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Master's Thesis:

Assessment of Selected Micropollutants and the Effect of Rain Events in Wastewater Treatment Plant and Its Receiving Water Body

Submitted by:

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Declaration of Authorship

I hereby certify that this thesis has been composed by me and is based on my own work, unless stated otherwise. No other person's work has been used without due acknowledgement in this thesis. All references and verbatim extracts have been quoted, and all sources of information, including graphs and data sets, have been specifically acknowledged.

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Abstract

Frequent detection of micropollutants in municipal wastewater raise the concern of these non-regulated pollutants and their adverse effects on aquatic life. The lack of comprehensive investigation and regulations in water policies regarded to micropollutants behavior may lead to the contamination of water resources. In contemplation of extending the groundwork for future water policies, an assessment of the behavior of micropollutants such as pharmaceuticals, industrial chemicals, personal care products and pesticides have been accomplished. Observation of the diurnal behavior, effect of rain events and combined sewer overflows, evaluation of comportment of conventional parameters and heavy metals with micropollutants and an estimation of average diurnal load per capita have been the objectives of this study.

The influent and effluent of the wastewater treatment plant of Herbolzheim, its receiving water body and the combined sewer overflows in its catchment area have been investigated. In regard to non-polar substances, gas chromatography and mass spectrometry has been applied, whereas high performance liquid chromatography was used for polar micropollutants.

Comparative demonstration of conventional parameters affirms the reliability of results to be compared with the micropollutants. Influent of Triclosan seems to follow a similar pattern as turbidity; moreover, the fluctuation of the ammonium and pharmaceuticals appears to be resemblance due to the same source of diffuse. Furthermore, the elimination percentage for different substances ranges from no degradation for substances such as Carbamazepine, to almost complete removal of 99% for the Ibuprofen. Correlation between the spectral absorption coefficient and the pharmaceuticals as well as turbidity and Triclosan seems to be strong; additionally the strength of the correlation among ammonium and the pharmaceuticals is related to the frequency of consumption of pharmaceuticals.

The average effluent concentrations of this study in comparison with other studies in Europe and the state of Baden-Württemberg have been introduced. Influent load fluctuations seem to be almost constant for several substances, hence an average estimation of influent load per capita has been investigated and compared with other studies. Comportment of heavy metals and metals such as potassium and micropollutants is evident. Ultimately, the concentrations of micropollutants in combined sewer overflows in multiple cases are higher than the effluent and even of the influent of the wastewater treatment plant, which implies the necessity of the treatment before discharge into the water body. Enforcement of regulations will enhance the protection of water resources and diminish the pollutants from the diffuse sources.

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List of Abbreviations

WWTP: Waste water treatment plant

CSO: Combined sewer overflow

TSS: Total suspended solid

PCB: Polychlorinated biphenyl

DDT: Dichlorodiphenyltrichloroethane

GC-MS: Gas Chromatography – Mass Spectrometry

HPLC: High Performance – Liquid Chromatography

PE: Population Equivalent

COD: Chemical Oxygen Demand

TOC: Total Organic Carbon

SAC: Spectral Absorption Coefficient

Chapter 1. Introduction

1.1. Background

Freshwater resources are unevenly distributed and only account 3% of the earth's water. Most of it is in icecaps and glaciers (69%) and groundwater (30%), while all lakes, rivers and swamps combined only account for a small fraction (0.3%) of the earth's total freshwater reserves (UNEP, 2002). The pursuit of cognition of the consumed water source, and where its destination will be in the aquatic environment, is an observation which might give a notion about how the human society consumes, and whether that consumption fits into the natural rehabilitation of the natural aquatic systems or not.

Observing the rainfall as a source of freshwater reveals some important aspects for consideration: the reliability, accuracy and precision. First, considering the climate change and its all effects on the uneven precipitation and the procrastination of rainfall in the future indicates of how unreliable the precipitation can be. Second, considering the total rainfall, as a source of freshwater is not very accurate, since the rainfall over the ocean constantly merges into the seawater and categorizes as non-potable water. From 509,000 Km^3 precipitations, only 119,000 Km^3 (less than 25%) is over land, and the rest (more than 75%) is precipitated over sea (WBCSD, 2005). Third, in order to be precise, the quality of the freshwater has to be considered. Suspended chemicals in the air and the pollution on the roads, and pesticides on the farm fields threaten the water quality of precipitation over land and the run off to the sewage.

Water pollution is an important topic since it is essential to health, and an alarming 3,900 children die each day due to dirty water or poor hygiene (WBCSD, 2005). Freshwater withdrawals have tripled over the last 50 years. Demand for freshwater is increasing by 64 billion cubic meters a year (UNESCO, 2009). While alternative methods to secure water supply such as basins and reservoirs have inevitable negative environmental impacts (EEA, 2009), treated wastewater will play a significant role in future of water resources (Azizi, 2015).

Unavoidable amount of water refluxes back to the environment and the other part is collected into the sewage, and whether treated or not will be discharged into the surface water. There are two types of sewer: separate sewer systems and combined systems (Steinmetz, 2014). The more elegant view of urban drainage recently is keen on increasing the permeable areas in order to reduce the total amount of wastewater in the sewage. The major discharge points are direct industrial discharges (with or without treatment), wastewater treatment plants (WWTPs), separate storm sewers, combined sewer overflows (CSOs), smaller discharge pipes and surface runoff (Renge, Khedkar and Bhoyar, 2012).

Measurements indicate that treatment is indeed vital for wastewater since the dilution is far above the rehabilitation threshold of nature; therefore in order to protect water bodies from contamination, wastewater treatment plants and environmental policies and guidelines are substantial. The primary goal of biological wastewater treatment is to remove organic matter from water, because it leads to oxygen consumption when emitted into the aquatic environment (Metzger, 2015).

Nowadays, there are treatment plants in Germany, which are running for many years, and regulations, which ensure accidents such as the foam in the river Neckar in 1960, will not reoccur. Detergents discharged from the factories into the river formed a foam layer on the surface preventing sunlight to pass through the water.

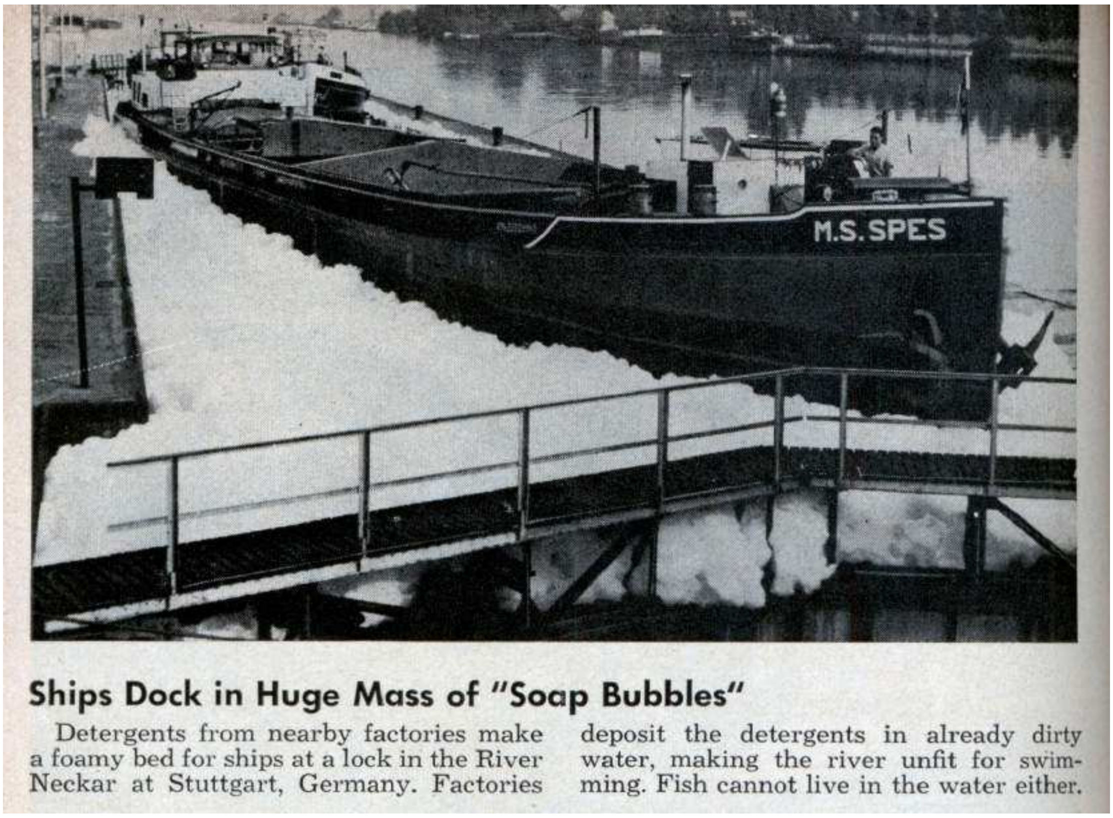


Figure 1: Accident in the river Neckar in 1960

Source: www.blog.modernmechanix.com

In order to realize whether the actual regulations are sufficiently strict, the precision and accuracy of the measuring devices has to increase as well as the researches on any abnormal observation.

There has been much discussion in recent years of new environmental consequences of pollutants, such as fish feminization (Jobling & Tyler, 2003). This is partly a result of the chronic introduction of endocrine disrupting chemicals. These include, along with the body's natural hormones, pharmaceuticals used for their hormonal effect, such as contraceptives and anti-diabetic drugs (Siegrist, Joss & A. Ternes, 2014). A hormonal side effect is also attributed to certain pharmaceuticals such as β-siosterol (control of cholesterol level, also called phytoestrogen as it is widely distributed in plants) and clenbuterol (asthma relief agent) (2014). Endocrine effects are reported also for nonylophenol (surfactant metabolite) and industrial chemicals such as Bisphenol A and phthalates (2014).

The definition of Micropollutants and the hazardous aspects of them towards the environment and human health are described in the following section, furthermore the thesis objectives and goals together with the list of selected micropollutants, which will be taken into consideration are presented and discussed.

1.2. Statement on Current Issues Regarding Micropollutants

Lately by improving the quality of products in order to have a thriving quality of life, plenty of miscellaneous chemicals have been used in the market. Today more than 100,000 different chemicals are registered in the European Union (EU), of which some 30,000 are distributed in the market in quantities in excess of one ton per year (Giger, 2002). Due to progressive advancement of chemical analysis, more organic compounds in lower concentrations (µg/L and ηg/L and lower) are being detected in aquatic environment. These mentioned contaminants are termed 'micropollutants'. Micropollutants can derivate from pesticides, personal care products, surfactants, industrial chemicals, etc., and are not readily degraded in WWTPs due to the nature of their continuous introduction and persistency, hence they are discharged either in the dissolved states or sorbed onto suspended solids (TSS) into the receiving water bodies.

Only in the last two decades has the focus of environmental chemistry research been extended from the more 'classic' environmental micropollutants such as PCBs (Polychlorinated biphenyl), DDT (Dichlorodiphenyl-trichloroethane), dioxins and pesticides to the so-called 'emerging pollutants', although these have been released for much longer (Siegrist, Joss & A. Ternes, 2014). Prominent among emerging pollutants are pharmaceuticals, hormones, and cosmetic ingredients (PPCP) as well as biocides that enter the environment mainly through regular domestic use and in municipal wastewater (2014). Additional compounds leaching out from electrical products (flame retardants) or used to create inert surfaces (perfluorinated compounds) also give reason for concern. Hospital wastewaters contribute significantly but not to a major extent, to the total pharmaceutical and biocide loads. Some polar pollutants (e.g. lipid regulators, carbamazepine and iodinated X-ray contrast media) might even pass through common drinking water treatment processes (2014).

1.3. Objectives

The main issues related to the frequent occurrence of recalcitrant compounds are their simultaneous presence as complex mixtures and the long-term exposition that can lead to serious chronic effects, as reported by several studies (Kidd et al., 2007; Santos et al., 2010), their constant but imperceptible effects can gradually accumulate, finally leading to irreversible changes on both wildlife and human beings (Daughton and Ternes, 1999; Jjemba, 2006).

In contemplation of prioritizing micropollutants under the Water Framework Directive of Europe, European-wide monitoring surveys are essential. In this study, the catchment area of Herbolzheim, existing CSOs, influent and effluent of the WWTP and its receiving water bodies have been investigated, conducive to assessing the behavior of selected micropollutants. The objectives of the study are:

- To assess the conventional parameters and comportment of them among each other and micropollutants
- To investigate the occurrence of micropollutants and its concentration variations in influent, effluent of WWTP and CSOs
- To observe the behavior of the load during the day under dry and wet weather conditions
- To evaluate the effect of rain events and CSOs on the micropollutants fluctuations
- To accomplish an estimation over average diurnal load of micropollutants per capita
- To consider heavy metals variations and their resemblance to micropollutants
- To classify the conventional parameters and micropollutants with corresponding behavior

Reaching the objectives of the study, can contribute to the parallel studies and researches which have been carried out about the characteristics of the micropollutants, their possible degradation through the conventional treatments, their hazardous aspects regarded to their load or concentrations, and in conclusion its contribution to the research studies, which may have been substantial for further policy, regulation and restrictions rules.

1.4. Selected Micropollutants

Regardless of micropollutants inferior concentrations, the complexity of their existence and bioaccumulation of them make further studies over their features way more significant. Establishing a decent selection of competent micropollutants requires experience and adequate reference studies as a background. Hence, in this study a list of noteworthy micropollutants from various sources have been decided by Dr. Bertram Kuch to be investigated and inspected. Different categories for micropollutants, which have been accomplished in this study, are pharmaceuticals, industrial chemicals, personal care products and pesticides.

1.4.1. Pharmaceuticals

Ibuprofen and its degradation products, Ibuprofen-OH and Ibuprofen-COOH, Carbamazepine, Lidocaine, Naproxen, Metoprolol, Sulfamethoxazole and Gabapentin are the nine various pharmaceuticals that have been sifted to be among the list of micropollutants, which are to be investigated in this study. Ibuprofen is a chiral, propionic acid derivative, which exhibits analgesic, fever-reducing, and anti-inflammatory action comparable to, and even surpassing that of aspirin and acetaminophen. Ibuprofen is an important nonprescription drug, and is the third-most popular drug in the world. It is marketed under the trade names of Advil and Motrin (EPA, 2009).

