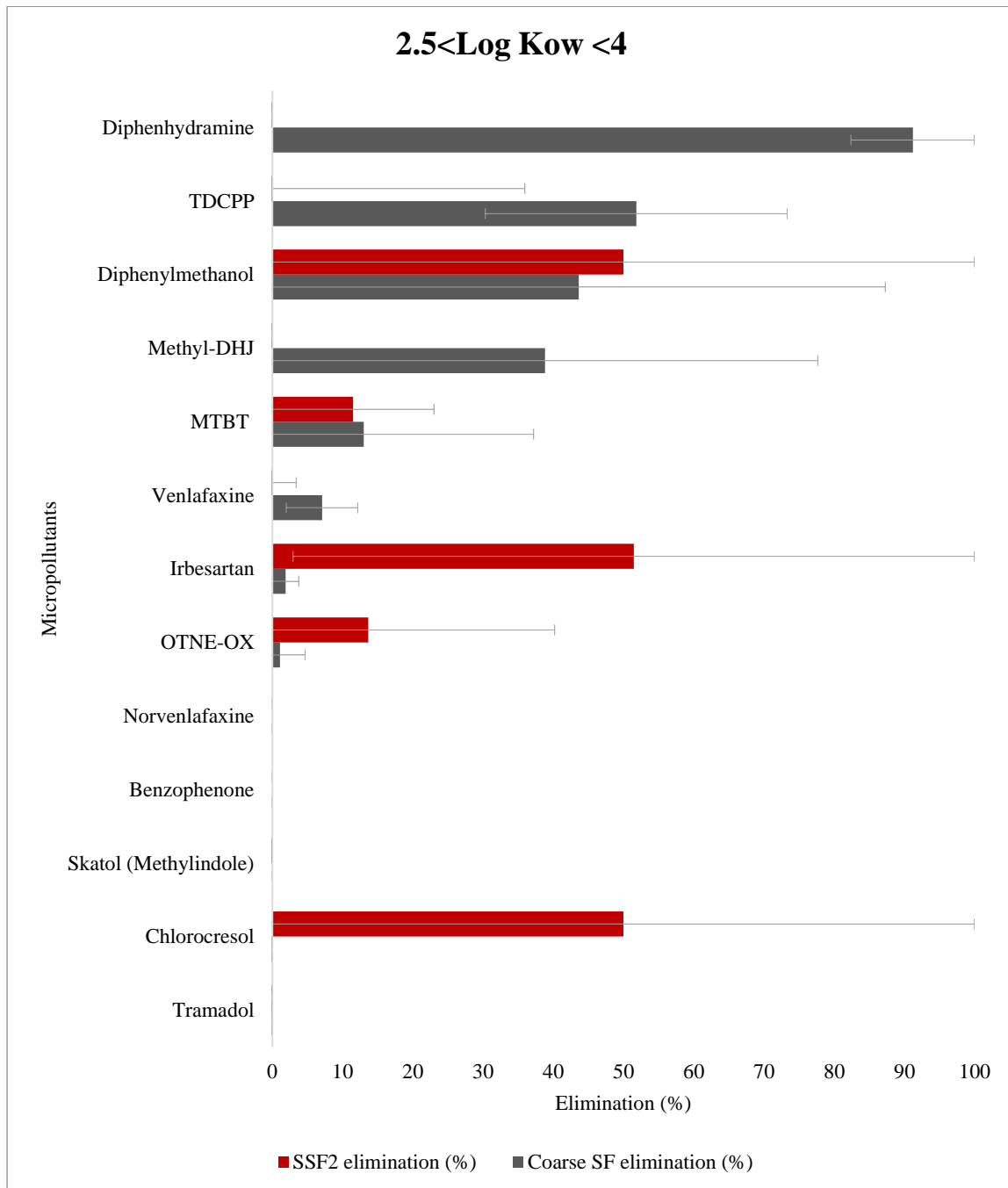


Figure 4.8. Removal of MPs with $2.5 < \text{Log } K_{ow} < 4$ from wastewater by Coarse SF and SSF2

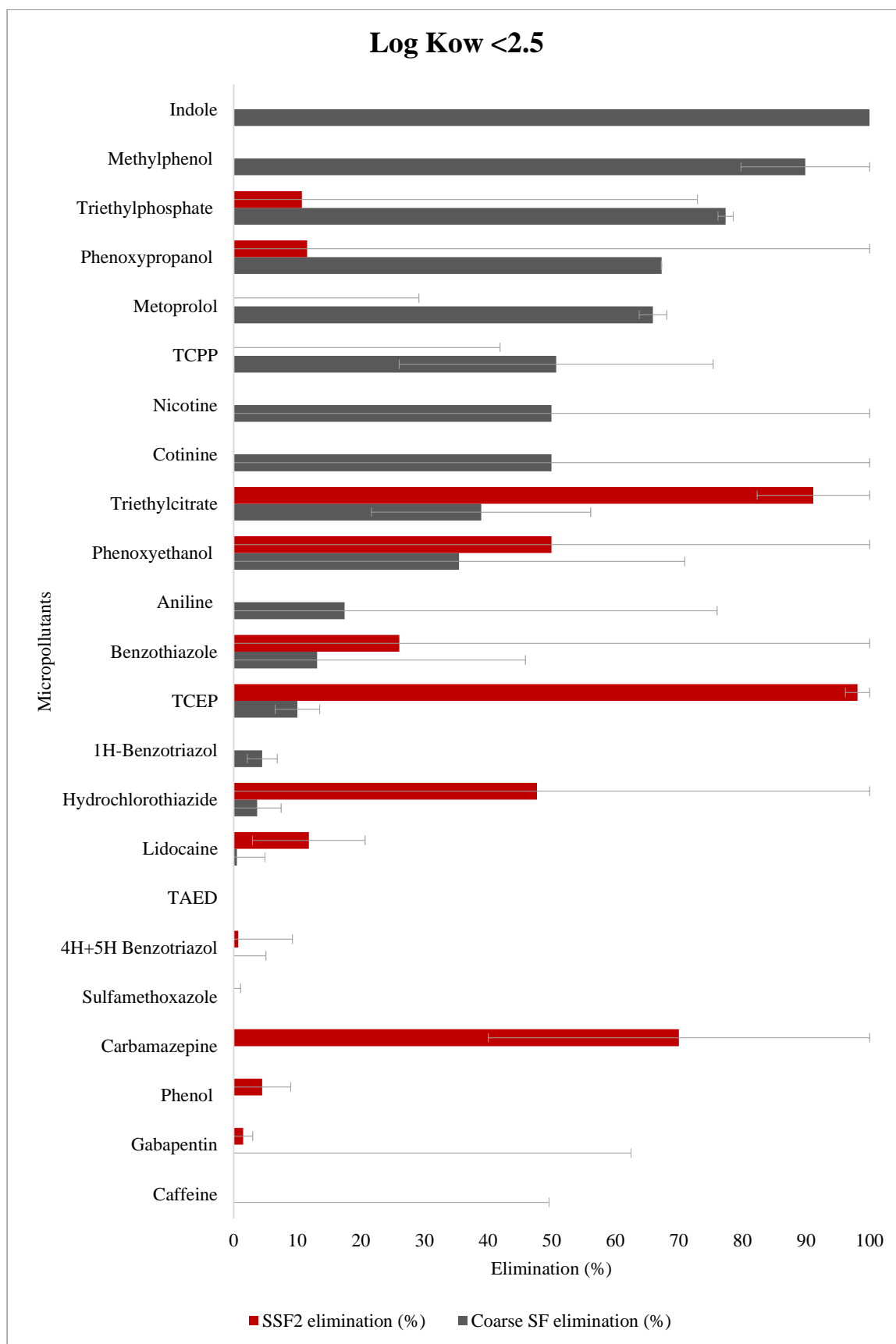


Figure 4.9. Removal of MPs with Log Kow <2.5 from wastewater by Coarse SF and SSF2

4.1.1.2. Influence of Polarizability

Polarizability is the ability of a compound to turn into an electrical dipole due to a distortion in its electron configuration. The higher distortion ability leads to more polarizability of the molecule.

Figure 4.10 provides information on sorption capability of the aliphatic compounds (micropollutants with no aromatic rings) and the effect of polarizability. As it is shown from the graph, Removal efficiencies differ from one compound to the other even by considering all of them to be in the same group of aliphatic compounds. However, the correlation between the compounds in the same family such as Siloxane D4 and Siloxane D5; TCPP, TDCPP and TBEP implies that increasing the polarizability among the aliphatic compounds with similar structure can lead to an increase in removal efficiency (Table 4.1). Sorption of aromatic compounds with 3 aromatic rings is also slightly affected by polarizability in a way that removal by the sand filter is increased by increasing more polarized compounds (Figure 4.11).

It is also noted that increasing the number of aromatic rings can, negatively impact the average removal efficiency of micropollutants (Figure 4.10 and Figure 4.11).

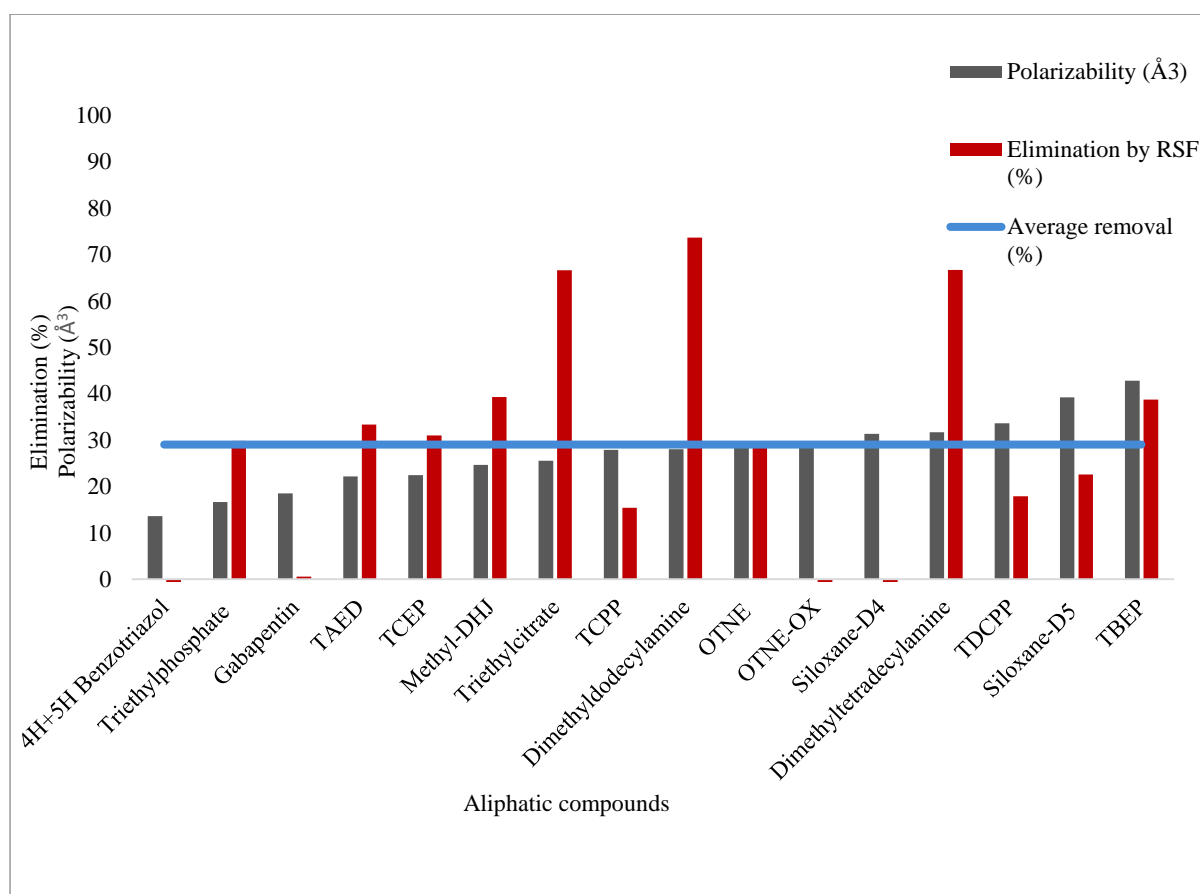


Figure 4.10. Influence of polarizability on the removal of aliphatic compounds by RSF