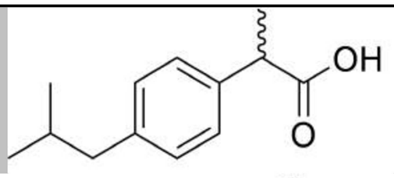
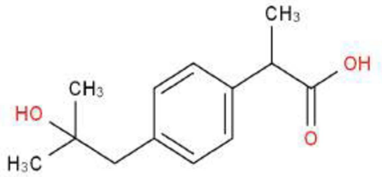
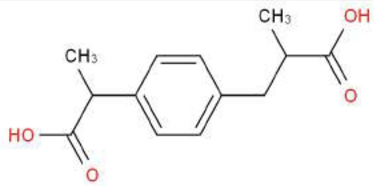
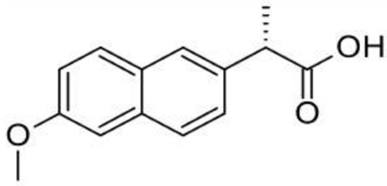
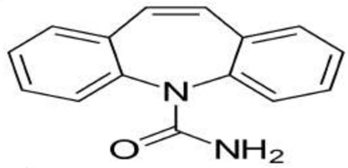
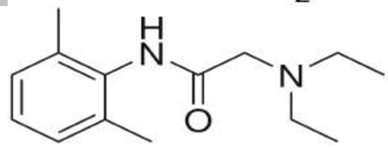
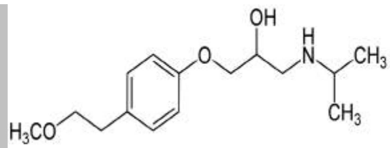
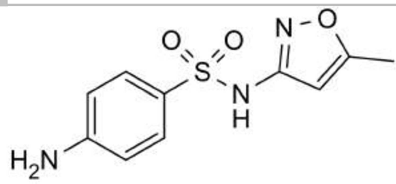
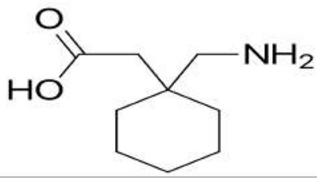
Ibuprofen-OH and Ibuprofen-COOH are the alcohol and acid of the Ibuprofen, which may have a distinct behavior than their parent compound. They are more likely to be found in the wastewater since, the higher the number of OH-groups; the better is the solubility in water (Metzger, 2015). Ibuprofen's physiochemical properties (i.e. high water solubility, low volatility) suggest a high mobility in the aquatic environment, and consequently, it is a commonly detected PPCP in the environment. However, it is not very persistent and behaves differently in comparison to some other pharmaceutical compounds (EPA, 2009).

Carbamazepine is an anticonvulsant. It works by decreasing nerve impulses that cause seizures and pain, and it is used to treat seizures and nerve pain such as trigeminal neuralgia and diabetic neuropathy as well as bipolar disorder (ASHP, 2015). Similarly, Lidocaine works by preventing nerves from transmitting painful impulses to the brain, causing loss of feeling during certain procedures. It is an anesthetic; it may be also used for other conditions as determined by a doctor (FDA, 2016). On the other had, Naproxen is a non-steroidal anti-inflammatory drug (NSAID) of the propionic acid class (the same class as Ibuprofen) that relieves pain, fever, swelling, and stiffness (Rossi, S, 2013). All these pharmaceuticals could be prescribed and consumed by the patients, which they all ended up being discharged to the wastewater and found in the influent of WWTPs.

Metoprolol, marketed under the trade name Lopressor among others, is a selective $\beta 1$ receptor blocker medication (ASHP, 2014). It is used to treat high blood pressure, chest pain due to poor blood flow to the heart, and a number of conditions involving an abnormally fast heart rate. It is also used to prevent further heart problems after myocardial infarction and to prevent headaches in those with migraines (2014). Furthermore, Sulfamethoxazole is an antibacterial prescription combination medicine approved by the U.S. Food and Drug Administration (FDA) to treat certain infections, such as: Acute exacerbations (worsening) of chronic bronchitis; Urinary tract and acute ear infections; Shigellosis; Diarrhea and Pneumocystis carinii pneumonia (PCP) (FDA, 2016). Additionally, Gabapentin is recommended as one of a number of first line medications for the treatment of neuropathic pain in diabetic neuropathy, post-herpetic neuralgia, and central neuropathic pain (Attal N et al., 2010). In conclusion, any pharmaceutical on this list is excreted from human body to the aquatic environment after being ingested; hence, tracing such pollutants shall reveal a relation to the consumption of pharmaceuticals and their introduction to the WWTP.

The table 1 is illustrating the chemical properties of each compound.

Table 1: Selected pharmaceuticals

Name	Chemical Formula	Structure	Application
Ibuprofen	$C_{13}H_{18}O_2$		Fever-reducing Anti-inflammatory
Ibuprofen-OH	$C_{13}H_{18}O_3$		
Ibuprofen-COOH	$C_{13}H_{16}O_4$		
Naproxen	$C_{14}H_{14}O_3$		Non-steroidal Anti-inflammatory
Carbamazep-ine	$C_{15}H_{12}N_2O$		Anticonvulsant
Lidocaine	$C_{14}H_{22}N_2O$		Anesthetic
Metoprolol	$C_{15}H_{25}NO_3$		β-Blocker
Sulfamethox-azole	$C_{10}H_{11}N_3O_3S$		Antibacterial
Gabapentin	$C_9H_{17}NO_2$		Epilepsy Neuropathic pain

Source: www.chemicalize.org

1.4.2. Industrial Chemicals

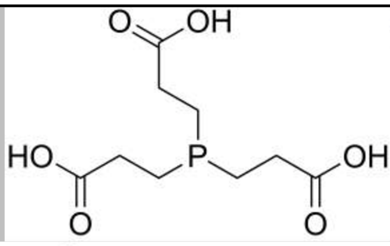
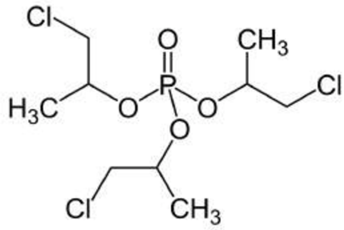
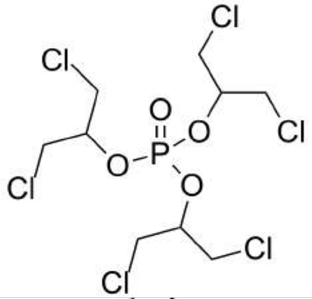
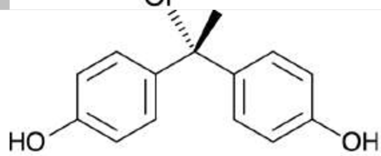
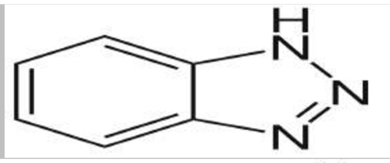
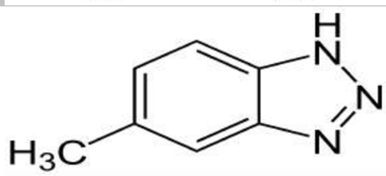
The second group of micropollutants has a different source than pharmaceuticals. Small businesses, factories and industrial parks introduce the main industrial chemicals into the wastewater. The chemicals such as TCEP, TCPP, TDCPP, Bisphenol A are among them, however, 1H-Benzotriazole and Tolytriazoles are among the industrial chemicals, which are sourced largely from households.

The chemicals such as 1H-Benzotriazole and Tolytriazoles prevent undesirable surface reactions and are widely used as an effective corrosion inhibitor for copper and its alloy. The main origin of these chemicals are dishwasher tablets; moreover the increasing trend of using dishwashers has an unavoidable impact on WWTPs, assuming 1 dishwasher tablet contains about 2 grams of phosphorus, and one dishwasher cycle per day for a family of four, will correspond to a load of 0.5 gP/(C.d) in the wastewater, which is an increase of the current load by about 25% (Steinmetz, 2014).

The applications of TCEP are as flame retardant and plasticizer as well as reducing agent in biochemical and molecular biology (Ruegg et al., 1977). Furthermore industrial chemicals, TCPP and TDCPP are used as an additive flame retardants, and have been measured in indoor air and dust, detected in the environment in streams, sewage influent and effluent, and in addition in human tissues, i.e. Adipose tissue and seminal plasma (OEHHA, CA, 2011).

Table 2 includes chemical properties and applications of the selected industrial micropollutants.

Table 2: Selected industrial chemicals

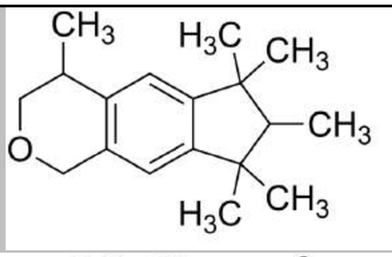
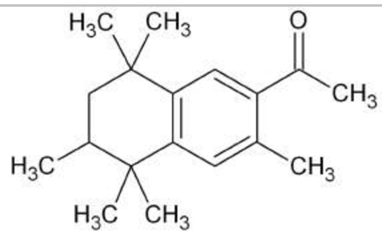
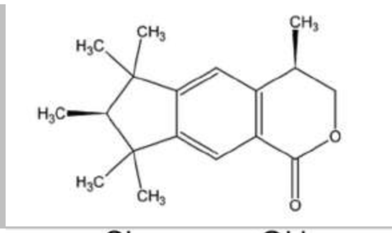
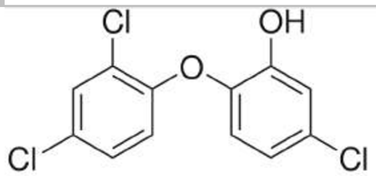
Name	Chemical Formula	Structure	Application
TCEP	$C_9H_{15}O_6P$		Plasticizer Reducing agent
TCPP	$C_9H_{18}Cl_3O_4P$		Flame retardant
TDCPP	$C_9H_{15}Cl_6O_4P$		Flame retardant
Bisphenol A	$C_{15}H_{16}O_2$		Endocrine disrupter
1H-Benzotriazole	$C_6H_5N_3$		Corrosion inhibitor
Tolytriazoles	$C_7H_7N_3$		Corrosion inhibitor

Source: www.chemicalize.org

1.4.3. Personal Care Products

Personal care products are the basis of the daily sanitary routine in the existing communities, and substances such as perfumes, shampoo, cosmetics, detergents, cleaning products and air fresheners are among the products that these micropollutants can derivate from. Galaxolide (HHCB), Tonalide (AHTN), HHCB-Lactone and Triclosan are the compounds, which their corresponding existence have been identified and examined in this study. The application of mentioned products are briefly overviewed in the Table 3.

Table 3: Selected personal care products

Name	Chemical Formula	Structure	Application
HHCB	$C_{18}H_{26}O$		Polycyclic musk
AHTN	$C_{18}H_{26}O$		Polycyclic musk
HHCB-Lac	$C_{13}H_{16}O_4$		
Triclosan	$C_{12}H_7Cl_3O_2$		Disinfectant

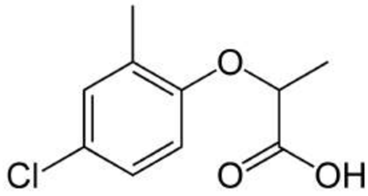
Source: www.chemicalize.org

1.4.4. Pesticides

A pesticide is any substance or mixture of substances used to destroy, suppress or alter the life cycle of any pest (EPA, 2016). Pesticides not only can be a naturally derived or synthetically produced substance, but also can be an organism, for example, the bacterium Bacillus thuringiensis that is used to control a number of insect pests, or even a genetically modified crops (2016).

The main diffuse source of pesticides is from the run-off of farm fields into the sewage and or industrial wastewater. In this study, Mecoprop is the main herbicide investigated. The chemical structure of the compound and its main application is seen in the table 4.

Table 4: Selected pesticides

Name	Chemical Formula	Structure	Application
Mecoprop	$C_{10}H_{11}ClO_3$		Herbicide

Source: www.chemicalize.org

As covered in this chapter the importance of the investigation on the hazardous aspects of micropollutants is revealed, furthermore, a concrete objectives over the engrossing aspects of inspection and multiple paths for anticipation of the existence of micropollutants has been decided, additionally, a selection of micropollutants from various sources have been chosen for further evaluation. In the next chapter, site description, methodology and the process leading to assessment of micropollutants have been carried out.

Chapter 2. Methodology

In the first chapter, micropollutants has been defined and the necessity of prediction of their behavior to have a clear projection on water resource management has been presented. In order to detect the micropollutants there are two common methods available, Gas Chromatography – Mass Spectrometry (GC-MS) and High Performance – Liquid Chromatography (HPLC). The application of GC-MS is in regard to non-polar substances whereas the HPLC method is mostly used for polar substances (Kuch, 2016). Both of these methods have been carried out in this thesis to assess micropollutants. In spite of the fact that there are more sophisticated and expensive methods for appraising micropollutants, the driving force behind choosing these methods were not only the unfeasibility of other methods but also the fact that GC-MS and HPLC are the most common used in the field.

In this study 136 samples from the WWTP Herbolzheim along with 6 samples from its receiving water body have been collected between the months of March until August of the year 2016 to be analyzed.

2.1. Location

Herbolzheim WWTP is located near the city Herbolzheim, in the state of Baden-Württemberg, southwest of Germany. The WWTP is 15,000 PE (Population Equivalent) and its effluent is conducted directly with a pipe to the river Elz, Elz is a 90 km river which is a right tributary of the river Rhine, it rises in the Black Forest and reaches the river Rhine near Lahr at the border of Germany and France (Figure 2).