Table 4.1. Influence of polarizability on the removal of similar aliphatic compounds from RSF

Aliphatic MPs	Polarizability (\AA^3)	Removal by RSF (%)
Siloxane-D4	31.33	0
Siloxane-D5	39.16	22.57
TCPP	27.89	15.41
TDCPP	33.63	17.84
TBEP	42.77	38.70

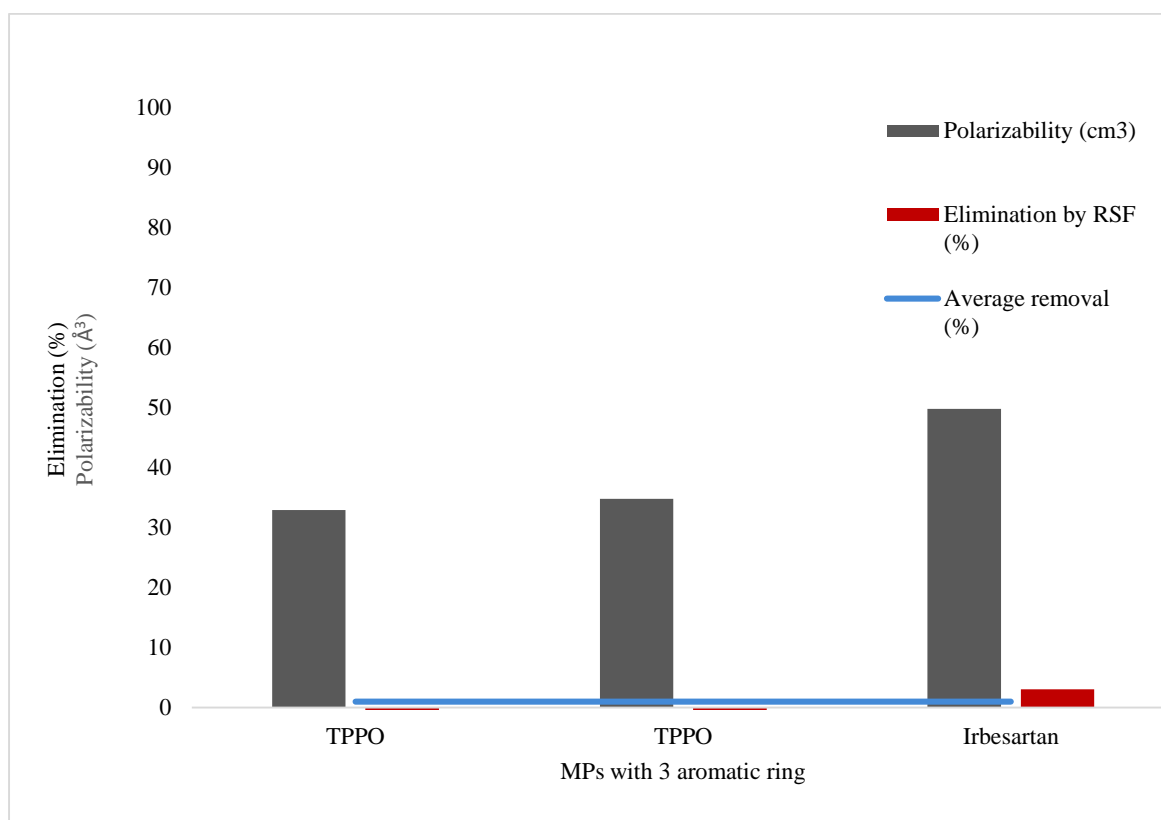


Figure 4.11. Influence of polarizability on the removal of aromatic compounds with 3 rings by RSF

4.1.2. Comparison between the removal efficiencies of the sand and trickling filters (sorption and biodegradation)

As mentioned previously, the trickling filter 1, rapid sand filter and slow sand filter locating in unit 1 are followed by each other. Biodegradation and sorption of micropollutants can be compared by the differences between removal efficiencies of the sand filters and the trickling filter (Figure 4.12).

For micropollutants showing high elimination capability by trickling filter despite having low hydrophobicity, biodegradation is the dominant mechanism. Examples of these compounds are Skatol, TAED and Phenol.

Compounds having a relatively better removal by sand filters correspond to those that have high adsorption capability if their hydrophobicity is high such as Candesartan and Traseolide.

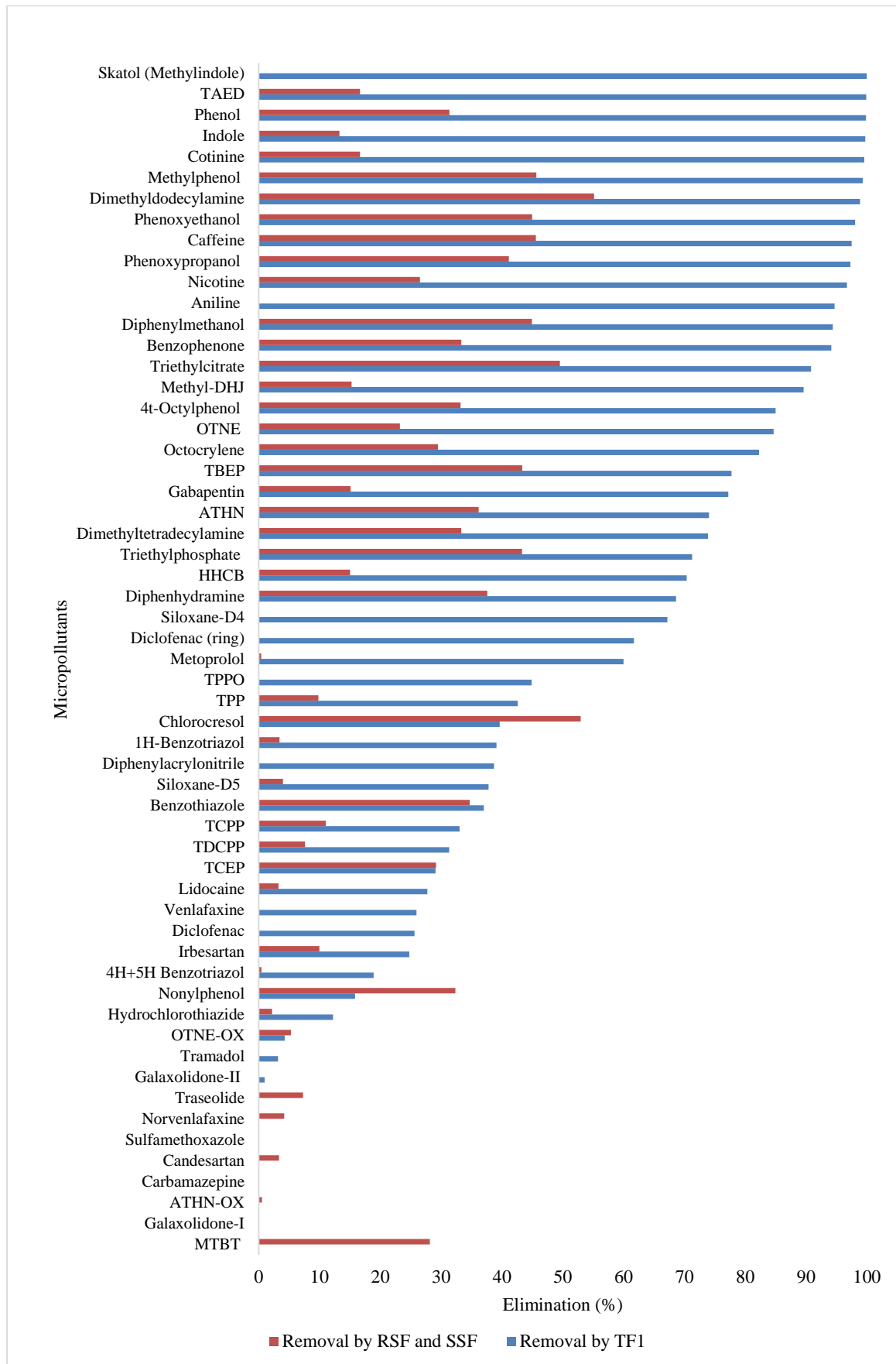


Figure 4.12. Comparison of the removal efficiencies of the sand and trickling filters

4.1.3. Influence of molecular orbital energies on the removal of Micropollutants by Trickling Filters and Sand Filters.

Band gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) has been used as an index of kinetic stability. Compounds having large HOMO-LUMO gap correspond to high kinetic stability and low chemical reactivity since they are not intended to add electrons to a high-energy LUMO, to extract electrons from a low-energy HOMO, and therefore to form the active complex of any reaction [49].

As it is shown in Figure 4.13 to Figure 4.15 for TF1, increasing the gap between HOMO and LUMO results in divergent elimination or efficiency of the trickling filter.

The highest MP band gap in each approach corresponding to the filter efficiency is represented in Table 4.2.

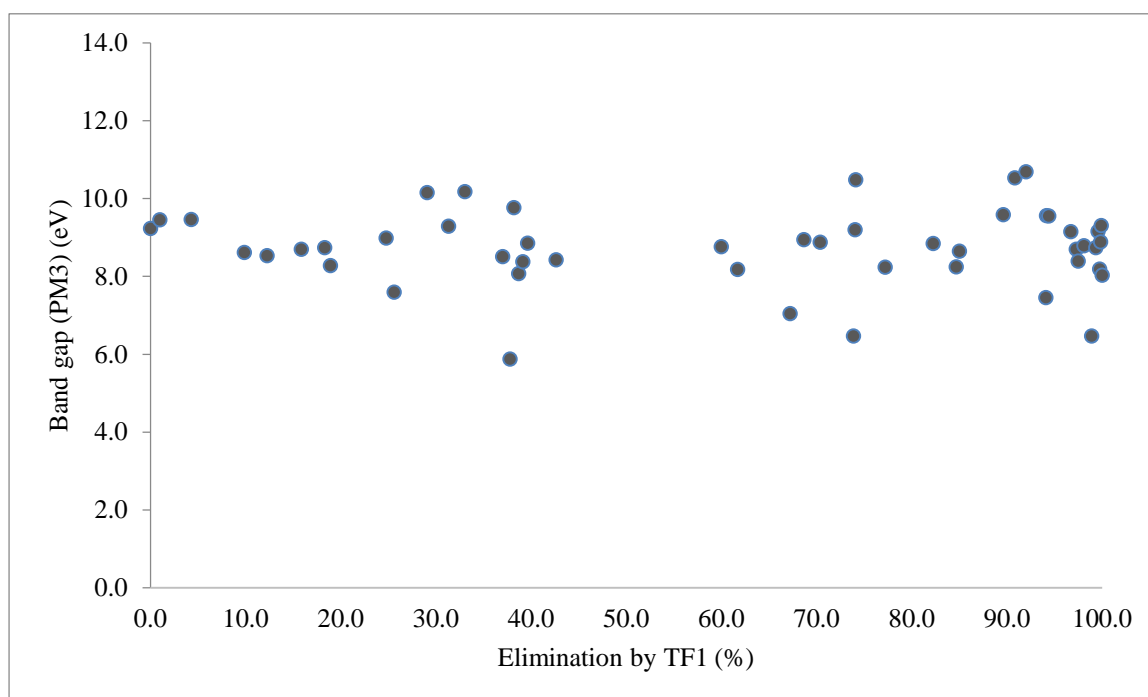


Figure 4.13. Influence of band gap (PM3 approach) on MP removal by TF1

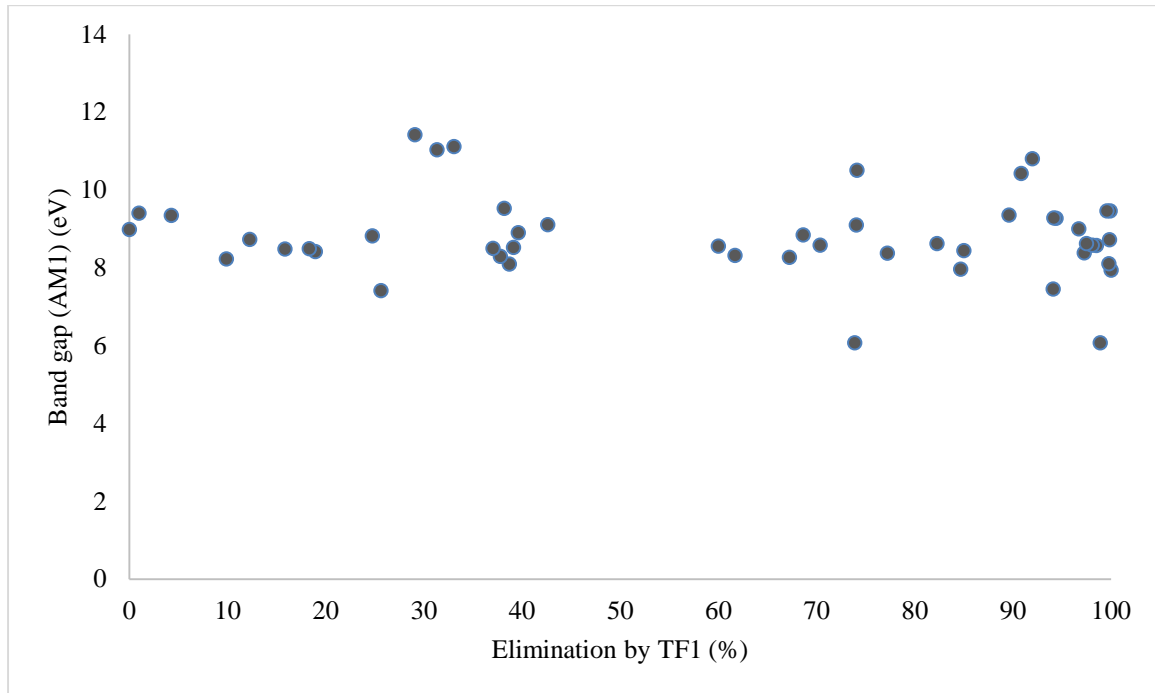


Figure 4.14. Influence of band gap (AM1 approach) on MP removal by TF1

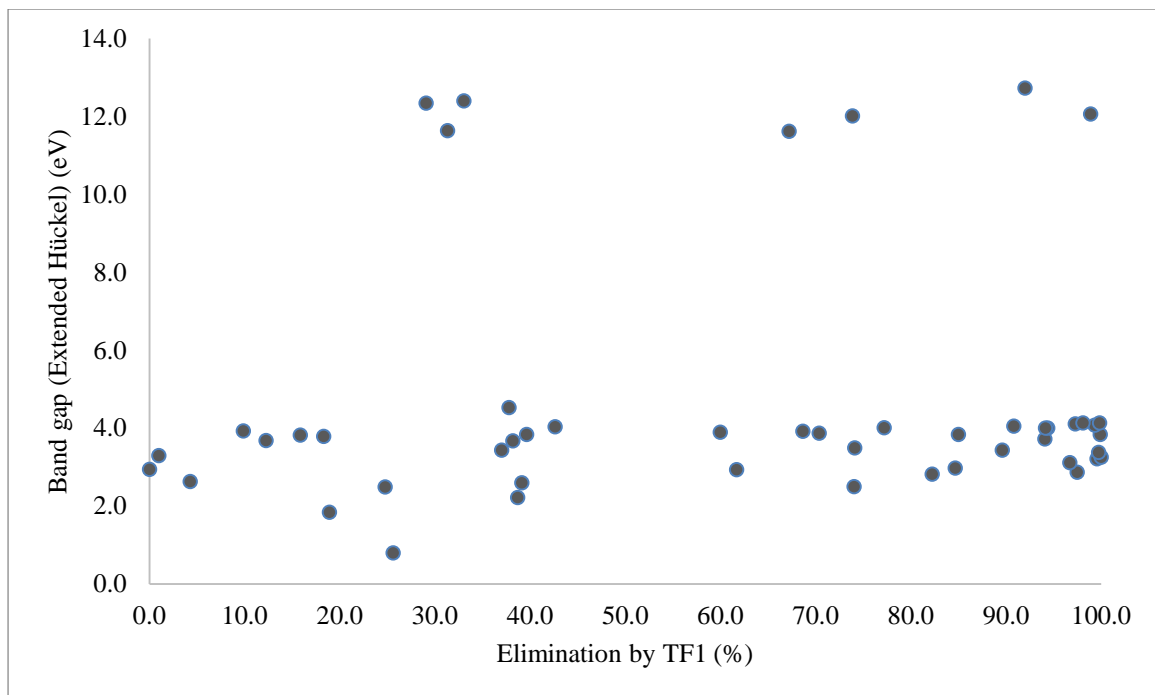


Figure 4.15. Influence of band gap (Extended Hückel approach) on MP removal by TF1

Table 4.2. MPs with high band gap

	Micropollutants	Elimination by TF1 (%)	Band gap energy (eV)
PM3 approach	TCEP	29.1	10.2
	TCPP	33.1	10.2
	TBEP	77.8	10.5
	Triethylcitrate	90.8	10.5
	Triethylphosphate	71.3	10.7
AM1 Approach	Triethylcitrate	90.8	10.4
	TBEP	77.8	10.5
	Triethylphosphate	71.3	10.8
	TDCPP	31.3	11.0
	TCPP	33.1	11.1
	TCEP	29.1	11.4
Extended Hueckel	Siloxane-D4	67.2	11.6
	TDCPP	31.3	11.6
	Dimethyltetradecylamine	73.9	12.0
	Dimethyldodecylamine	98.9	12.1
	TCEP	29.1	12.3
	TCPP	33.1	12.4
	Triethylphosphate	71.3	12.7

Figure 4.16 and Figure 4.17 indicate all of the compounds with respect to their band gap energy and efficiency in trickling filter TF1 and rapid sand filter RSF. According to the graphs, the micropollutants elimination capability of the filters resulted from the experiment and the band gap energy of the molecules do not follow a specific trend. However, by comparison of the compounds with similar structure, such as Siloxanes and Benzotriazoles it is concluded that higher band gap energy of the micropollutants can result in a decrease in their removal by the filters.

Examples of these groups of compounds can be seen in Table 4.3.

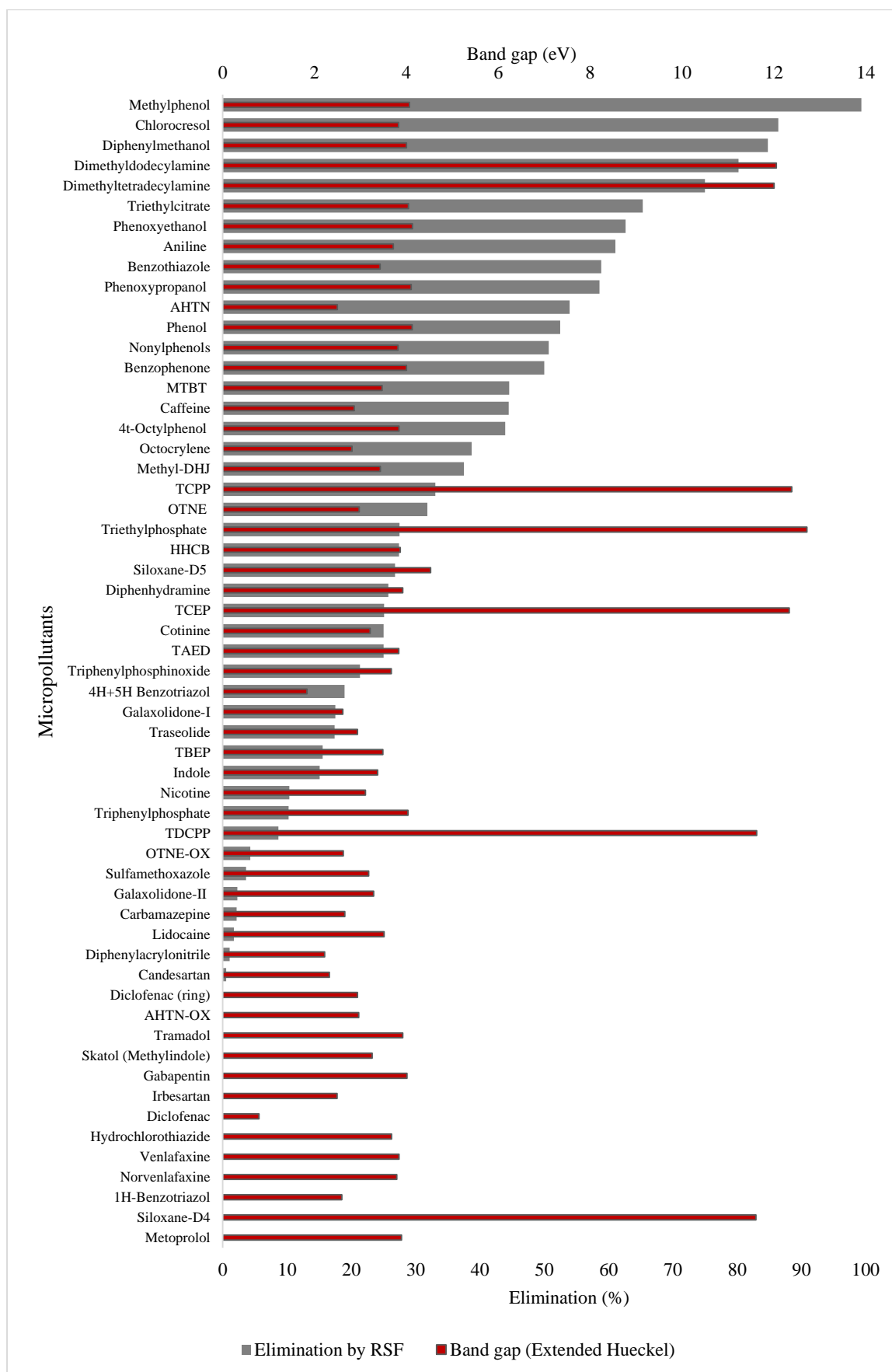


Figure 4.16. Influence of the band gap on the removal of MPs by RSF

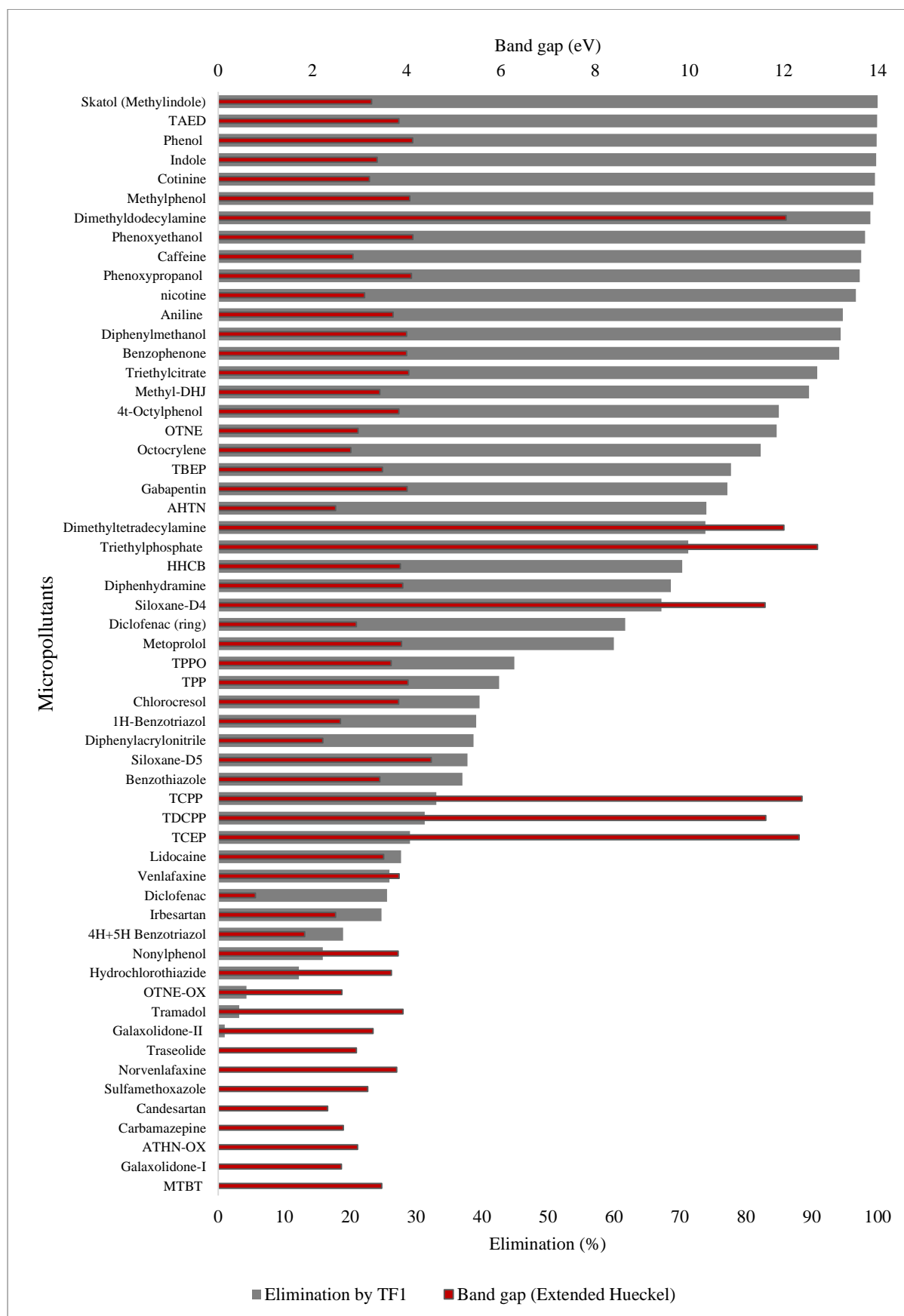


Figure 4.17. Influence of the band gap on the removal of MPs by TF1

Table 4.3. Influence of the band gap on the removal of MPs by RSF

Micropollutants	Band gap (eV)	Elimination in RSF (%)
Siloxane D4	11.610	0
Siloxane D5	4.525	26.799
1H-Benzotriazole	2.593	0
4H+5H Benzotriazole	1.836	18.927