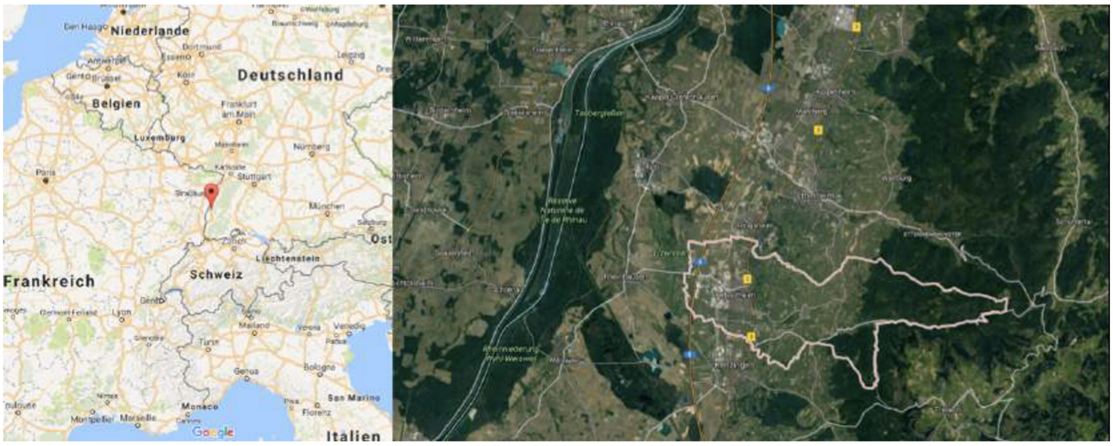


Figure 2: Site Location

Source: www.maps.google.de

Based on the census in the year 2010, population of the city was more than 10,000 (Leo-BW.de, 2017). Figure 3 is illustrating the land use of the area Herbolzheim. Table 5 is the general information about the Herbolzheim WWTP.

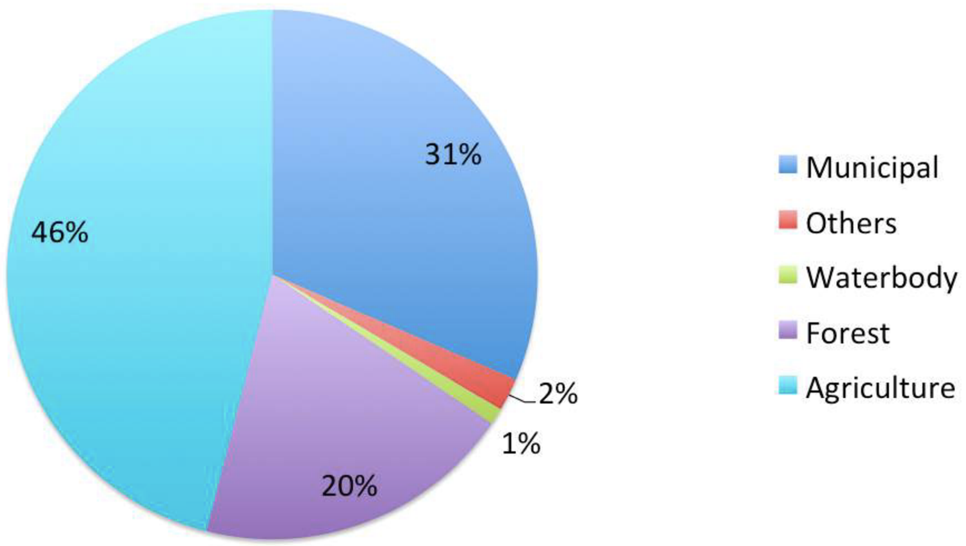


Figure 3: Land use of the area Herbolzheim

Source: www.leo-bw.de

Table 5: General information on WWTP Herbolzheim

Name of WWTP	Herbolzheim
PE (year 2000)	15,000
Treatment	Activated Sludge
Water Consumption	180 L/ca.d
Infiltration	25 L/s
Specific load per inhabitant	60 g BOD5/ca.d
Average Q dry weather	57 L/s
Q combined	160 L/s
Dry weather influent	2,100 m^3/d
Maximum influent	13,000 m^3/d
Degradability efficiency	97 %
Primary sludge volume	20 – 30 m^3/d
Nitrogen elimination	86 %
Phosphorus elimination	93 %
Electricity consumption	430,000 kWh/a

2.2. Sample Collection

Samples, which have been processed in this study, are containing influent and effluent sets of daily sample series for the week of 22.03.2016 through 28.03.2016, and 4 series of 24-hour samples from 4 different days, from April through August of the year 2016, and 24 samples from retention basins, and 6 samples from multiple points in the receiving water body. Table 6 and 7 are the representative information about days of sampling, discharge and the precipitation.

Table 6: Diurnal samples of the week

Sample	Date	Time (From)	Time (To)	Q (m^3)	Precipitation (mm)
HZ_01	22.03.2016	08:00	08:00	2101	
HZ_02	23.03.2016	08:00	08:00	1929	
HZ_03	24.03.2016	08:00	08:00	1804	0.1
HZ_04	25.03.2016	08:00	08:00	5025	5
HZ_05	26.03.2016	08:00	08:00	2539	1
HZ_06	27.03.2016	08:00	08:00	3184	2
HZ_07	28.03.2016	08:00	08:00	4525	5

Table 7: 24-Hourly information of the second day

Sample	Date	Time (From)	Time (To)	Q (m^3)	Precipitation (mm)
HZ_Z_20	23.07.2016	16:45	18:45	403.2	0.3
HZ_Z_21	23.07.2016	18:45	20:45	396	
HZ_Z_22	23.07.2016	20:45	22:45	417.6	
HZ_Z_23	23.07.2016	22:45	0:45	360	
HZ_Z_24	24.07.2016	0:45	2:45	324	
HZ_Z_25	24.07.2016	2:45	4:45	554.4	1
HZ_Z_26	24.07.2016	4:45	6:45	792	
HZ_Z_27	24.07.2016	6:45	8:45	763.2	
HZ_Z_28	24.07.2016	8:45	10:45	770.4	
HZ_Z_29	24.07.2016	10:45	12:45	777.6	
HZ_Z_30	24.07.2016	12:45	14:45	432	
HZ_Z_31	24.07.2016	14:45	16:45	374.4	

2.2.1. Sampling Strategy

Two methods of sampling have been applied: grab sampling and composite sampling.

Grab Sampling:

In order to have no floating particle, skim or upper stream variations, a very well mixed grab sampling from adequate depth has been accomplished for the samples of CSOs as well as the tributaries. Tributaries creeks and river samples have been grabbed along the water body, from the creek Kirnbach, at the joint of tributaries Kirnbach and Bleichbach, before Bleichbach reaches the river Elz, as well as before and after the effluent point of WWTP along the river Elz. These samples were gathered on 21st of March.

Composite Sampling:

All the influent and effluent samples have been collected with this method. Mixing of different laps and intervals until achieving a well representative of the average values during the time span is the most important factor in this step, the diurnal samples have been taken from 08:00 to 08:00 of every 24 hours and the 24-hourly samples are grabbed every 2 hours in order to have a proper distribution throughout the day, which allows a very distinct observation of the effect of rain events and or the CSOs on the influent and effluent fluctuations.

2.3. Sample Readiness

All the samples arrived have to pass along a process in order to be able to be assessed by different methods; Dr. Bertram Kuch has developed the following hierarchical process and planning of the necessary substances and values required to conduct the thesis's objectives.

2.3.1. Sample Separation

In the first place, samples, which are in the volume of 0.5 liter to 4 liters, should be separated according to the required volume for each process. A set of samples for HPLC, 2 sets containing of neutral and acidified for GC-MS, the samples have been acidified by dropping one or two drops of H_2SO_4 to decrease their pH to the range of 2 – 3.5, one set for determining heavy metals and one set for measuring the conventional parameters such as: COD (Chemical Oxygen Demand), TOC (Total Organic Carbon), Ammonium, SAC (Spectral Absorption Coefficient), pH, Temperature, conductivity and Turbidity. Figure 4 illustrates the separation process.

Figure 4: Separation process

Source: Riyahi

2.3.2. Internal Standards

Internal standards are solutions with intentional concentrations of substances, which will be added to the samples in order to distinguish a range of unknown substances based on the deliberate known concentration in internal standards (Kuch, 2016). Standards should be cooled down to the room temperature furthermore after being added identically, have been stirred for 30 minutes (Figure 5). Table 8 includes the essential internal standards and their respective volume and concentrations.

Figure 5: Syringing internal standards

Source: Riyahi

Table 8: Essential internal standards and their volume

	Internal Standard	Volume (μL)	Concentration (ng/μL)
Neutral	AHTN D^3	300	1.1 in Methanol
	Caffeine	300	2.154 in Methanol
	PAK mix	300	1 in Toluene
	Carbamazepine D^{10}	50	10.5 in DCMI
	Terbutryn D^5	50	4.2 in Methanol
	Lidocaine D^{10}	50	9.9 in DCM
Acidic	Bisphenol A D^{16}	300	1.08 in Methanol
	Triclosan D^3	100	1 in DCM
	Diclofenac D^4	50	8.7 in DCM
	Naproxen D^3	50	6.32 in Methanol
	Mecoprop D^3	50	8.88 in Methanol

2.3.3. Liquid – Liquid Extraction

Based on the (D. Law & A. Todd, 2008), liquid – liquid extraction is an essential tool in the analytical laboratory. Utilizing an unequal component dispersion between two separate liquid phases in order to segregate substances of a solution is the act of liquid – liquid extraction, which usually is done by intimately mixing the two immiscible phases, allowing for the selective transfer of solute(s) from one phase to the other, then allowing the two phases to separate.

In this process dichloromethane has been chosen as the solvent. 40 mL of dichloromethane with density of 1.325 g/mL has been added to the samples and shook for few minutes gently in order to prevent emulsion, as can be seen, since the density of water is less than dichloromethane it will arise to top of the funnel, hence the desired substances has been introduced to the solvent they could be collected from the bottom outlet of the funnel. In the same fashion, another round of 40 mL dichloromethane will be introduced in order to wash any possible particle of the substance; finally the gained 80 mL solution is collected in a chemical globular bulb to be processed in the rotary evaporator. Figure 6 is illustrating the process in a schematic way.

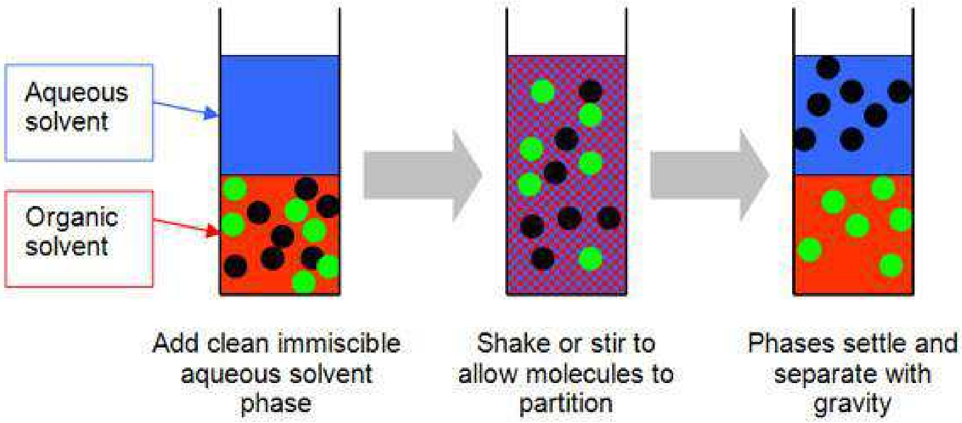


Figure 6: Schematic process in liquid - liquid extraction

Source: www.faculty.ksu.edu.sa

2.3.4. Rotary Evaporator

By diminution of pressure inside the attaching chemical globular bulb into the rotary evaporator, dichloromethane can evaporate at the room temperature. Rotation of the sample in a warm water bucket increases the pace of evaporation while it prevents decreasing the temperature of the sample. 80 mL of the dichloromethane has to be reduced to roughly 10 mL. Figure 7 shows the rotary evaporator and its warm water bucket, the temperature of the water is set around 40 degrees Celsius.

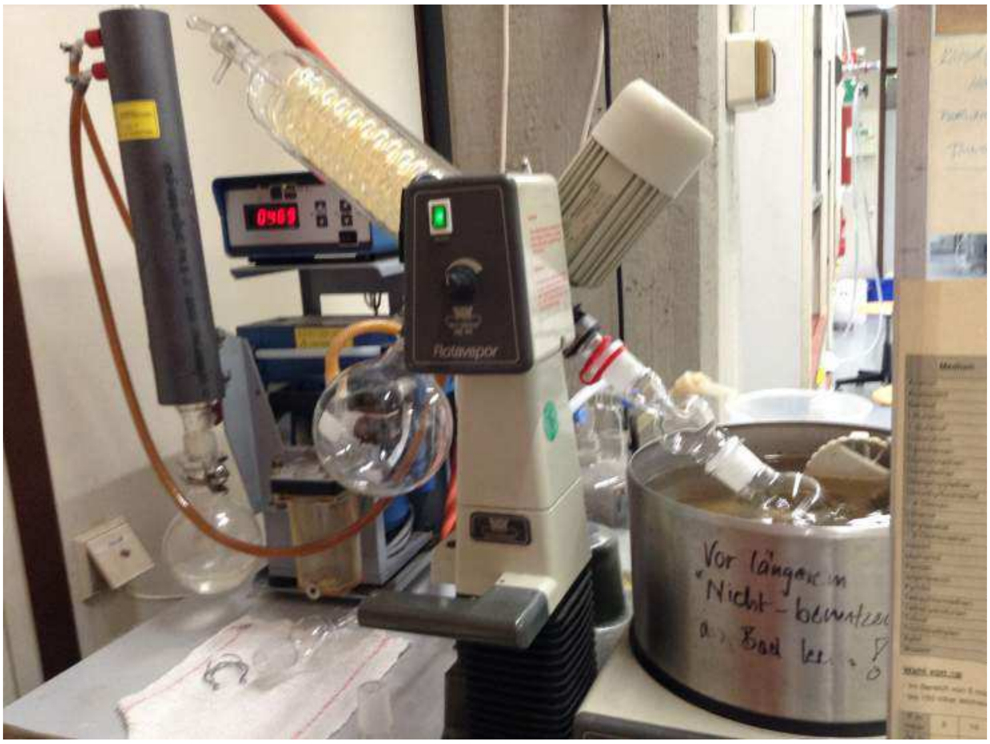


Figure 7: Rotary evaporator

Source: Riyahi

2.3.5. Sample Dewatering

Drying agents (also called desiccants) come in various forms. A desiccant is a hygroscopic substance that induces or sustains a state of dryness in its vicinity (UCLA, 2016). Many organic solvents are immiscible with aqueous solutions, but they are able to dissolve significant amounts of water because of their polarity. Commonly used drying agents are all in their anhydrous form (2016).

$$A + n\,H_2O \;\rightleftharpoons\; A * (H_2O)_n$$

Anhydrous sodium sulfate has been used as desiccant; the existence of water in the samples will cause clumps. Additionally in order to obtain all the possible micropollutants from the samples, the entire inner surface of the holder should be rinsed once more with dichloromethane. Finally the whole solution is syringed into a vial.