4.2. Correlation between physical-chemical and/or quantum properties of the compounds

In this section, the physical-chemical behavior of the selected compounds such as band gap energy, octanol-water coefficient, number of aromatic rings, organic-carbon partition coefficient, bioconcentration factor, solubility and polarizability are compared and plotted to each other. As the mentioned properties play a key role in the projection of the micropollutants degradation through filters, their consideration is accomplished.

4.2.1. Band gap and number of aromatic rings

Increasing the number of aromatic rings results in the convergent Band gap energy in all three approaches of PM3, AM1 and Extended Hueckel. The maximum number of rings belongs to Candesartan with 5 aromatic rings (Figure 4.18, Figure 4.19 and Figure 4.20).

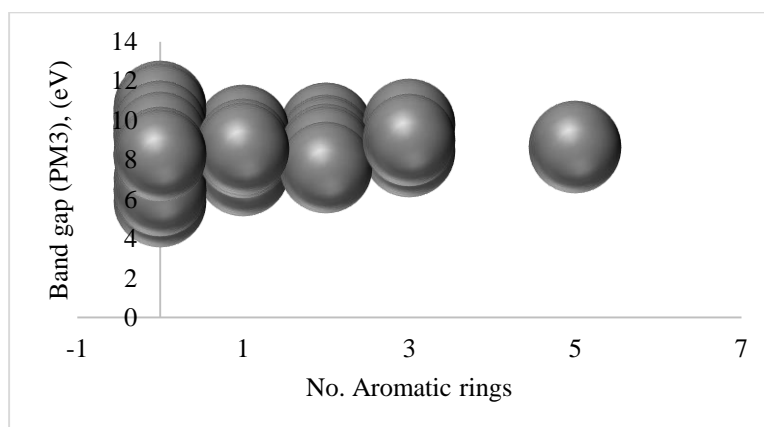


Figure 4.18. Correlation between the band gap (PM3 approach) and the number of aromatic rings

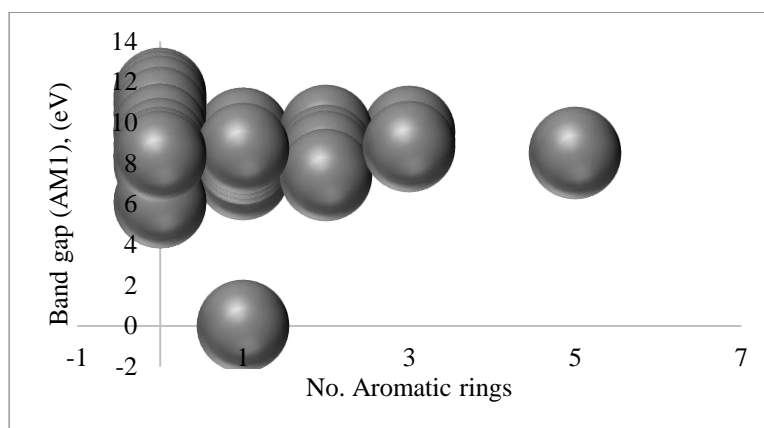


Figure 4.19. Correlation between the band gap (AMI approach) and the number of aromatic rings

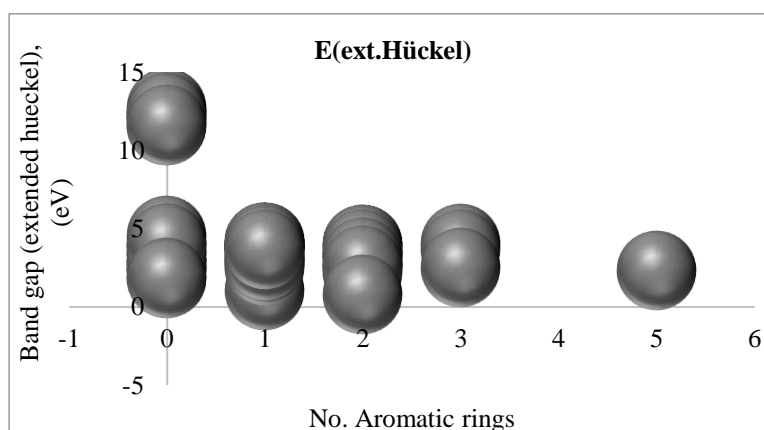


Figure 4.20. Correlation between the band gap (Extended Hückel approach) and the number of aromatic rings

4.2.2. Band gap and hydrophobicity

Table 4.4 shows the relation between Octanol-water coefficient which is an index of hydrophobicity and band gap of the compounds having high energy gap, measured in Extended Hückel approach. The relation between Log Kow and band gap energy implies that increasing band gap can lead to a fall in reactivity or sorption. However, band gap does not have any significant effect on the sorption of other investigated compounds.

Table 4.4. Correlation between band gap (extended Hückel approach) and Log Kow for compounds with high gap

Compounds with high band gap	Log Kow	Band gap (Extended Hückel) (eV)
Siloxane D4	4.43	11.6
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)	3.26	11.6
Dimethyl-tetradecylamine	4.65	12
Dimethyl-dodecylamine (DMDA)	3.38	12.1
Tris-(2-chloroethyl)-phosphate (TCEP)	1.42	12.3
Tris(2-chloropropyl) phosphate (TCPP)	2.38	12.3
Tris-(3-chloropropyl)-phosphate (TCPP)	2.58	12.4
Triethylphosphate	1.02	12.7

4.2.3. Octanol-water and Organic-carbon partition coefficients

Organic-carbon partition coefficient (K_{oc}), is a measure of the partitioning of a chemical between the solid and aqueous phases of the environment and a useful term for predicting the transport of chemicals in the environment. It is defined as the ratio of adsorbed compound per unit weight of organic carbon to the concentration of the compound in aqueous. According to the literature K_{oc} is correlated to K_{ow} for hydrophobic compounds, hence, more likely to partition into organic matter or living organisms (bioaccumulation) [31]. Since there are many hydrophobic compounds in wastewater a good correlation between these two terms is indicated (Figure 4.21).

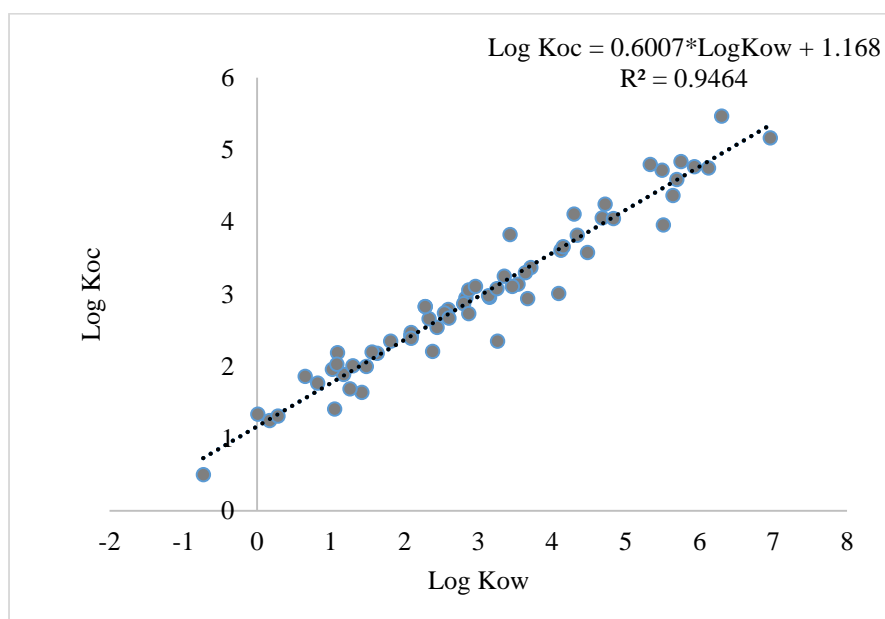


Figure 4.21. Correlation between organic-carbon and octanol-water coefficient.

4.2.4. Octanol-water partition coefficient and Solubility

Solubility is reversely proportional to the Octanol-water partition coefficient implying that, with increasing hydrophobicity, solubility in water decreases (Figure 4.22).

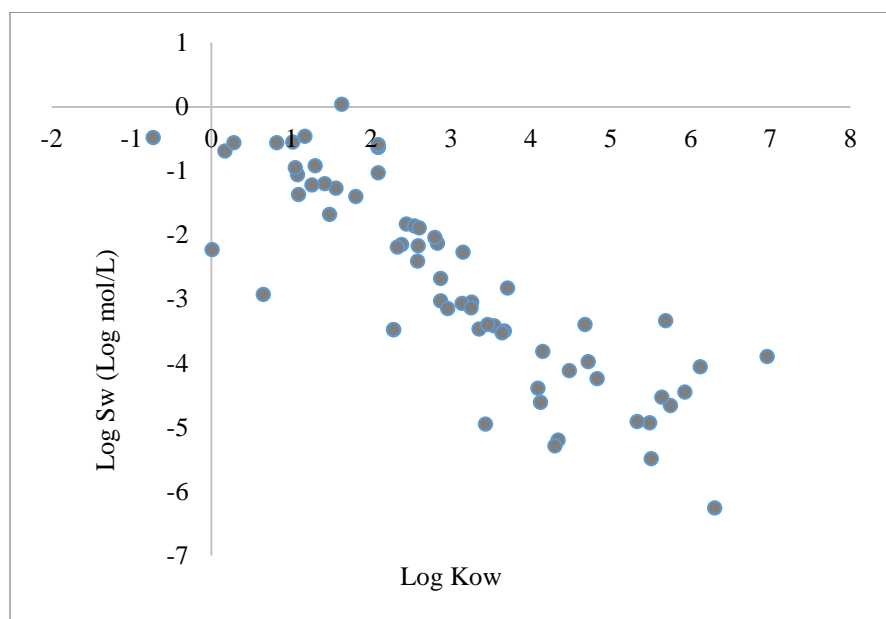


Figure 4.22. Correlation between solubility and octanol-water coefficient

4.2.5. Octanol-water coefficient and Bio-concentration factor

The bioconcentration factor is the ratio of the concentration of the micropollutants in aquatic organisms, following direct uptake from the environment, to the concentration of the same micropollutants in the surrounding environment [50]. Bioconcentration factor of the selected micropollutants in the current study is predicted from the Octanol-water partition coefficient (Figure 4.23).

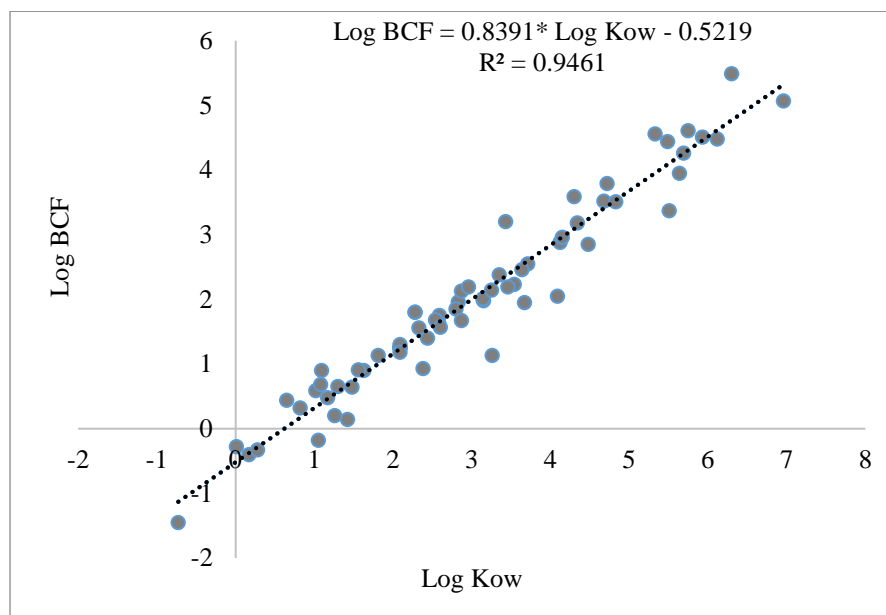


Figure 4.23. Correlation between bioconcentration factor and octanol-water coefficient

4.2.6. Polarizability and molecular weight

Figure 4.24 illustrates that polarizability is highly dependent on the physical properties of the molecule such as molecular weight. This correlation between polarizability and the molecular weight is assumed to be due to the higher distance from the nucleus for heavier compounds.

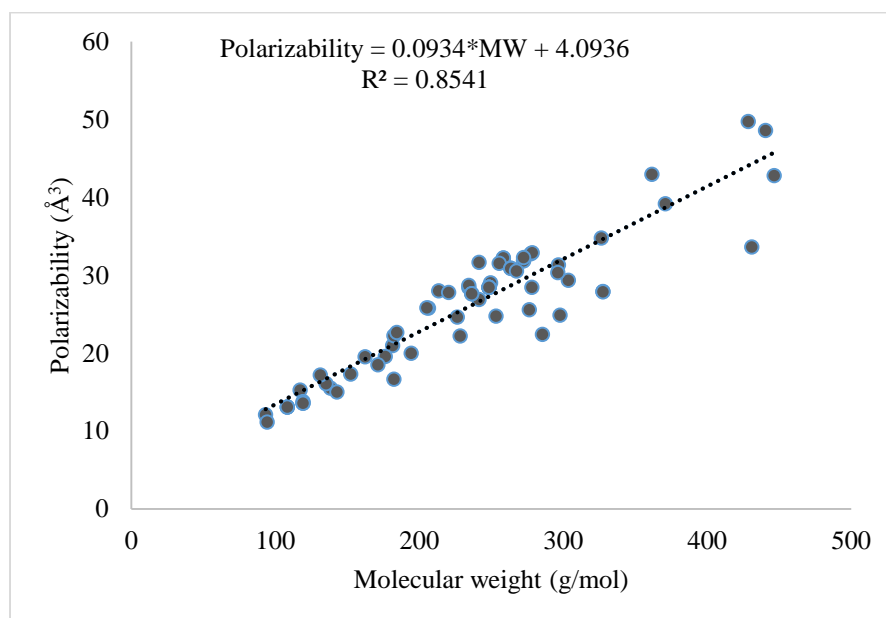


Figure 4.24. Correlation between polarizability and molecular weight

4.3. Control parameters of the process

The measured conventional parameters of the process such as SAC, DOC and conductivity could cast some light on the micropollutants behavior and especially can be a pathway to monitor the processes in which these emerging pollutants are involved. Thus, fluctuations of these parameters and their affiliation among each other are provided.

4.3.1. Spectral absorption coefficient (SAC)

Figure 4.25 provides information on SAC reduction from influent to the effluent of different filters measured by 1cm path length. Negative SAC reduction in TF1 from 190 to 240 nm is observed, explaining the biotransformation effect.

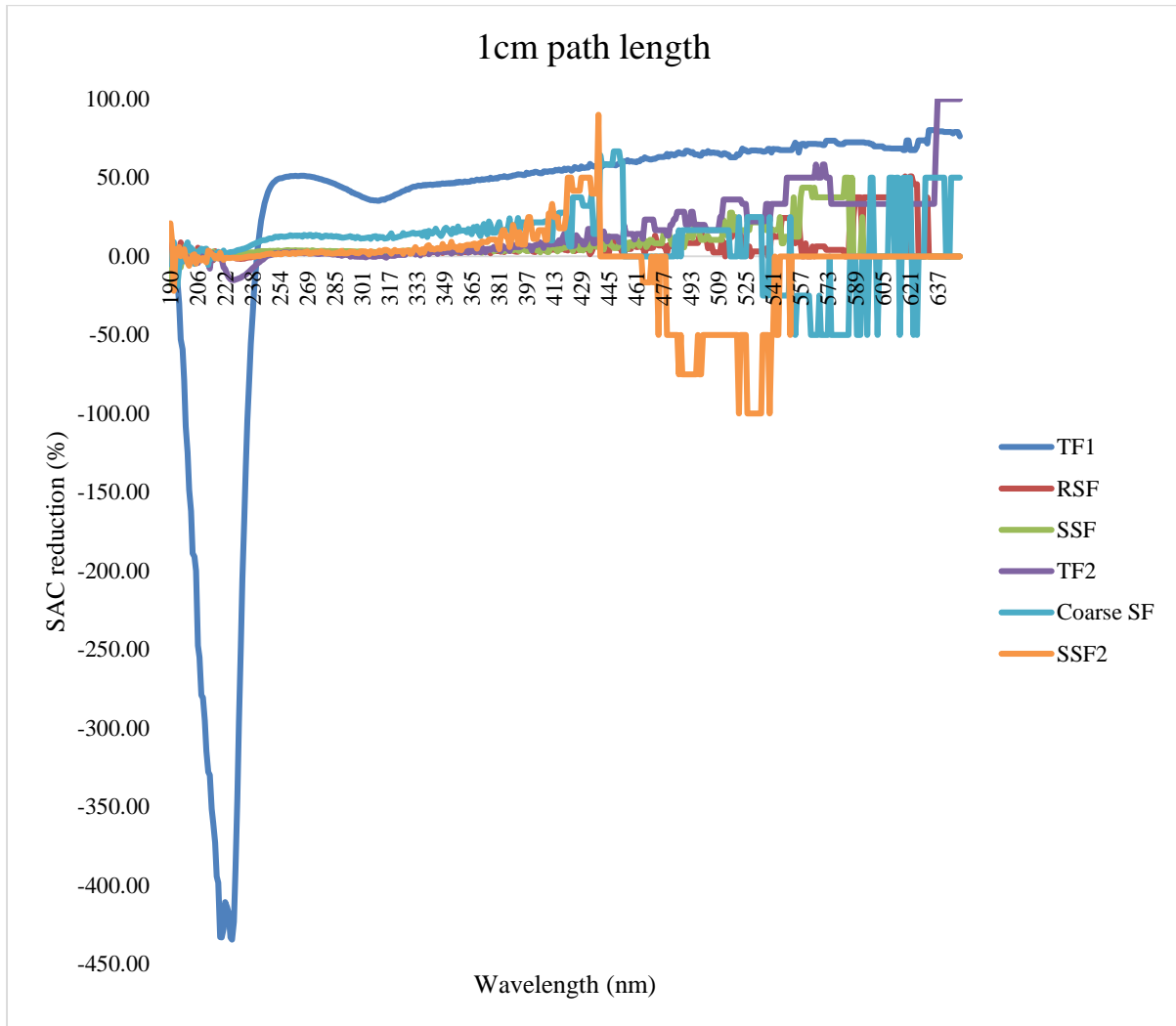


Figure 4.25. SAC removal and wavelength through the sand and trickling filters (1cm path length)

Figure 4.26 demonstrates the relative SAC reduction for trickling filters and sand filters measured by 5 cm path length. As it is shown, among all of the filters TF1 having a high amount of particles provides the highest SAC reduction.

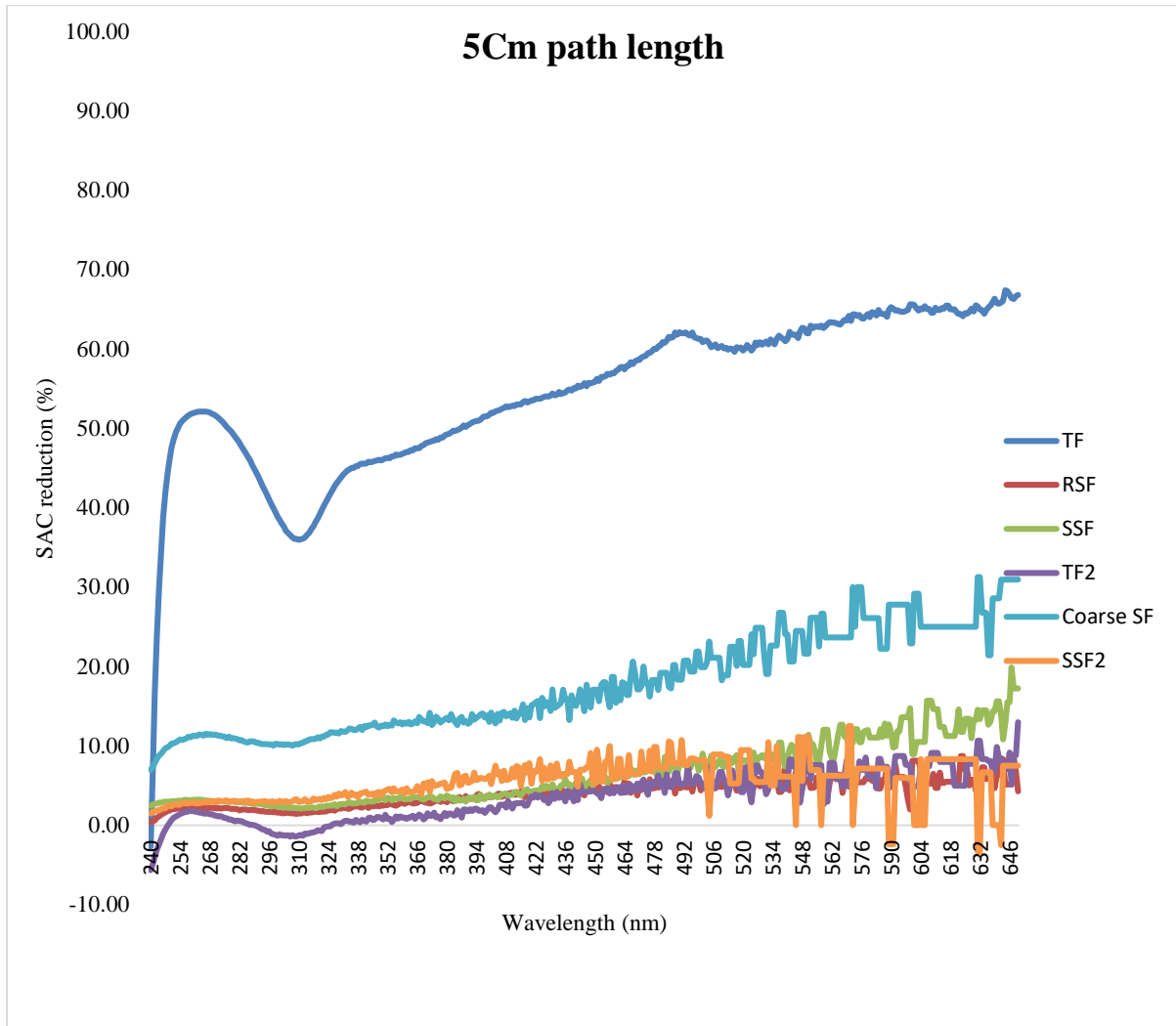


Figure 4.26. SAC removal and wavelength through the sand and trickling filters (5 cm path length)

4.3.2. Dissolved organic carbon (DOC)

SAC fluctuation measured by spectrophotometer can be applied in order to predict the ability of the filters to remove DOC. Figure 4.27 demonstrates the similar behavior of DOC and SAC at 254 nm in each sample and each filter. TF1 provides the highest amount of SAC as well as DOC reduction in all samples.