2.3.6. Sample concentration

The final sample volume for GC-MS has to be 100 μL. Further evaporation of the samples is done with the help of Nitrogen gas stream in the vial, which creates a partial pressure diminution over the top surface, forcing the dichloromethane to evaporate. In the long run, the process will cool off the sample, which will decelerate the evaporation. Therefore samples are heated constantly in the device with the temperature around 39 degrees Celsius. The process and the device are presented in the Figure 8.

Figure 8: Evaporation by Nitrogen gas

Source: Riyahi

2.3.7. Gas Chromatography – Mass Spectrometry

Based on the (Kuch, 2016), the system of GC-MS is containing two main parts with different processes, first the part gas chromatography and second mass spectrometry. Only 1 μL of the sample will be injected to the device to be processed.

Liquid sample is injected to a glass tube, which will be heated up to 210 degrees Celsius in order to evaporate the sample. Helium gas stream from top of the glass tube is bellowed as a driving force to insert the gaseous sample into a column. The column is 30 meters long with outer diameter of 250 micrometer and inner diameter of 0.25 micrometer. The column is from granite and it is coated with a thin layer of lining as a liquid in the inner tube with boiling temperature of 400 degrees. Based on the size and polarity, the inner coating can discrete different substances. Passing the first 5 cm of column all samples condense to liquid again. At time = t0 all the particles, for instance A, B and C are at the same position in the column, they all will be driven through the column by the force of Helium gas. Alongside the column the particles will separate because of different time of interaction with the coating, the more volatile and smaller the size, the quicker they will reach the end of the column. Figure 9 presents the particle's journey in the column.

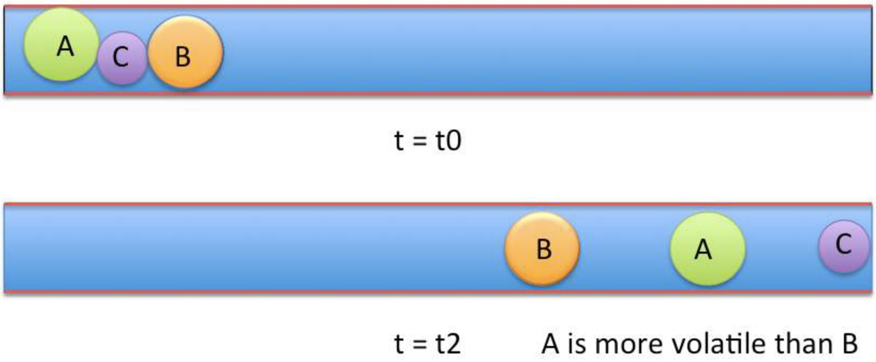


Figure 9: Process along the column

Source: Riyahi

Before the substances entre a box with a very high vacuum pressure, they will be heated up to 280 degrees in order to have them all in gaseous phase. The very high velocity generates a beam of particles, which they will be blasted with electrons, causing a positively charged ion beam. The beam passes through a magnetic as well as an electric field and will be deviated. Based on the consistency of energy E = ½ mV^2 and also assuming almost constant velocity for the particles, the only factor effecting the deviation is the mass of particles.

In the last section positively charged ions will insert in the final tube and will produce an electric pulse, the number of pulses represents the number of atoms. Correspondingly by knowing the number of atoms and the degree of deviation, amount and mass of the particle can be investigated. Figure 10 illustrates the process.

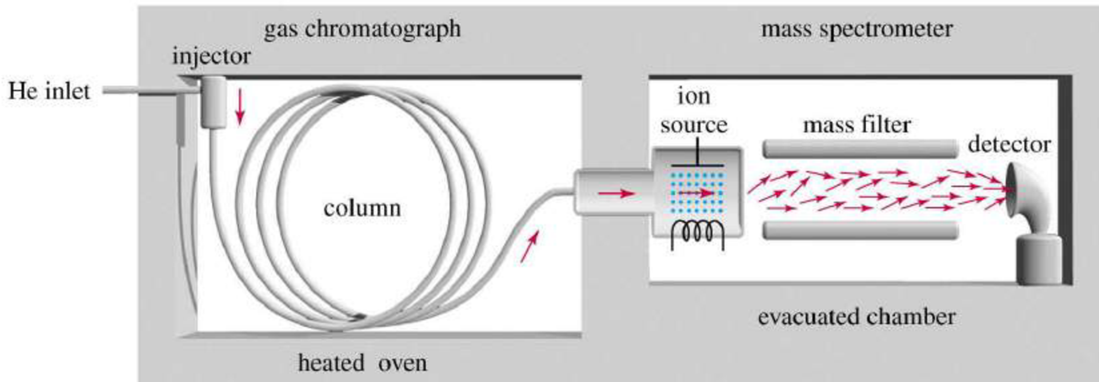


Figure 10: The process inside the GC-MS

Source: www.intechopen.com

A mass spectrum is generated from the information sent to the computer. The intensity of pulses will be plot in a time span for different masses resulting a 3D graph. For any individual mass spectrum, integral of the area underneath the abundance – time will be representative of the concentration by comparing each to a reference unique spectrum. Figure 11 and 12 are the schematic view of the results for GC-MS and the GC-MS device itself respectively.

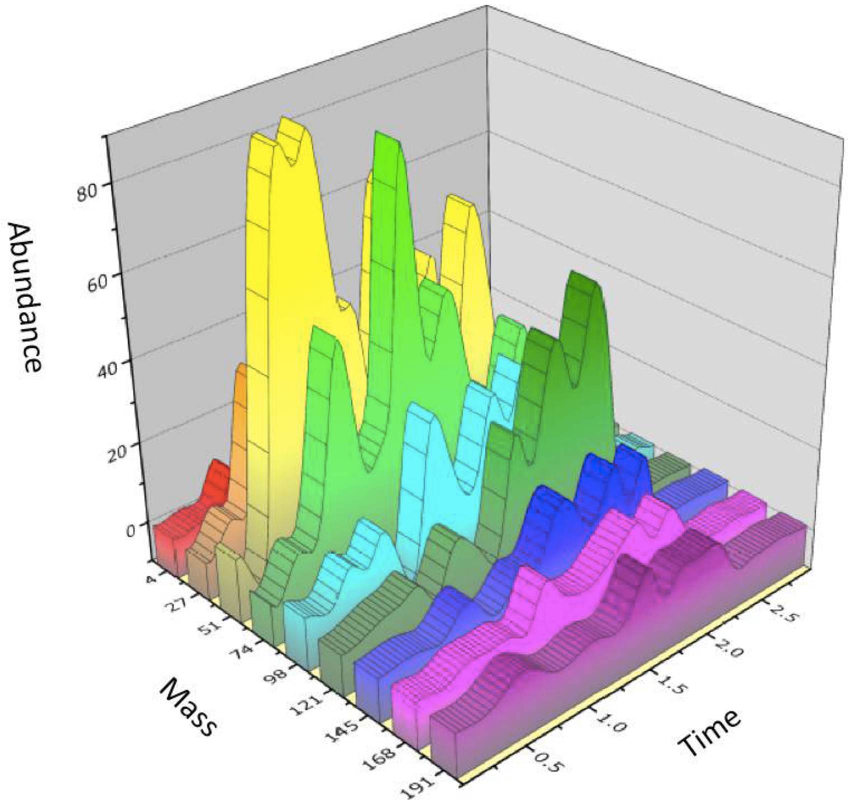


Figure 11: Schematic results of GC-MS

Source: Modified by Riyahi

Figure 12: GC-MS device

Source: Riyahi

2.4. Quantification and Analysis

By the same token in last section, and establishing an internal standard as the unique spectrum, while its concentration is known; in order to determine the concentration of the desired component, first, by comparing each substance to the reference library, and then the integral of the area below the curve, concentration shall be assessed using the given formula:

$$C = [(A_n/A_{IS})/V]*F$$

C: Substance concentration (μg/L)

A_n: Integral of area of native compound

A_{IS}: Integral of area of internal standard

V: Sample volume (mL)

F: Mass of the internal standard (ng)

The integration and quantification of the results have been done with the MSD ChemStation software. As shown in the figure 13, by extracting the desired ion, the abundance will appear on the Y-axis while X-axis is the time span. Accordingly, retention time and the area can be investigated with the software. Carbamazepine is the inspected substance in this figure.

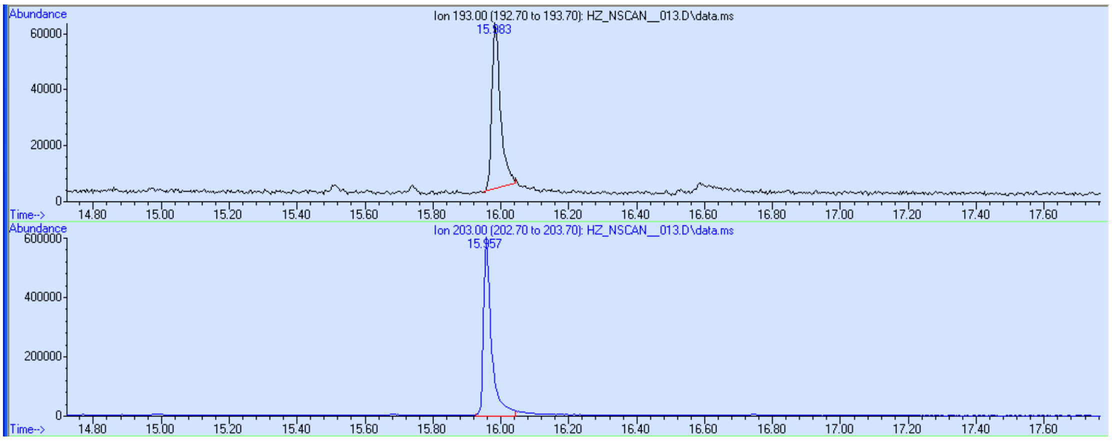


Figure 13: Carbamazepine peaks for the native and standard peak selected in the software MSD ChemStation

Source: Riyahi

Individual ions investigated have their special retention time, each peak occurred at the retention time is representative of the inspected micropollutant. Table 9 is the retention time for each native compound and its associated internal standard.

Table 9: Qualification and the retention time

Substance	F (ng)	Qualifier ion (m/z)	Retention time (min)	Internal standard ion (m/z)	Retention time (min)
Carbamazepine	525	193	15.995	203	15.969
Lidocaine	495	86	13.310	96	13.260
HHCB	330	258	12.894	261	12.921
AHTN	330	258	12.935	261	12.921
HHCB – Lac	330	257	14.881	261	12.921
TCEP	1945	249	12.581	188	12.924
TCPP	2345	277	12.620	188	12.924
TDCPP	2945	381	15.524	188	12.924
Triclosan	100	302	14.335	305	14.322
Mecoprop	445	228	10.147	231	10.138
Ibuprofen	105	161	10.029	172	10.136
Ibu – OH	210	118	11.724	172	10.136
Ibu – COOH	315	205	12.658	172	10.136
Naproxen	495	244	14.644	247	14.631
Bisphenol A	300	241	14.006	252	13.956

Given these points, after collection of all samples from WWTP, tributaries and CSOs, from different locations, the only common system of assessing micropollutants has been chosen, the samples have gone through a systematic separation as well as preparation, until they reached to the GC-MS processor. The results produced with the device with the use of its library, deliver the concentration in samples.

With knowing the concentrations of various micropollutants in each sample, further investigation of the correlation and codependence of the samples, as well as their pattern could be considered in order to fulfill the study’s objectives. The results and discussions of micropollutants fluctuations and behavior are described in next chapter.

Chapter 3. Results and Discussion

In the previous chapter the techniques available and their advantage and disadvantages were discussed as well as the path for assessing the concentration of micropollutants. In this chapter the outcome of the research exercise is presented. As mentioned in the Chapter 1, objectives of the study are:

- To assess the conventional parameters and comportment of them among each other and micropollutants
- To investigate the occurrence of micropollutants and its concentration variations in influent, effluent of WWTP and CSOs
- To observe the behavior of the load during the day under dry and wet weather conditions
- To evaluate the effect of rain events and CSOs on the micropollutants fluctuations
- To accomplish an estimation over average diurnal load of micropollutants per capita
- To consider heavy metals variations and their resemblance to micropollutants
- To classify the conventional parameters and micropollutants with corresponding behavior

With the intention of fulfilling the research objectives, a mutual behavior analysis of the conventional parameters in conjunction with comportment of micropollutants, along with micropollutants elimination are presented and discussed. Furthermore, the corresponding correlation among standard parameters and micropollutants, as well as the average diurnal load and concentrations are given. Additionally, some arguments about the existence of a relation among heavy metals and conventional parameters and micropollutants along with the load and concentrations in multiple CSOs are considered.

3.1. Conventional Parameters

The measured conventional parameters such as COD, TOC, Ammonium, SAC and turbidity could shed a light on the projection of the micropollutants behavior, hence consideration of their fluctuations and their affiliation among each other has been applied. A comprehensive investigation of conventional parameter fluctuations have been accomplished, following are the evidence of some of the most pertinent figures of the findings.

3.1.1. Spectral Absorption Coefficient

The spectral absorption coefficient is one of the inherent optical properties that influence the reflectance of aquatic systems (Mitchell et al., 2000). The plotted SAC values should follow a certain manner in order to be reliable to correlate with the other conventional parameters. Figure 14 is the spectra of absorption in different wavelengths.