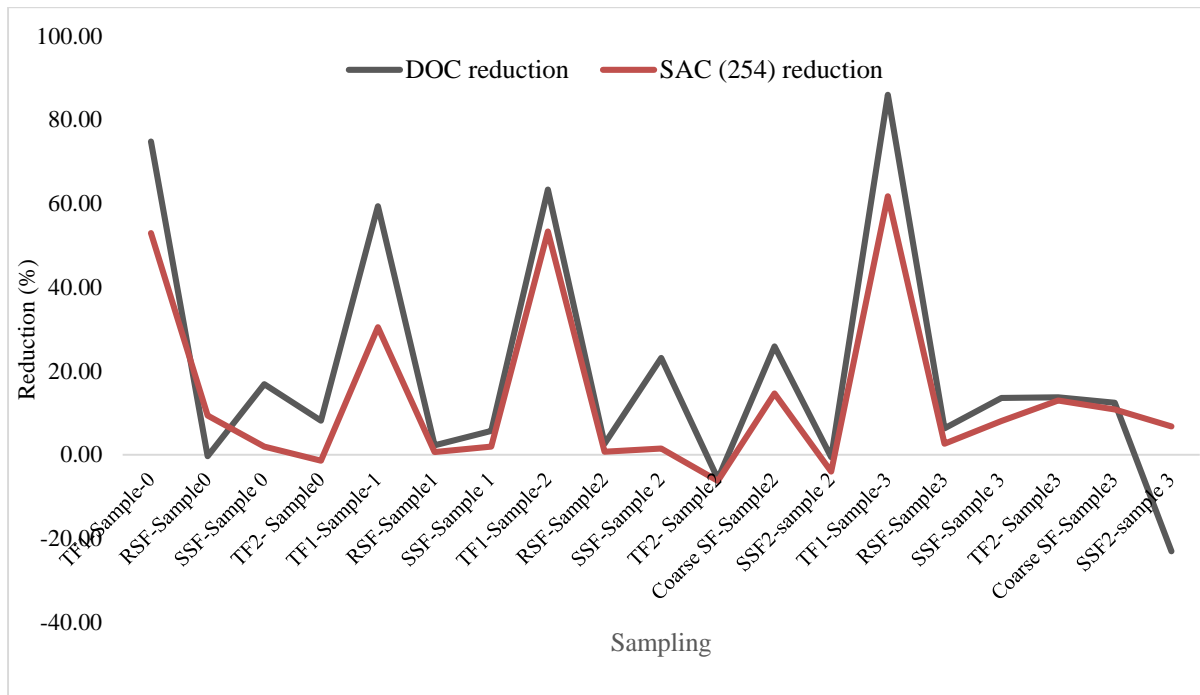


Figure 4.27. Correlation between DOC reduction and SAC (254) reduction for different samples

4.3.3. Conductivity

Conductivity is a general indicator of water quality, regarding the amount of dissolved salt, and can be applied to control processes in the wastewater treatment that cause changes in total salt concentration and thus change the conductivity. The fluctuation of conductivity in the wastewater can be caused by the variation of the ion content. Ions causing conductivity consist of hydrogen H^+ , hydroxide OH^- and nutrients such as phosphate and nitrate. Contribution of these ions to conductivity is a function of pH [5].

Conductivity in the influent of the trickling filter1 has the highest amount which implies the high amount of nutrients and ions in this filter. However, conductivity in TF1 has been declined by 20% showing the amount of biological treatment and nutrient removal in the same filter (Figure 4.28).

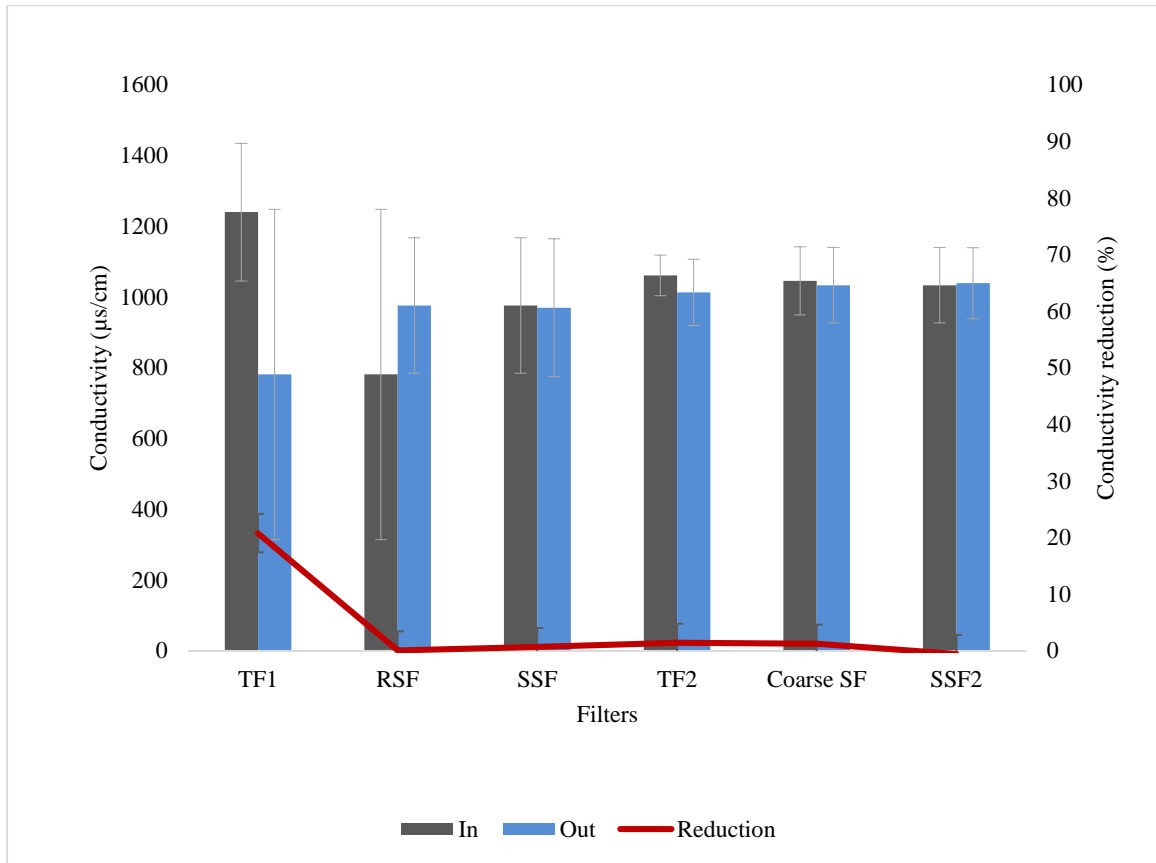


Figure 4.28. Changes of conductivity in various filters

5. Conclusion and future recommendations

The purpose of this study was to determine the environmental fate and effect of various organic micropollutants and examine the efficiency of the trickling and sand filter for the elimination of micropollutants from wastewater considering different physical-chemical properties affecting the removal. Four experiments were conducted, and the properties and removal behavior of 60 diverse micropollutants from the sand and trickling filter effluent were assessed. The 60 selected micropollutants were from the groups of personal care products, pharmaceuticals, industrial chemicals, pesticides/herbicides, and others. The sampling points were the influent and effluent of trickling filters, rapid sand filters and slow sand filters in the LFKW wastewater treatment plant. The removal of dissolved organic compounds and UV absorbance, as well as conductivity, were also measured. The conclusions obtained by this work are provided as the following:

- ❖ The interpretation and comparison of the results of studies depend on the scale and operation mode of the process. Therefore, the information retrieved from real scale studies can significantly differ from those obtained from batch experiments. Nonetheless, the investigated compounds in these kinds of experiments can be extrapolated to the real scale for modeling application [29]. For instance, the size of the sampling (for estimation of error) and the operational conditions should be considered. Given the experiments of this study were performed during the winter time in Germany, the cold weather can negatively affect the biodegradation of the organic compounds.
- ❖ Trickling filter 1 with the influent of raw wastewater provides better removal efficiency than trickling filter 2 which processes the pre-treated wastewater due to the higher number of particles.
- ❖ The removal efficiencies of the sand and trickling filters differ from one compound to the other and are related to the physical-chemical characteristics of the micropollutants. It has been even observed that the elimination rates vary among the compounds despite having similar physical-chemical properties such as Octanol-water coefficient or band gap. However, concerning the factors influencing the removal behavior of micropollutants some general rules can be derived as follows:
 - **Chemical structure:** Compounds with complex structures (e.g., functional groups), show higher resistance to biodegradation processes. For example, Galaxolide (HHCB) shows significantly higher removal than Galaxolidone I (HHCB Lactone I) and Galaxolidone II (HHCB Lactone II) by the trickling filter. Moreover, Siloxane D4 is observed to have higher removal (67%) than Siloxane D5 (38%) by the trickling filter. On the other hand, Siloxane D5 with a higher number of Alkyl groups shows better elimination by the sand filter (23%) compared to Siloxane D4 (0%).
 - **Hydrophobicity:** High amount of Octanol-water coefficient ($\text{Log } K_{ow} > 4$) as an index of hydrophobicity indicates good sorption ability of the sand filters. Accordingly, all micropollutants with the same property show at least some amount of sorption in rapid sand filter, slow sand filter or both. An exception is for Diclofenac, which shows no adsorption in neither of the mentioned filters despite having a great pH-independent-

Log Kow which is 4.48. (Figure 4.4 in subchapter 4.1.1) The lack of sorption in sand filter for this compound can be correlated to the pH-dependent-Log Kow at pH=7.4 which is 1.37. Therefore, in order to enhance the removal of this compound, advanced treatment approaches such as sorption on activated carbon in addition to the trickling filter process are suggested.