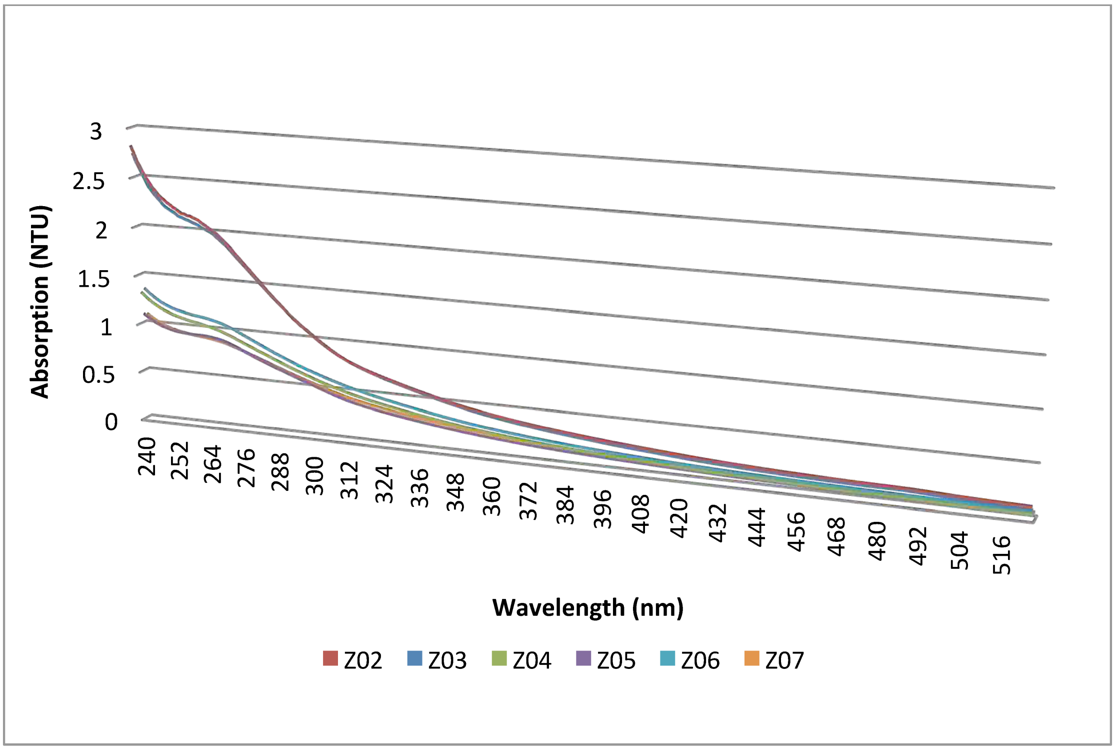


Figure 14: SAC representative area for different influent samples

The observed area for SAC seems to follow the usual pattern, meaning the integral of the area should relate with other conventional parameters. As shown in the Figures 15-17, SAC has similar fluctuations as the TOC and COD, similar behavior has been observed among other data sets. Additional graphs showing diurnal and hourly, influent and effluent of the parameters above can be found in Appendix A.

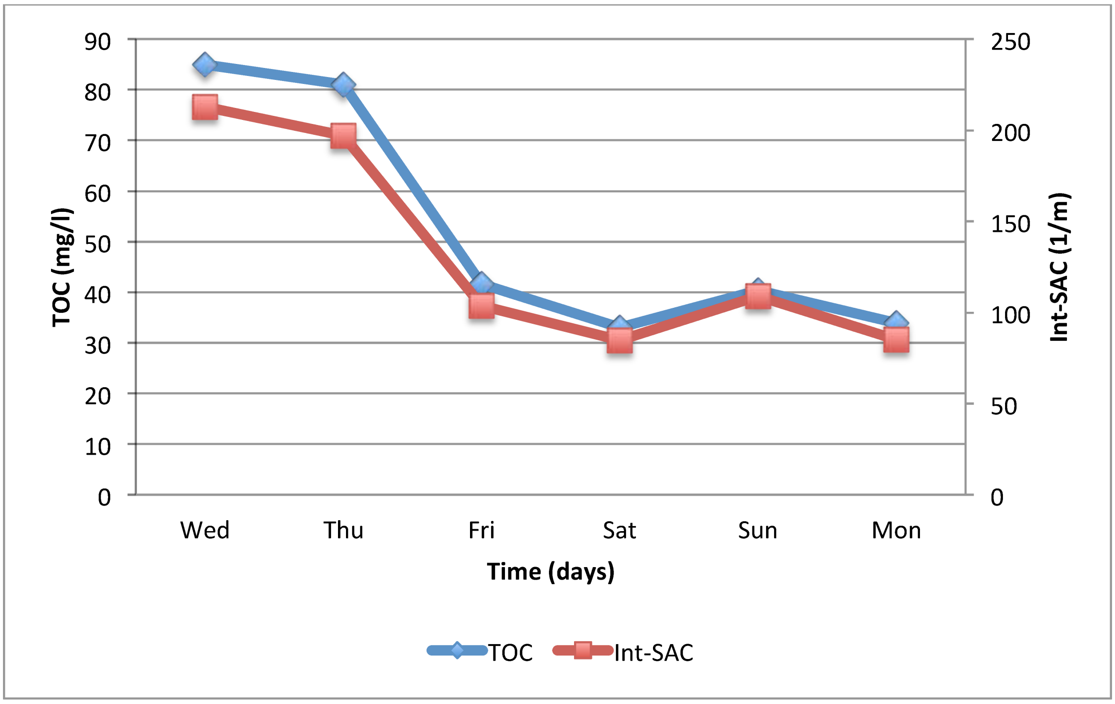


Figure 15: Diurnal influent of TOC and integral of SAC

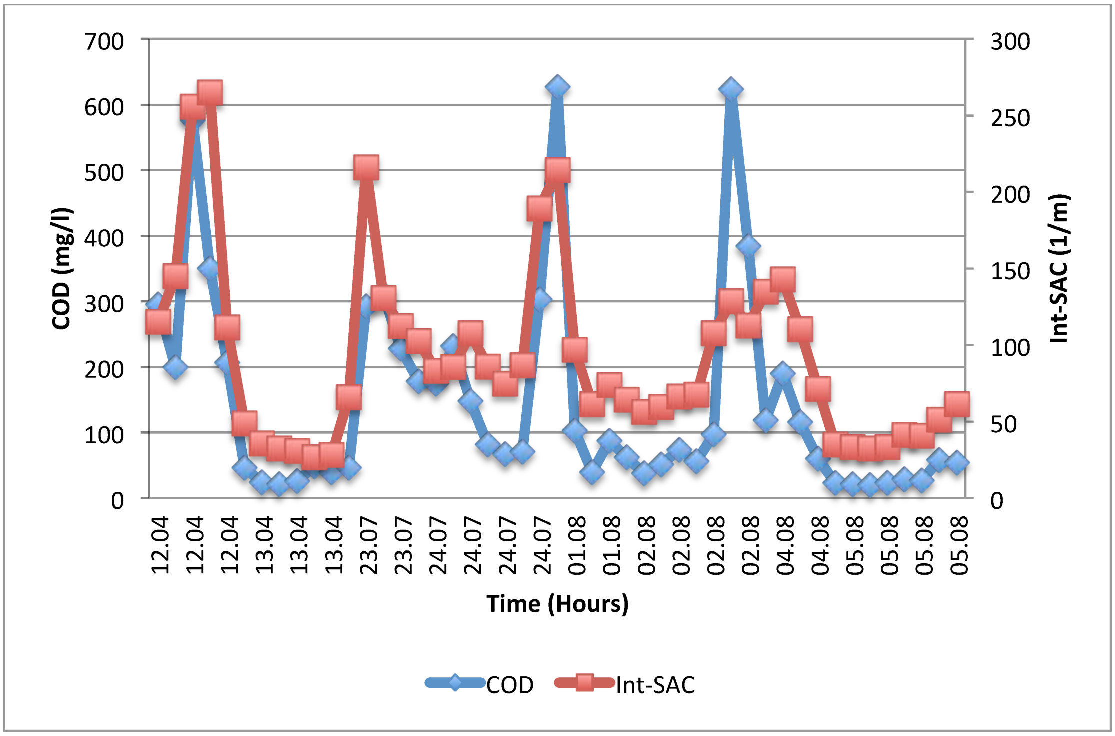


Figure 16: Hourly influent of COD and integral of SAC

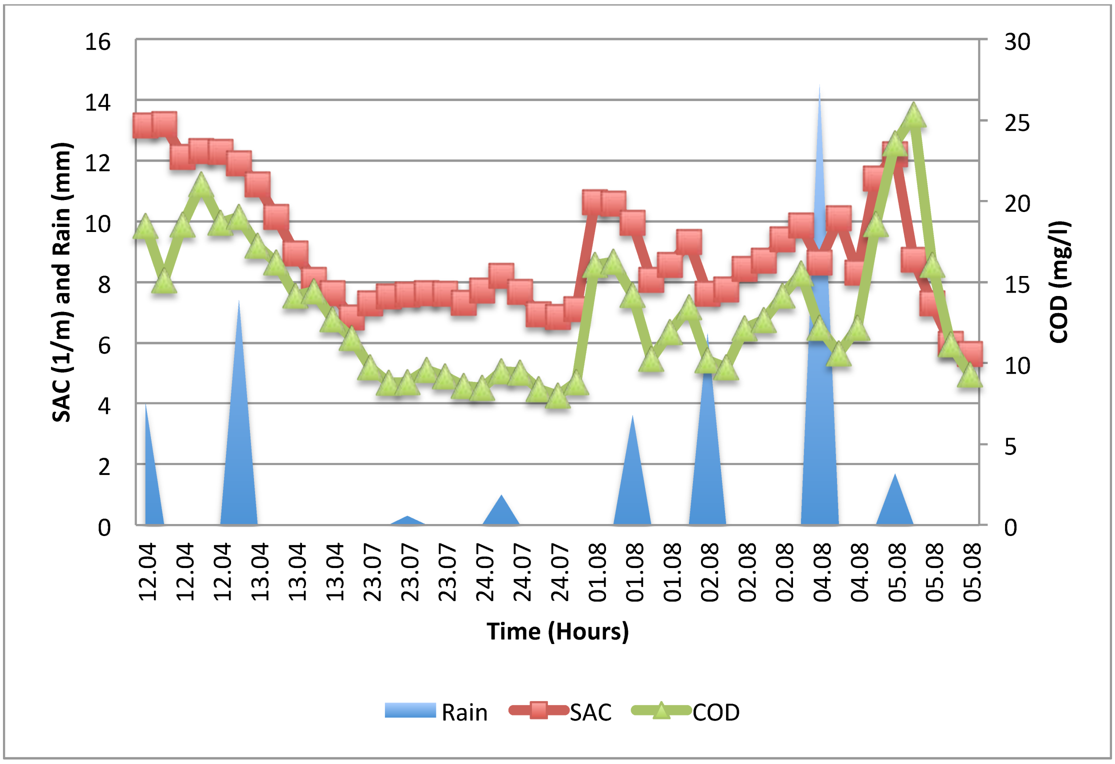


Figure 17: Hourly effluent of SAC and COD

3.1.2. Ammonium

The main source of NH4-N in the sewage is urine, and investigating the ammonium influent, its fluctuations in contrast with rain and its correlation with other chemical substances, makes ammonium a key parameter in this study. Following are the graphs for NH4-N and its loads for diurnal and hourly influent and effluent of the WWTP (Figures 18-21).

As can be seen in the Figure 18 rain has an impact not only on the influent but also on the effluent load for ammonium in the WWTP; moreover, turbidity has a fairly similar fluctuation with the ammonium, which implies the turbulence in the sewage may cause the increase in suspended solids and ammonium, Figure 19. As discovered in the chapter “3.1.1” SAC, which is the representative of the yellow color in WWTP, has a strong relation with the NH4-N concentrations as well as loads throughout daily and hourly behavior, the resembling trends illustrated in the Figures 20 and 21 are the evidence of such affiliation. Ammonium graphs related to the mentioned parameters shall be found in Appendix A.

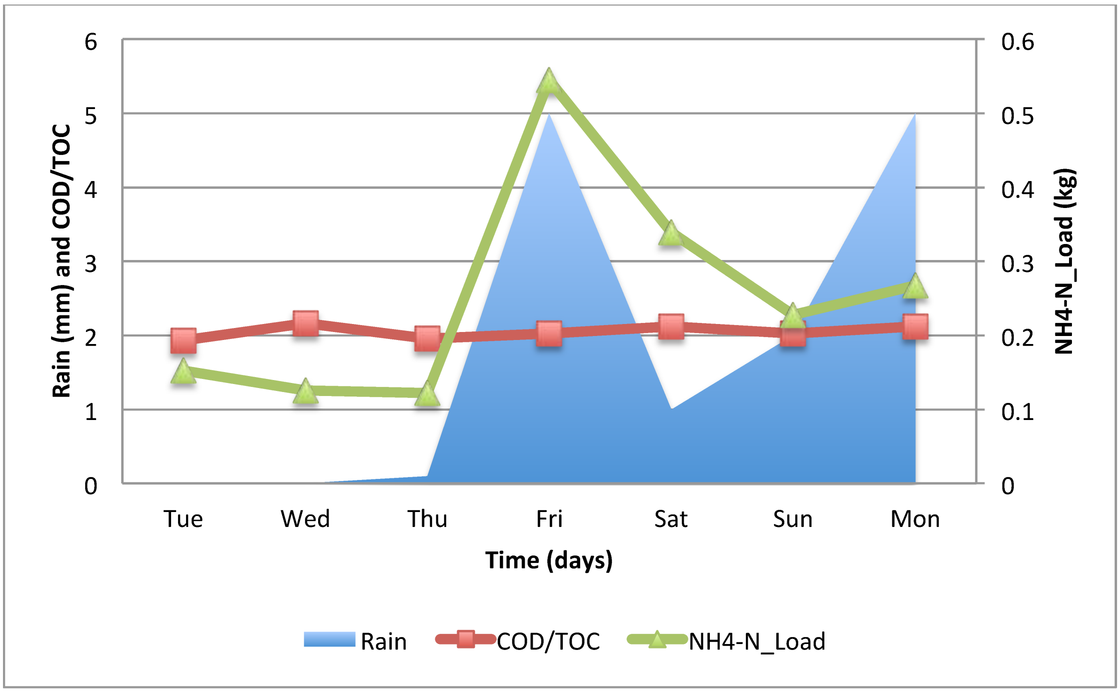


Figure 18: Diurnal effluent of ammonium and COD/TOC

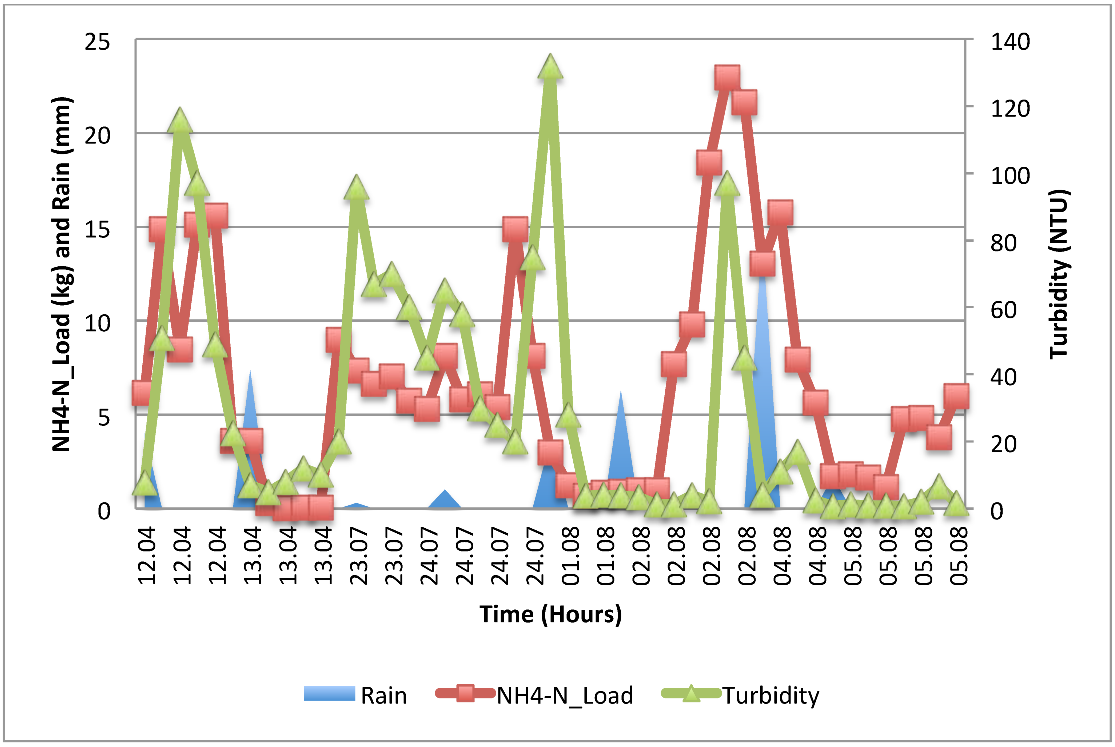


Figure 19: Hourly influent of load of the ammonium and turbidity

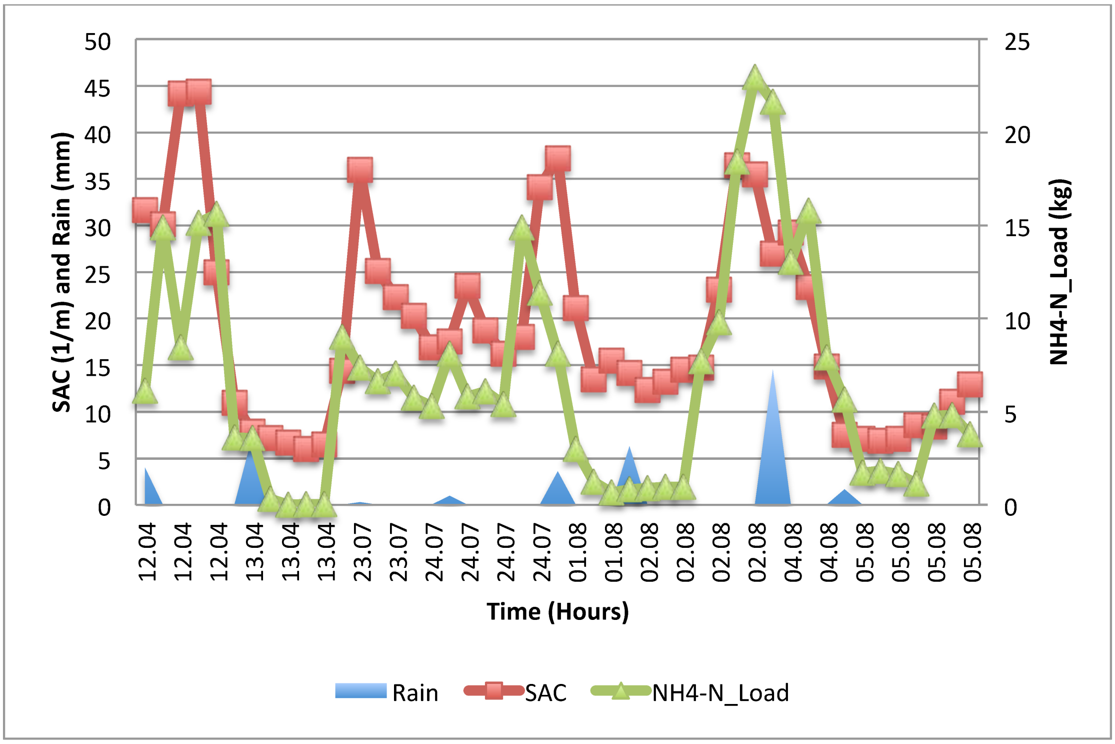


Figure 20: Hourly influent of SAC and the load of ammonium

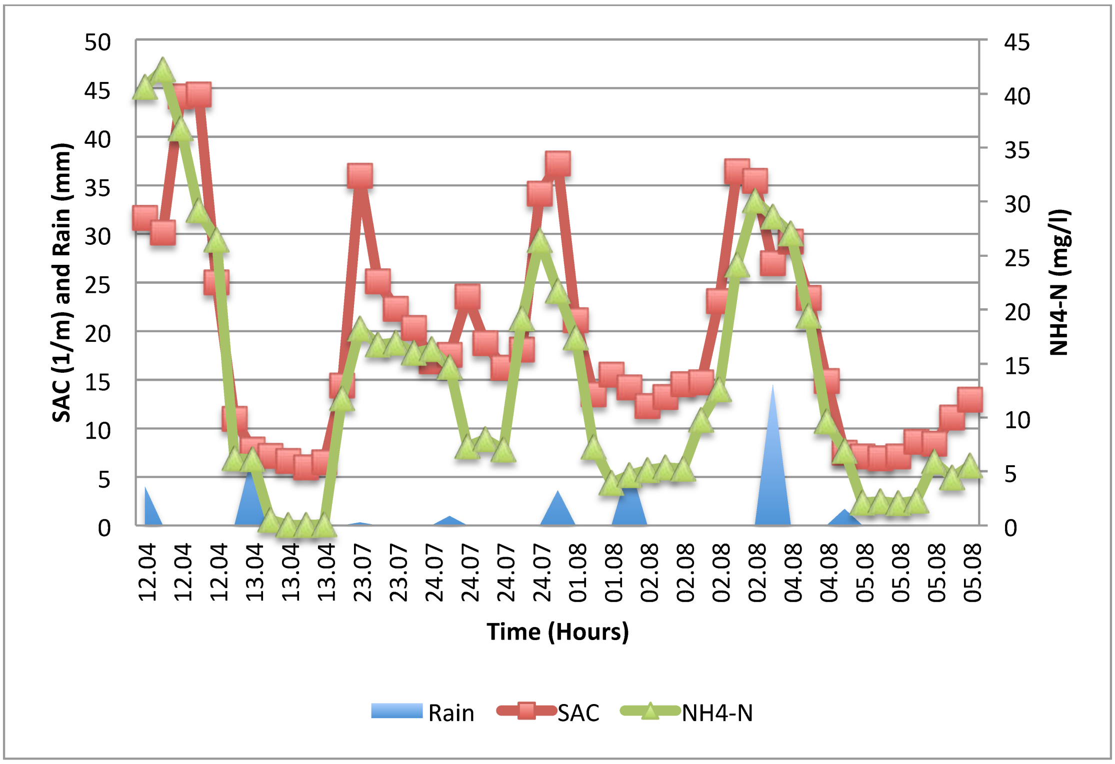


Figure 21: Hourly influent of SAC and the concentration of ammonium

3.1.3. Chemical Oxygen Demand and Total Organic Carbon

Based on Dr. Kuch, measuring the Total Organic Carbon (TOC) is a direct assessment of the amount of organics in the water. A Chemical Oxygen Demand (COD) test oxidizes all organics except for those, which are totally resistant to dichromate oxidation, and is widely used in wastewater monitoring, design, modeling and plant operational analysis (Kuch, 2016). Based on the stoichiometry, the COD/TOC ratio should be approximately the molecular ratio of oxygen to carbon, which is 2.66, and any values higher than that is evidence of a poor oxidization. In the organic compounds with the schematic formula of:

$$C_nH_mO_x$$

$$[O] \rightarrow \text{n } CO_2 + 0.5\text{m } H_2O$$

Indicating, the lower the value of x, the higher the ratio of COD/TOC, resulting a devastated oxidized mixture (2016). In the Figures 22-25 various combination of different parameters in regards to COD and TOC are illustrated.