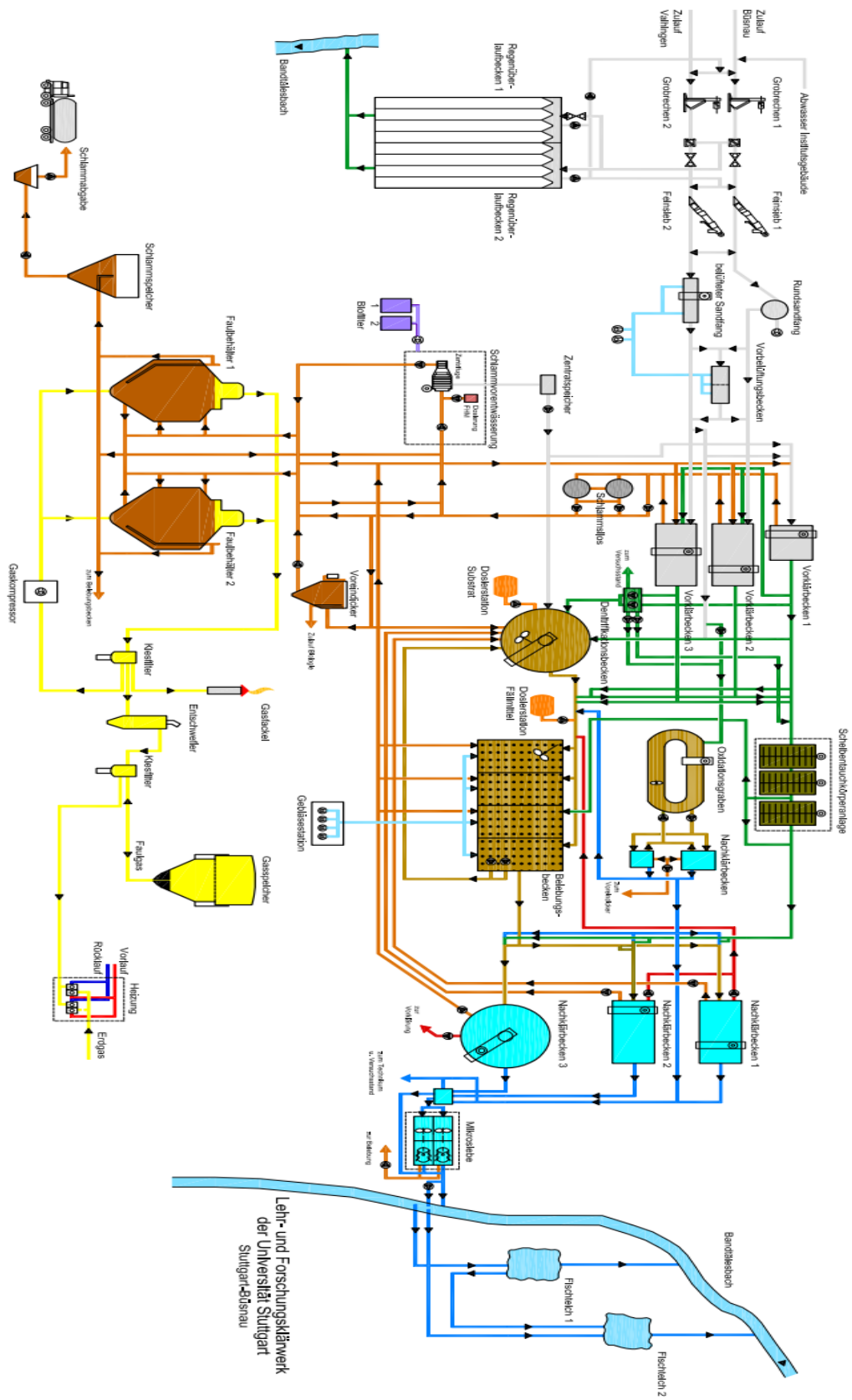
- **Polarizability:** It is concluded that the elimination of similar compounds having the same number of aromatic rings is positively affected by their polarizability characteristic. As the polarization of the micropollutant increases, forming an electrical dipole becomes more likely. This leads to greater sorption potential.
 - **Band gap energy:** Micropollutants show a wide range of elimination as a function of the HOMO-LUMO band gap. However, a comparison of the compounds with similar structure or properties respecting the band gap and elimination implies that increasing the band gap can negatively affect the removal. For instance, Siloxane D4 with zero removal in rapid sand filter has a higher band gap compared to Siloxane D5 with 27% removal in the same filter. High band gap energy, implies the compounds low reactivity and high stability, and it is the reason for low removal efficiency in such compound (D4).
- ❖ **Formation:** Some pollutants such as MTBT are formed during the filtration process by the trickling filter. This compound is originated from the newly implemented pipes and installations into the wastewater and is poorly to moderately biodegradable. The micropollutant management methods, as well as advanced treatment processes, can be applied for controlling and removing this contaminant. Moreover, AHTN-Oxide, Galaxolidone I and Galaxolidone II are transformation products of AHTN and Galaxolide which are applied as polycyclic musks. Despite the formation of these micropollutants by trickling filter, they are relatively adsorbed by the following sand filter.
- ❖ Conventional methods such as the sand and trickling filter can be economically and efficiently excellent approaches for the treatment of many emerging contaminants. Relatively hydrophobic contaminants such as DMDA and DMTDA are well removed by sorption on the rapid sand filter and slow sand filter. Easily biodegradable pollutants such as TAED, Phenol, Indole, Cotinine, Methyl-phenol and Caffeine are also well removed by biodegradation. More hydrophilic and poorly biodegradable pollutants are not well removed during conventional treatments. Hence, the removal efficiency of some micropollutants can be enhanced by applying the advanced processes such as ozonation and adsorption on activated carbon (Table 5.1). However, yet the importance of the conventional treatment approaches for making the advanced technologies more efficient, should not be underestimated.

Table 5.1. Classification of the treatment approaches based on the MPs removal mechanism

Classification			
Biodegradation	Sorption	Treatment approach	Micropollutants (Example)
No	No	AOP	Sulfamethoxazole
Yes	No	Trickling filter	TAED
No	Yes	AOP, sand filter	Traseolide, Galaxolidone I
Yes	Yes	Sand and trickling filter	DMDA, Caffeine

- ❖ **Micropollutant management:** Besides the existing treatment approaches, micropollutants can be either managed by regulation and substitution, user awareness, optimal application, choice of chemicals with lower environmental impacts and technical solutions in wastewater treatment plants [1].

Appendix



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Stuttgart-Adornau

Figure 1. LFKW Wastewater treatment plant

Table 1. Classification and physical-chemical properties of the selected organic micropollutants

MP Abbr.	Formula	Class/Type	Molecular Weight (g/mol)	LogD (pH = 7,40)	LogP (1)	LogP LogP
D4	C8H24O4Si4	PCP	296.62	4.43		4.43
D5	C10H30O5Si5	PCP	370.77	5.00		5.00
PhE	C8H10O2	PCP	138.16	1.30	1.16	1.34
PCMC	C7H7ClO	PCP	142.58	2.83	2.89	2.82
DMDA	C14H31N	PCP	213.40	3.38	5.91	5.60
TAED	C10H16N2O4	PCP	228.25	-0.73	-1.61	0.00
DHJ	C13H22O3	PCP	226.31	2.87	2.50	3.06
OTNE	C16H26O	PCP	234.38	4.72	5.28	4.22
Tras	C18H26O	PCP	258.40	5.49	6.14	5.01
HHCb	C18H26O	PCP	258.40	5.93	6.23	5.82
AHTN	C18H26O	PCP	258.40	5.75	6.37	5.47
HHCb-lactone	C18H24O2	PCP	272.38	5.64	5.50	5.70
HHCb-lactone 2	C18H24O2	PCP	272.38	4.83	4.92	4.74
OctC	C24H27NO2	PCP	361.48	6.30	7.53	5.48
AHTN-OX	C18H24O2	PCP	272.38	4.15	4.19	4.11
OTNE-OX	C16H24O2	PCP	248.36	3.54	3.23	3.80
OTNE-OX	C16H24O2	PCP	248.36	3.64	3.54	3.73
OTNE-OX	C16H24O2	PCP	248.36	3.14	2.95	3.41
OTNE-OX	C16H24O2	PCP	248.36	3.46	3.18	3.71
OTNE-OX	C16H24O2	PCP	248.36	3.25	3.12	3.44
NIC	C10H14N2	Pharmaceuticals	162.23	-0.37	0.72	0.86
DPM	C13H12O	Pharmaceuticals	184.23	2.80	2.74	2.82
DPH	C17H21NO	Pharmaceuticals	255.35	2.34	3.66	3.72
LDC	C14H22N2O	Pharmaceuticals	234.34	1.81	2.36	2.32
TRA	C16H25NO2	Pharmaceuticals	263.38	0.52	2.51	2.55
ODT	C15H23NO2	Pharmaceuticals	249.35	0.06	1.86	2.27
VLX	C17H27NO2	Pharmaceuticals	277.40	1.43	2.91	3.33
TCS	C13H9Cl3O2	Pharmaceuticals	303.57	5.51	4.74	5.75
NVNF	C16H25NO2	Pharmaceuticals	263.38	-0.12	2.37	2.82
CBZ	C15H12N2O	Pharmaceuticals	236.27	2.28	2.67	2.17
DCF ring	C14H9Cl2NO	Pharmaceuticals	278.13	4.09	3.00	4.52
Meto	C15H25NO3	Pharmaceutical	267.36	-0.29	1.79	1.82
SFX	C10H11N3O3S	Pharmaceutical	253.28	-0.55	0.89	0.58
GBP	C9H17NO2	Pharmaceutical	171.24	-1.42	1.19	1.00
DCF	C14H11Cl2NO2	Pharmaceutical	296.15	1.37	4.06	4.61
Irbes	C25H28N6O	Pharmaceutical	428.53	1.46	4.51	2.81
Cand	C24H20N6O3	Pharmaceutical	440.45	0.18	5.02	3.88
HCT	C7H8ClN3O4S2	Pharmaceutical	297.74	0.00	-0.07	0.03
ANL	C6H5NH2	Industrial chemicals	93.13	1.17	0.94	1.25
PhOH	C6H6O	Industrial chemicals	94.11	1.63	1.48	1.67
PCR	C7H8O	Industrial chemicals	108.14	2.09	1.94	2.13

MP Abbr.	Formula	Class/Type	Molecular Weight (g/mol)	LogD (pH = 7,40)	LogP (1)	LogP LogP
MCR	C7H8O	Industrial chemicals	108.14	2.09	1.94	2.13
OCR	C7H8O	Industrial chemicals	108.14	2.09	1.94	2.13
TEP	C6H15O4P	Industrial chemicals	182.15	1.02	1.08	0.99
PhP	C9H12O2	Industrial chemicals	152.19	1.56	1.51	1.57
MTBT	C8H7NS2	Industrial chemicals	181.28	2.87	3.10	2.78
BPh	C13H10O	Industrial chemicals	182.22	2.96	3.18	2.90
TCEP	C6H12Cl3O4P	Industrial chemical	285.49	1.42	0.48	1.79
TCPP	C9H18Cl3O4P	Industrial chemical	327.57	2.58	2.44	2.63
TCPP	C9H18Cl3O4P	Industrial chemical	327.57	2.38	1.53	3.07
TDCPP	C9H15Cl6O4P	Industrial chemical	430.90	3.26	1.79	3.71
TPP	C18H15O4P	Industrial chemical	326.28	4.12	4.10	4.13
TPPO	C18H15OP	Industrial chemical	278.28	3.67	2.87	4.11
TBEP	C18H39O10P	Industrial chemical	446.47	5.33	6.30	3.09
BTR	C6H5N3	Industrial chemical	119.12	1.44	1.14	1.58
5BTR	C6H5N3	Industrial chemical	119.12	1.26	0.57	1.75
4BTR	C6H5N3	Industrial chemical	119.12	1.05	0.06	1.75
BT	C7H5NS	Pesticides/Herbicides	135.19	2.09	2.01	2.13
IND	C8H7N	Pesticides/Herbicides	117.15	2.44	2.14	2.52
3-MI	C9H9N	Pesticides/Herbicides	131.17	2.59	2.60	2.58
Toct	C14H22O	Pesticides/Herbicides	206.32	4.68	4.93	4.56
PPT	C15H24O	Pesticides/Herbicides	220.35	6.12	6.19	6.09
Cot	C10H12N2O	Pesticides/Herbicides	176.22	0.17	-0.23	0.33
TBY	C10H19N5S	Pesticides/Herbicides	241.36	3.35	3.44	3.32
TEC	C12H20O7	others	276.28	1.09	1.49	0.92
DMTDA	C16H35N	Others	241.46	4.65	6.97	6.95
DPAN	C15H11N	Others	205.25	4.34	4.48	4.29
CAFF	C8H10N4O2	Others	194.19	0.28	-0.13	0.42

Table 2. Physical-chemical properties of the selected organic micropollutants 1

MP Abbr.	Polarizability (Å ³)	Molar Volume (cm ³)	No. of Hydrogen Bond Donors	No. of Hydrogen Bond Acceptors	No. of Rings	No. of Aromatic Rings
D4	31.33	310.08	0	4	1	0
D5	39.16	384.35	0	5	1	0
PhE	15.50	127.45	1	2	1	1
PCMC	15.01	116.09	1	1	1	1
DMDA	28.00	266.88	0	1	0	0
TAED	22.18	196.59	0	6	0	0
DHJ	24.64	229.87	0	3	1	0
OTNE	28.39	246.33	0	1	2	0
Tras	32.18	276.85	0	1	2	1
HHCb	31.82	273.21	0	1	3	1
AHTN	32.21	280.89	0	1	2	1
HHCb-lactone	31.87	269.71	0	2	3	1
HHCb-lactone 2	31.87	269.71	0	2	3	1
OctC	42.96	342.46	0	3	2	2
AHTN-OX	32.26	277.39	0	2	2	1
OTNE-OX	28.43	243.33	0	2	2	0
OTNE-OX	28.43	243.33	0	2	2	0
OTNE-OX	28.43	243.33	0	2	2	0
OTNE-OX	28.43	243.33	0	2	2	0
OTNE-OX	28.43	243.33	0	2	2	0
NIC	19.53	157.18	0	2	2	1
DPM	22.64	167.09	1	1	2	2
DPH	31.54	249.23	0	2	2	2
LDC	28.71	228.35	1	3	1	1
TRA	30.91	251.39	1	3	2	1
ODT	29.01	225.82	2	3	2	1
VLX	32.76	261.70	1	3	2	1
TCS	29.36	219.87	0	2	2	2
NVNF	30.87	246.75	2	3	2	1
CBZ	27.63	186.59	2	3	3	2
DCF ring	28.44	194.17	0	2	3	2
Meto	30.55	258.73	2	4	1	1
SFX	24.76	173.13	3	6	2	2
GBP	18.51	161.83	3	3	1	0
DCF	30.34	206.82	2	3	2	2
Irbes	49.73	328.25	1	7	5	3
Cand	48.58	310.52	2	9	5	5
HCT	24.86	175.80	4	7	2	1
ANL	12.09	91.71	2	1	1	1
PhOH	11.15	87.86	1	1	1	1