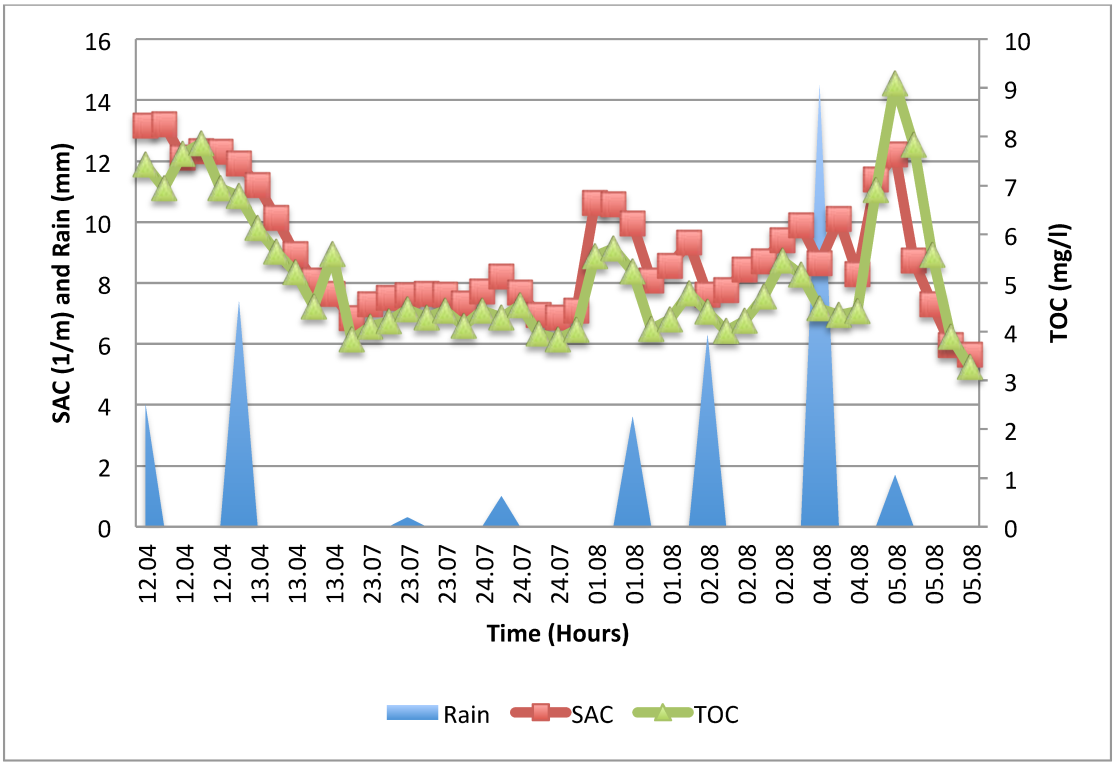


Figure 22: Hourly effluent of SAC and concentration of TOC

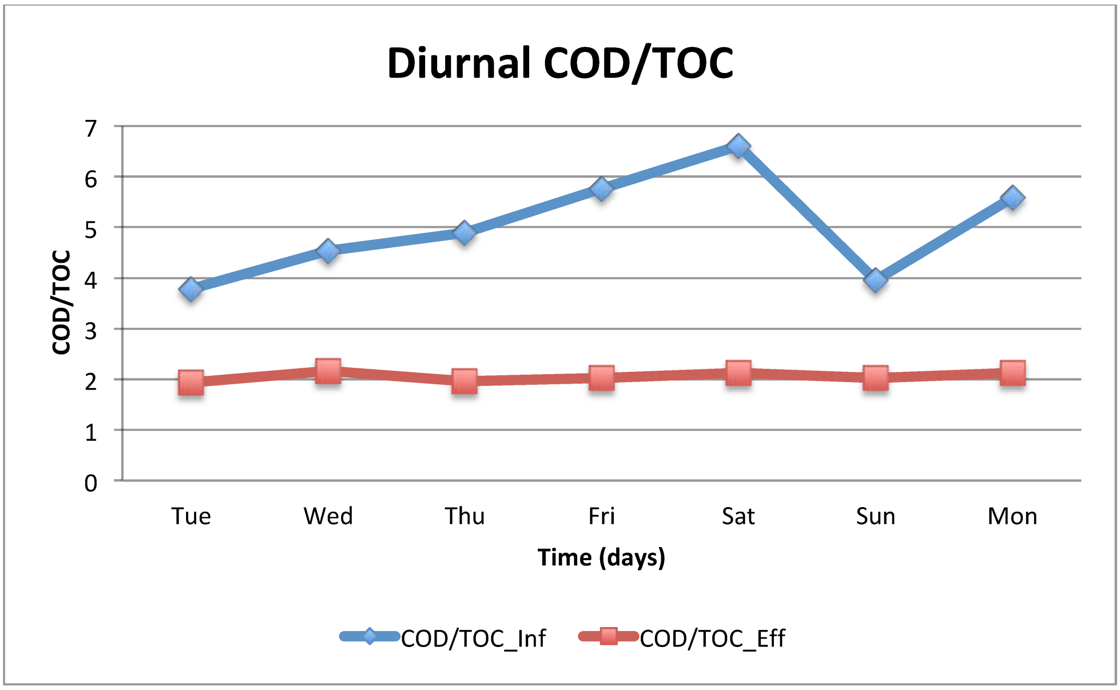


Figure 23: Diurnal ratio for COD and TOC

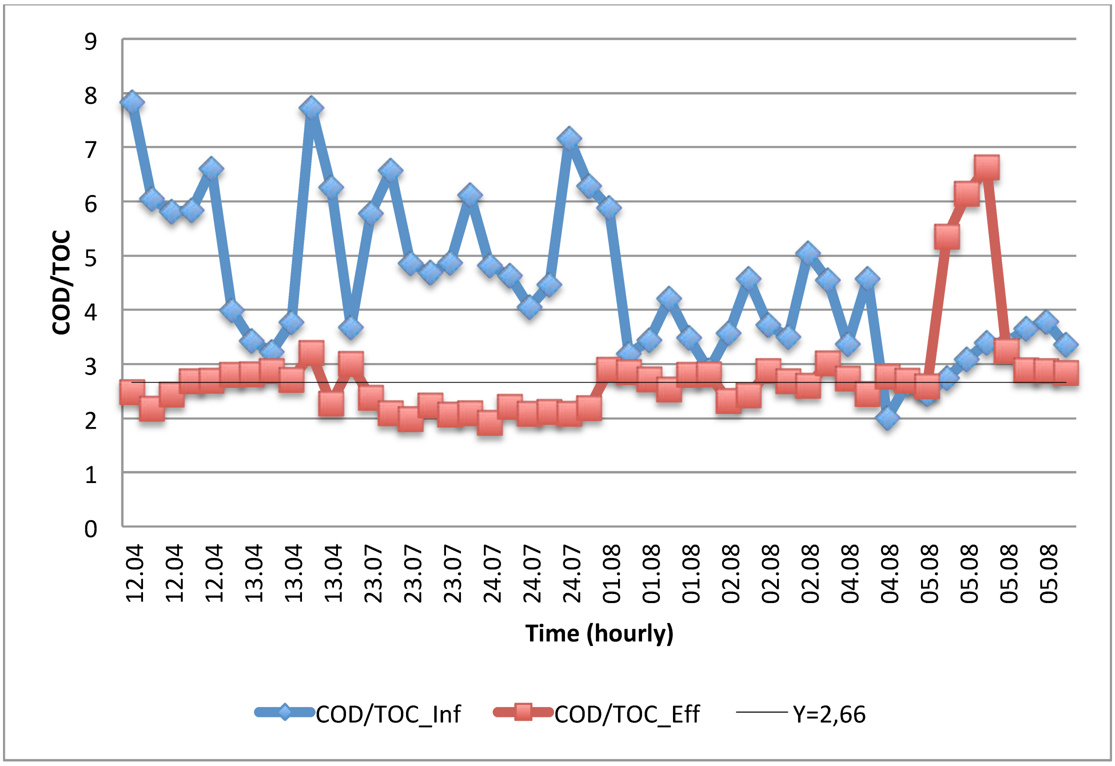


Figure 24: Hourly ratio for COD and TOC

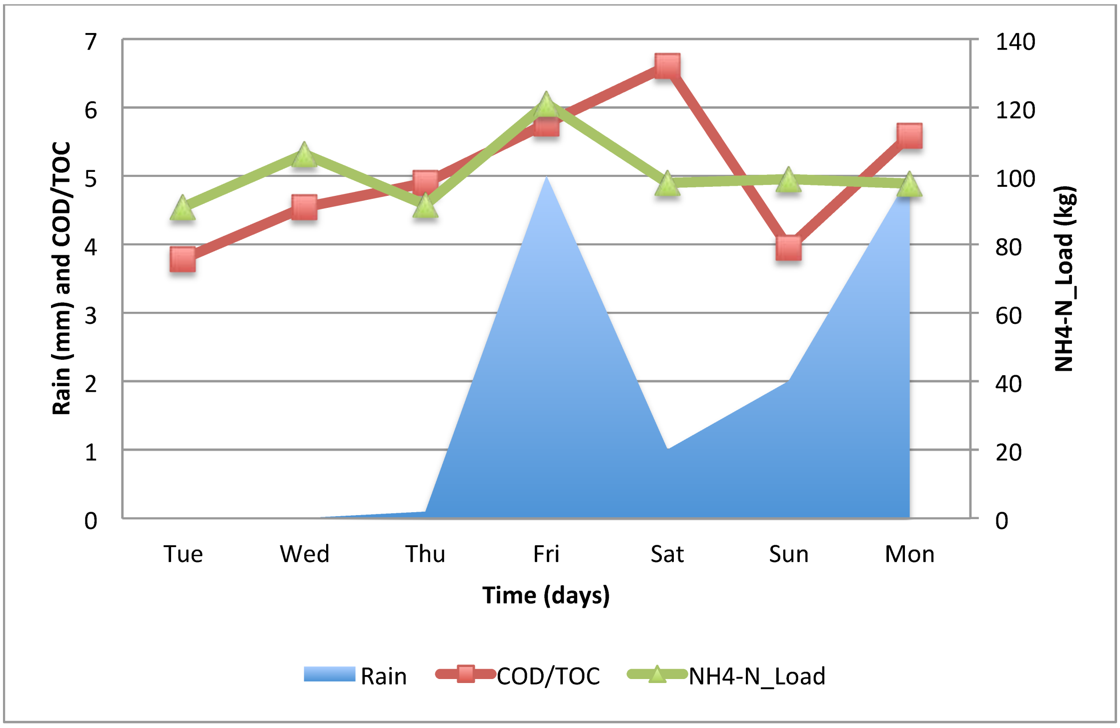


Figure 25: Diurnal influent of the load of the ammonium and COD/TOC

The fluctuations of COD and TOC are in a harmony with SAC. It is quite often when the ratio of COD/TOC in the influent is higher than 6, which may cause difficulties along the degradation process in the WWTP, however the WWTP is still working efficiently and reducing the effluent ratio below 2.66. As observed above, there was an incident on the 5th day of the month August, a malfunction in the secondary sedimentation tank leading the sludge through effluent, resulting the observed very high values for the ratio of COD/TOC as well as other parameters. Accordingly, the corresponding values from the incident are omitted in the Figure 25, in order to reach more realistic and noticeable fluctuations.

As can be seen in the Figure 25, the rain event on Friday has an immediate influence on the load of the NH4-N arriving to the WWTP, despite the fact that the peak for the ratio of COD/TOC happens with a delay; this can be explained since the settled sludge, along the sewer is the origin of the COD and TOC, it cause a delay for the particles to be driven into the WWTP by the flush of rain.

3.2. Comportment of Conventional Parameters and Micropollutants

In the following section analyzes of a correlation or reciprocal behavior among the conventional parameters and micropollutants have been accomplished.

3.2.1. Turbidity and Triclosan

Triclosan is an antibiotic, mainly driven into the WWTP because of rain events; therefore it is expected to increase by turbidity of the influent. Figures

26 and 27 are presenting the fluctuations of Triclosan concentration and turbidity.

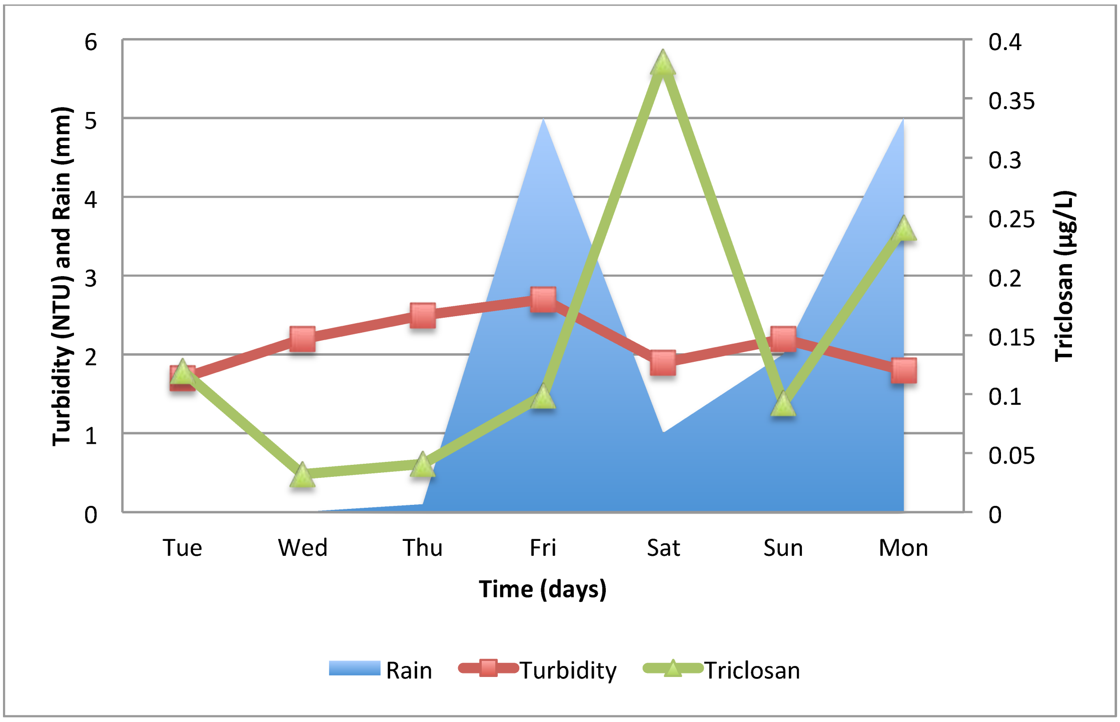


Figure 26: Diurnal effluent of the turbidity and Triclosan

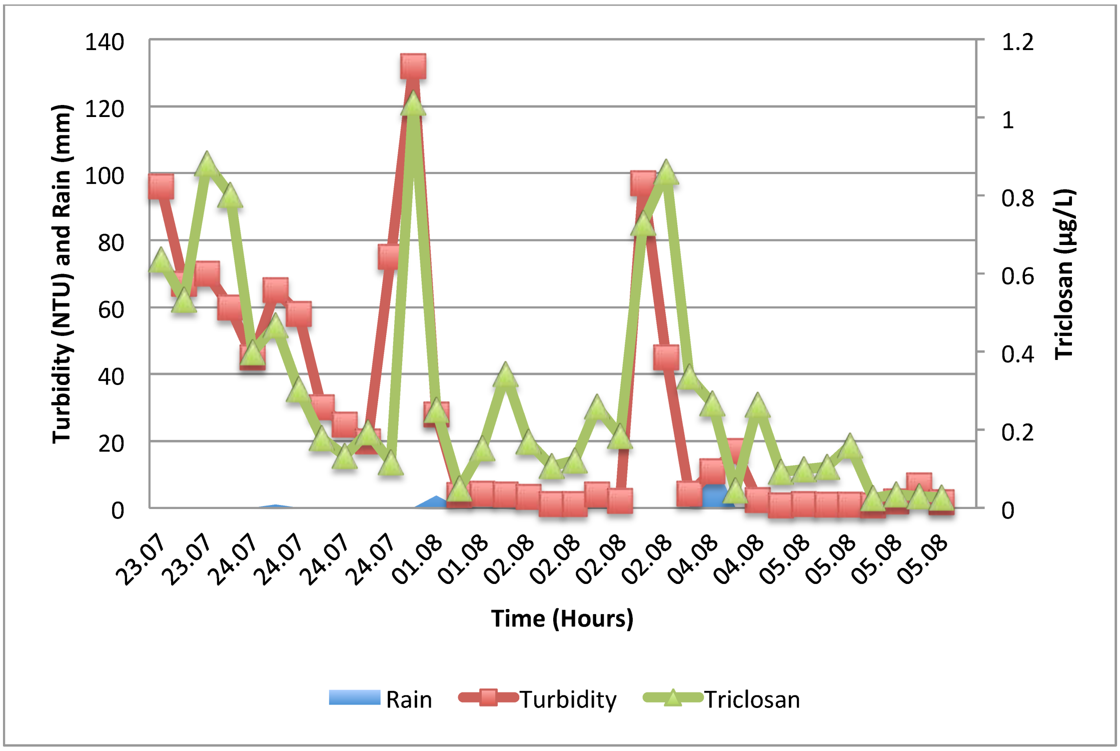


Figure 27: Hourly influent of the turbidity and Triclosan

As has been noted, regulations are leading the limitation of the conventional parameters concentrations in the effluent of the WWTPs; in contrast, in the absence of regulations for micropollutants concentration, the effluent values are neither regulated nor mitigated. Triclosan can be attached to the floating particles in the wastewater and reach the WWTP by the turbid suspended solids, peaks for the influent of the Triclosan and turbidity follow a similar pattern in the hourly influent. Diurnal influent and hourly effluent can be found in the Appendix B.

3.2.2. Ammonium and Pharmaceuticals

Pharmaceuticals are largely excreted from the patients to the sewage. The main provenance of pharmaceutical is urine; therefore a clear relation between the ammonium and pharmaceuticals is anticipated. Concentration of the Gabapentin and the load of ammonium have similar fluctuations throughout the day for the influence (Figure 28). Contrastingly, concentration of Lidocaine does not follow the same pattern with the load of ammonium (Figure 29). As can be seen in the Figure 30, Sulfamethoxazole follows a similar trend as Gabapentin against the ammonium. However the load of the ammonium for the effluent has drastically decreased due to the biological removal of nitrogen, yet no diminishing of Carbamazepine has occurred (Figure 31). Related graphs shall be found in Appendix B.