MP Abbr.	Polarizability (Å ³)	Molar Volume (cm ³)	No. of Hydrogen Bond Donors	No. of Hydrogen Bond Acceptors	No. of Rings	No. of Aromatic Rings
PCR	13.07	104.14	1	1	1	1
MCR	13.07	104.14	1	1	1	1
OCR	13.07	104.14	1	1	1	1
TEP	16.63	170.81	0	4	0	0
PhP	17.32	144.33	1	2	1	1
MTBT	20.97	137.48	0	1	2	2
BPh	22.22	167.55	0	1	2	2
TCEP	22.40	204.96	0	4	0	0
TCPP	27.91	254.48	0	4	0	0
TCPP	27.86	255.61	0	4	0	0
TDCPP	33.63	289.77	0	4	0	0
TPP	34.76	257.86	0	4	3	3
TPPO	32.87	236.20	0	1	3	3
TBEP	42.77	408.20	0	10	0	0
BTR	13.76	88.32	1	3	2	2
5BTR	13.58	85.96	0	3	2	0
4BTR	13.58	85.96	0	3	2	0
BT	16.08	106.25	0	1	2	2
IND	15.27	101.87	1	1	2	2
3-MI	17.19	118.15	1	1	2	2
Toct	25.78	220.63	1	1	1	1
PPT	27.80	236.23	1	1	1	1
Cot	19.58	153.68	0	3	2	1
TBY	26.90	212.73	2	5	1	1
TEC	25.56	234.62	1	7	0	0
DMTDA	31.67	299.90	0	1	0	0
DPAN	25.81	190.24	0	1	2	2
CAFF	19.97	133.40	0	6	2	1

Table 3. Physical-chemical properties of the selected organic micropollutants 2

MP Abbr.	Log BCF	Log Koc	Log S (pH = 7,40) (Log mol/L)	Log Sw/pH (Log mol/L)
D4	-	-	-	-
D5	-	-	-	--
PhE	0.65	2.01	-0.92	6.99
PCMC	1.96	2.95	-2.13	5.88
DMDA	4.26	4.59	-3.34	10.14
TAED	-1.45	0.5	-0.48	7
DHJ	1.67	2.73	-2.68	7
OTNE	3.79	4.25	-3.98	7
Tras	4.44	4.72	-4.93	7
HHCB	4.51	4.77	-4.45	7
AHTN	4.61	4.84	-4.66	7
HHCB-lactone	3.95	4.37	-4.53	7
HHCB-lactone 2	3.51	4.05	-4.24	7
OctC	5.49	5.47	-6.26	7
AHTN-OX	2.96	3.66	-3.82	7
OTNE-OX	2.23	3.14	-3.42	7
OTNE-OX	2.46	3.3	-3.53	7
OTNE-OX	2.01	2.98	-3.07	7
OTNE-OX	2.19	3.11	-3.4	7
OTNE-OX	2.14	3.08	-3.14	7
NIC	0.32	1.77	-0.56	11
DPM	1.85	2.87	-2.04	6.99
DPH	2.55	3.37	-2.83	9.95
LDC	1.56	2.66	-2.19	9.79
TRA	1.68	2.74	-1.86	10.79
ODT	1.18	2.39	-1.03	9.69
VLX	1.98	2.96	-2.27	10.42
TCS	3.37	3.96	-5.49	7
NVNF	1.57	2.67	-1.89	11.2
DCF ring	2.05	3.01	-4.39	7
Meto	1.13	2.35	-1.4	11.06
SFX	0.44	1.86	-2.93	4.56
GBP	0.68	2.03	-1.06	7.5
CBZ	1.8	2.83	-3.48	7
DCF	2.85	3.58	-4.12	4.34
Irbes	3.2	3.83	-4.95	5.02
Cand	3.59	4.11	-5.29	5.21
HCT	-0.28	1.34	-2.23	5.75

MP Abbr.	Log BCF	Log Koc	Log S (pH = 7,40) (Log mol/L)	Log Sw pH (Log mol/L)
ANL	0.48	1.89	-0.46	9.08
PhOH	0.9	2.18	0.04	4.91
PCR	1.25	2.43	-0.63	5.42
MCR	1.25	2.43	-0.63	5.35
OCR	1.25	2.43	-0.63	5.47
TEP	0.59	1.96	-0.55	7
PhP	0.91	2.2	-1.27	6.99
MTBT	2.13	3.06	-3.03	7
BPh	2.19	3.11	-3.15	7
TCEP	0.14	1.64	-1.2	7
TCPP	1.63	2.71	-2.41	7
TCPP	0.93	2.21	-2.15	7
TDCPP	1.13	2.35	-3.05	7
TPP	2.88	3.61	-4.61	7
TPPO	1.95	2.94	-3.5	7
TBEP	4.56	4.8	-4.91	7
BTR	0.64	2	-1.68	5.13
5BTR	0.2	1.69	-1.22	9.11
4BTR	-0.18	1.41	-0.95	9.19
BT	1.3	2.47	-0.59	7.23
IND	1.4	2.54	-1.83	7
3-MI	1.75	2.79	-2.17	7
Toct	3.52	4.06	-3.4	6.71
PPT	4.48	4.75	-4.06	6.89
Cot	-0.4	1.25	-0.69	9.02
TBY	2.38	3.25	-3.47	7.48
TEC	0.9	2.19	-1.37	6.45
DMTDA	5.07	5.17	-3.9	9.79
DPAN	3.18	3.82	-5.2	7
CAFF	-0.33	1.31	-0.56	7.14

Table 4. Band gap energies of the selected organic micropollutants

MP Abbr.	E(PM3) (eV)	Dipole moment (Pm3) (Debye)	E(AM1) (eV)	Dipole moment (Am1) (Debye)	E(ext.Hückel) (eV)	Dipole moment (ext.Hückel) (Debye)	Log P (Hyperchem)
ANL	7.452	1.568	7.455	1.585	3.714	7.73	-0.12
D4	7.037	0.004	8.269	0.010	11.610	0.06	–
PhOH	8.885	1.143	8.716	1.233	4.125	2.65	0.57
PCR	8.621	1.226	8.445	1.359	3.957	21.95	0.73
MCR	8.800	1.412	8.635	1.526	4.143	22.66	0.73
OCR	8.786	1.356	8.627	1.418	4.104	22.71	0.73
TEP	10.684	1.025	10.800	1.239	12.720	24.72	1.58
D5	5.876	2.005	8.295	1.174	4.525	90.53	–
PhE	8.782	0.742	8.576	0.595	4.133	44.96	0.16
PhP	8.698	1.234	8.385	1.375	4.102	54.27	0.57
BT	8.505	1.252	8.498	1.557	3.428	126.70	-0.19
IND	8.182	2.005	8.103	1.882	3.374	5.43	-0.24
NIC	9.151	2.630	8.997	3.068	3.108	65.95	0.09
3-MI	8.026	1.882	7.936	1.771	3.254	25.86	-0.08
PCMC	8.851	1.528	8.900	1.615	3.830	155.70	0.50
DMDA	6.461	1.088	6.072	0.942	12.056	29.46	4.53
MTBT	8.030	2.452	7.871	2.623	3.470	166.60	0.98
TAED	9.303	5.82E-06	9.456	4.84E-06	3.833	1.03E-05	-1.75
BPh	9.556	1.544	9.279	1.687	4.000	6.76	1.83
DPM	9.552	1.542	9.273	1.689	4.000	6.73	1.83
TEC	10.531	3.675	10.419	3.411	4.044	31.93	-0.10
DHJ	9.587	5.795	9.357	5.962	3.433	102.90	2.81
Toct	8.644	1.227	8.435	1.341	3.837	128.40	3.44
OTNE	8.242	2.513	7.959	2.505	2.970	26.85	4.35
DMTDA	6.463	1.084	6.070	0.945	12.008	34.39	5.33
PPT	8.698	1.150	8.480	1.300	3.818	232.10	3.90
Cot	9.155	3.295	9.463	4.415	3.210	31.30	-0.79
TCEP	10.154	1.356	11.415	2.074	12.335	17.15	2.67
TCPP	10.227	2.266	11.251	1.577	12.446	72.60	2.82
TCPP	10.123	2.179	10.969	1.115	12.341	29.80	3.90
Tras	9.230	3.055	8.980	3.174	2.935	81.92	4.03
HHCb	8.876	1.531	8.583	1.753	3.865	71.71	3.15
AHTN	9.197	2.969	9.099	3.165	2.493	77.11	4.14
DPAN	8.067	3.823	8.090	3.545	2.217	15.68	2.46
CAFF	8.391	3.903	8.617	3.711	2.862	27.52	-1.06
DPH	8.940	0.809	8.840	0.509	3.918	138.50	2.09
LDC	8.779	3.079	8.916	3.753	3.515	108.00	0.41
TBY	8.716	2.012	8.381	1.523	4.076	186.80	3.27
TRA	8.614	2.377	8.225	2.526	3.921	65.98	0.80
ODT	–	–	–	–	1.052	2318.00	0.77
VLX	8.699	2.205	8.299	2.624	3.840	86.75	1.05
TCS	8.264	1.081	8.299	1.256	3.672	156.40	-0.57

MP Abbr.	E(PM3) (eV)	Dipole moment (Pm3) (Debye)	E(AM1) (eV)	Dipole moment (Am1) (Debye)	E(ext.Hückel) (eV)	Dipole moment (ext.Hückel) (Debye)	Log P (Hyperchem)
NVNF	8.732	3.045	8.488	3.046	3.787	63.29	0.69
HHCB- lactone	9.191	5.057	9.124	5.453	2.615	113.80	3.14
HHCB- lactone 2	9.450	4.951	9.399	5.396	3.288	118.00	2.98
TDCPP	9.291	2.982	11.027	3.570	11.626	127.80	4.99
CBZ	8.371	3.250	8.314	3.644	2.679	14.80	-0.28
TPP	8.427	2.311	9.109	3.698	4.032	84.78	2.03
OctC	8.844	4.270	8.622	3.872	2.817	300.20	4.67
TPPO	9.764	3.586	9.523	5.061	3.671	35.87	-0.74
AHTN- OX	9.423	3.095	9.435	2.677	2.961	32.01	3.98
TBEP	10.482	4.630	10.507	5.891	3.486	111.30	5.34
DCF ring	8.176	2.006	8.314	2.157	2.933	168.70	-0.52
OTNE- OX	9.609	2.623	9.575	2.693	2.520	35.92	4.20
OTNE- OX	9.690	4.838	9.637	4.826	2.380	20.82	4.43
OTNE- OX	9.206	2.072	8.922	2.214	2.861	44.48	3.50
OTNE- OX	9.660	4.901	9.618	5.294	2.478	46.42	3.96
OTNE- OX	9.124	4.457	8.952	4.285	2.880	46.75	3.63
BTR	8.375	0.336	8.523	0.125	2.592	13.68	2.71
Meto	8.758	2.871	8.557	2.836	3.894	105.50	0.29
SFX	8.521	7.889	8.634	6.921	3.176	124.50	-1.54
GBP	8.233	2.305	8.376	2.227	4.010	38.90	0.96
DCF	7.593	5.051	7.409	1.507	0.791	182.20	-0.21
Irbes	8.985	2.055	8.815	2.934	2.490	254.80	4.38
Cand	8.654	2.547	8.507	2.954	2.323	104.10	2.53
HCT	8.533	7.202	8.730	9.200	3.676	164.10	-3.24
5BTR	8.345	6.648	8.487	6.971	1.871	20.04	2.27
4BTR	8.213	6.269	8.336	6.539	1.801	15.82	1.93

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