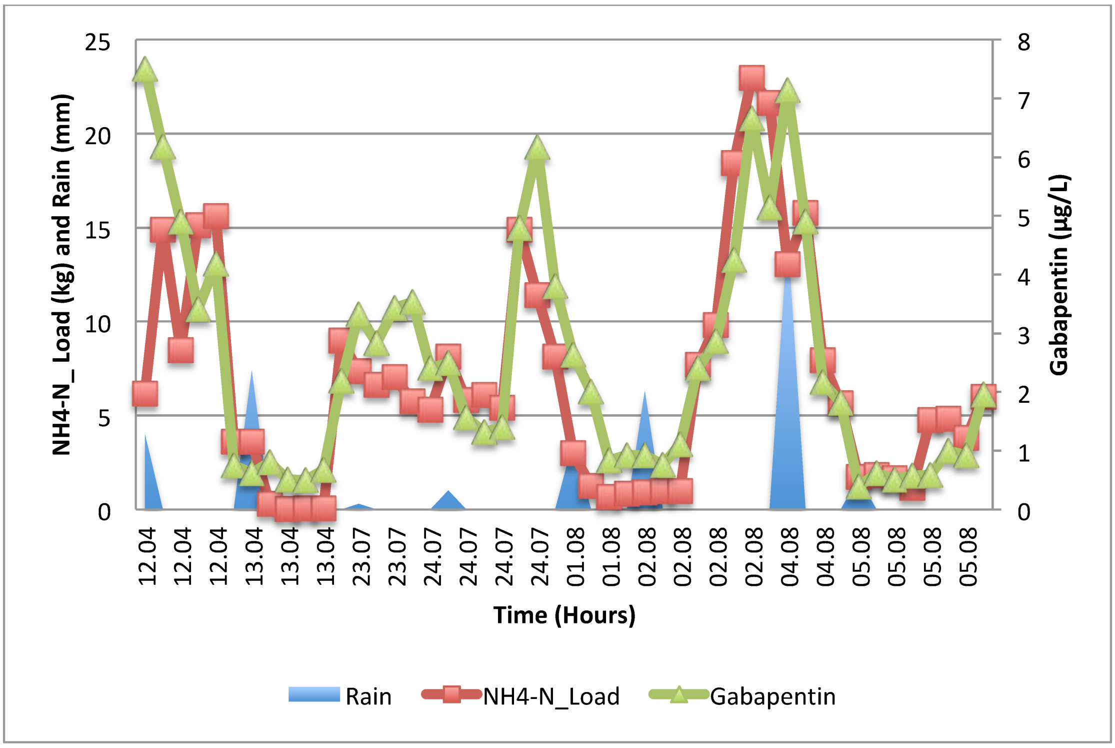


Figure 28: Hourly influent of the load of ammonium and concentration of Gabapentin

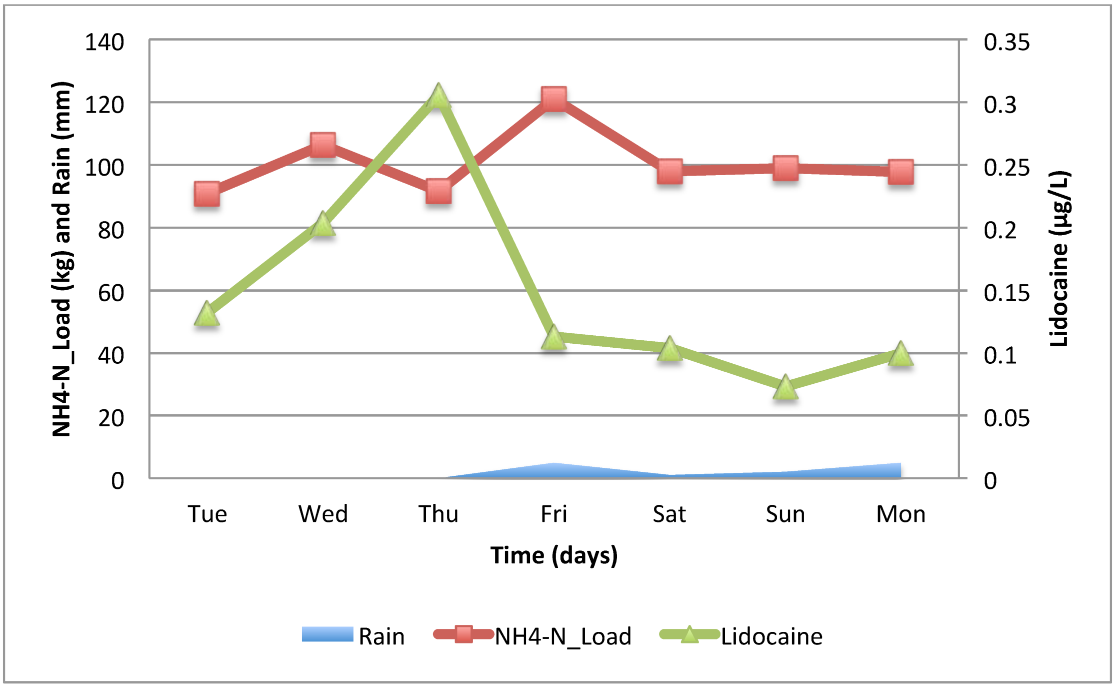


Figure 29: Diurnal influent of the load of ammonium and the concentration of Lidocaine

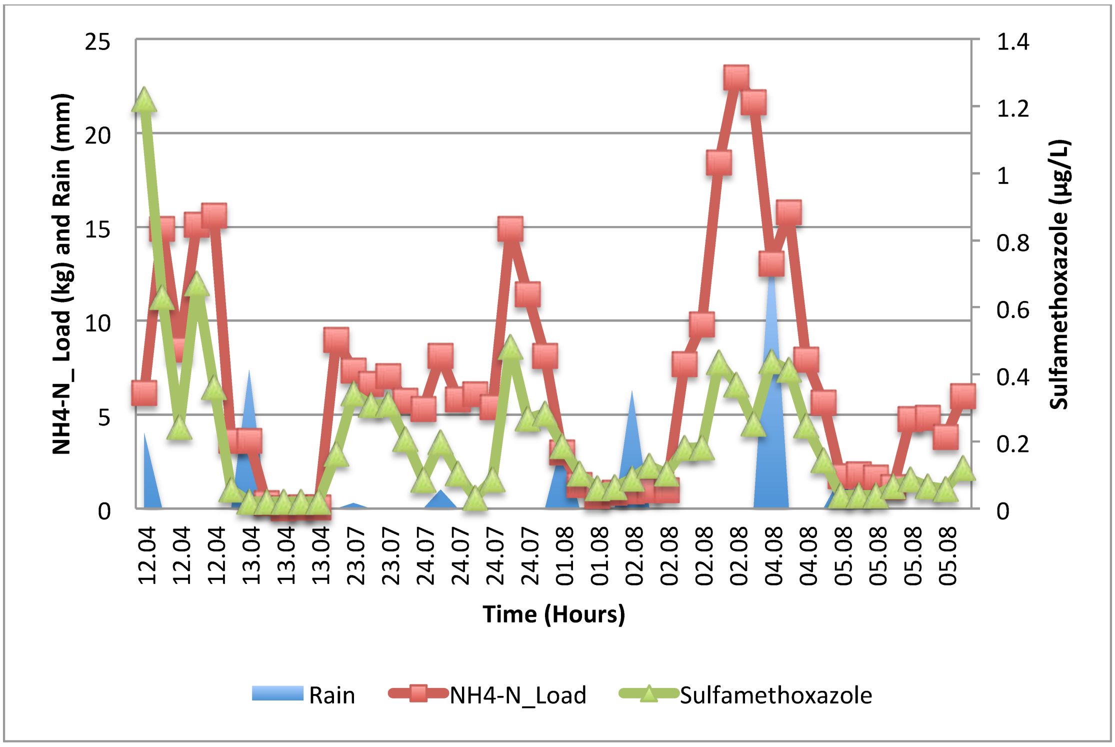


Figure 30: Hourly influent of the load of ammonium and the concentration of Sulfamethoxazole

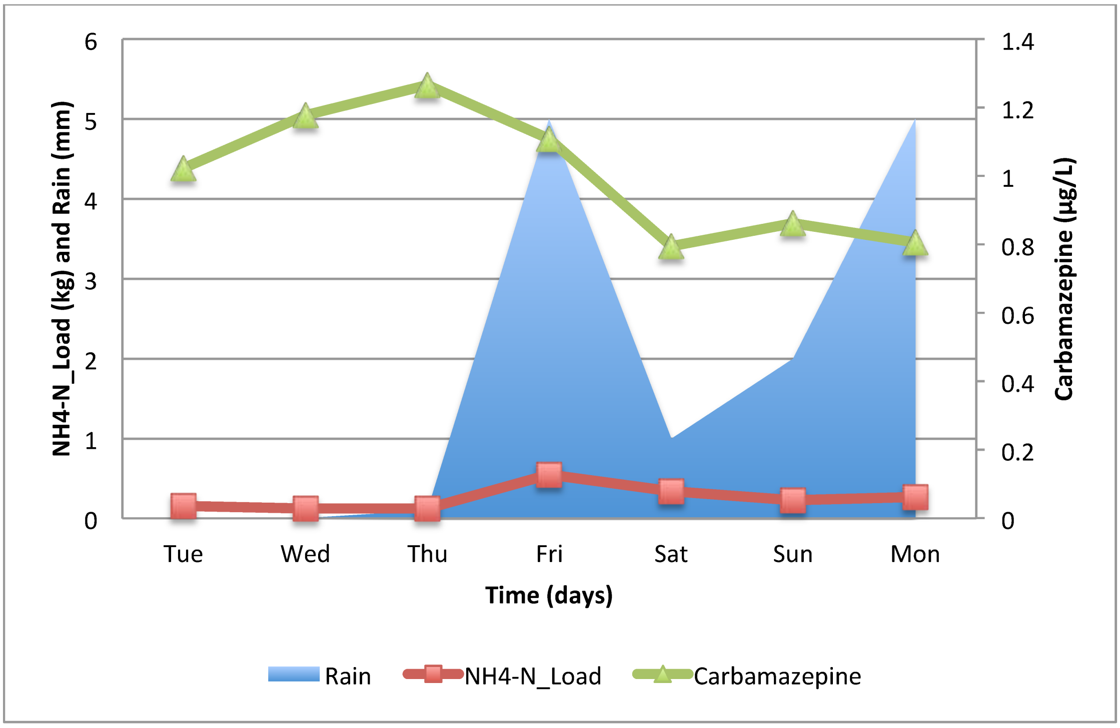


Figure 31: Diurnal effluent of the load of ammonium and concentration of Carbamazepine

3.3. Concentrations and Elimination of Micropollutants

In this section, concentration of influent and effluent of micropollutants as well as the percentage of elimination achieved by the activated sludge process during the WWTP is presented. In spite of the fact that the average elimination for conventional parameters such as COD, TOC are 93% and 84% respectively, and parameters such as NH4-N are up to 99% degraded, elimination of the micropollutants does not follow a decent pattern. Likewise the manner, substances like Gabapentin and Sulfamethoxazole are barely reaching the 50% elimination, while substances like Ibuprofen has shown a impressive elimination of 99%, and on the other hand, Carbamazepine has shown a total resistance against the conventional procedures for treatment.

Tables of influent and effluent concentrations and the graphs for fluctuations as well as the eliminations have been carried forward.

3.3.1. Concentrations

Tables 10 and 11 contain the minimum and maximum for the diurnal and hourly influent and effluent of the micropollutants for the pharmaceuticals and other micropollutants respectively. A large difference between the values of minimum and maximum of the Gabapentin as well as the Ibuprofen and its degradation products are diagnosed. The chemicals 1H-benzotriazole and Tolytriazoles in excess of Bisphenol A are also following the same trend, implying the more unreliability of their constant concentration to the WWTP. This could be influenced by their solubility in the water. Moreover, a huge gap between the influent and effluent concentrations of the Ibuprofen indicates its biodegradability in the conventional process of WWTP.

Table 10: Minimum and maximum of the diurnal and hourly influent and effluent of the pharmaceuticals

Micropollutant	Time	Influent (μg/l)		Effluent (μg/l)	
		Min	Max	Min	Max
Metoprolol	D	0.90	2.12	0.72	1.51
	H	0.10	1.62	0.04	1.02
Sulfamethoxazole	D	0.16	0.67	0.12	0.26
	H	0.02	1.22	0.01	0.42
Gabapentin	D	3.71	9.83	2.60	4.22
	H	0.39	7.50	0.72	3.40
Carbamazepine	D	0.61	0.89	0.80	1.27
	H	0.04	0.72	0.10	0.74
Lidocaine	D	0.07	0.31	0.12	0.32
	H	0.01	0.28	0.03	0.22
Ibuprofen	D	12.35	32.10	0.03	0.12
	H	0.67	21.28	0.00	2.36
Ibu-OH	D	40.19	70.55	0.03	0.24
	H	0.28	20.20	0.00	2.93
Ibu-COOH	D	55.84	99.97	0.25	1.14
	H	0.06	16.75	0.00	0.11
Naproxen	D	0.00	0.00	0.00	0.00
	H	0.21	2.14	0.03	0.56

Table 11: Minimum and maximum of the diurnal and hourly influent and effluent of the other micropollutants

Micropollutant	Time	Influent (μg/l)		Effluent (μg/l)	
		Min	Max	Min	Max
1H-Benzotriazole	D	4.07	12.27	1.41	2.26
	H	0.81	13.50	0.42	3.01
Tolytriazoles	D	0.41	1.43	0.43	0.79
	H	0.11	8.09	0.25	076
HHCB	D	0.19	0.19	0.10	0.14
	H	0.04	2.35	0.02	0.49
AHTN	D	-	-	0.10	0.14
	H	0.04	0.43	0.00	0.09
HHCB-Lac	D	-	-	1.23	3.36
	H	0.22	2.03	0.29	1.65
TCEP	D	0.44	0.86	0.17	0.41
	H	0.17	2.38	0.14	0.43

TCPP	D	0.34	1.76	0.37	1.47
	H	0.19	2.89	0.26	1.02
TDCPP	D	0.07	0.18	0.04	0.07
	H	0.03	0.44	0.04	0.12
Mecoprop	D	0.00	-	0.01	0.04
	H	0.00	0.27	0.01	0.18
Triclosan	D	0,06	0,22	0,03	0,38
	H	0,02	1,04	0,00	0,10
Bisphenol A	D	-	-	0,27	0,34
	H	0,05	18,30	0,04	3,26

3.3.2. Elimination

Figures 32 and 33 are presenting the diurnal elimination percentage under dry weather and wet weather along with the hourly wet weather for the pharmaceuticals and rest of the micropollutants respectively.

In most of the cases, diurnal elimination of the dry weather is higher than the wet weather; this phenomenon can be explained by the greater values of loads during the wet weather. However such a trend is not observed in the case of TDCPP and Triclosan. Ibuprofen has a decent degradation in all various cases. On the contrary Carbamazepine and Lidocaine have shown no removal in the effluent of the WWTP.

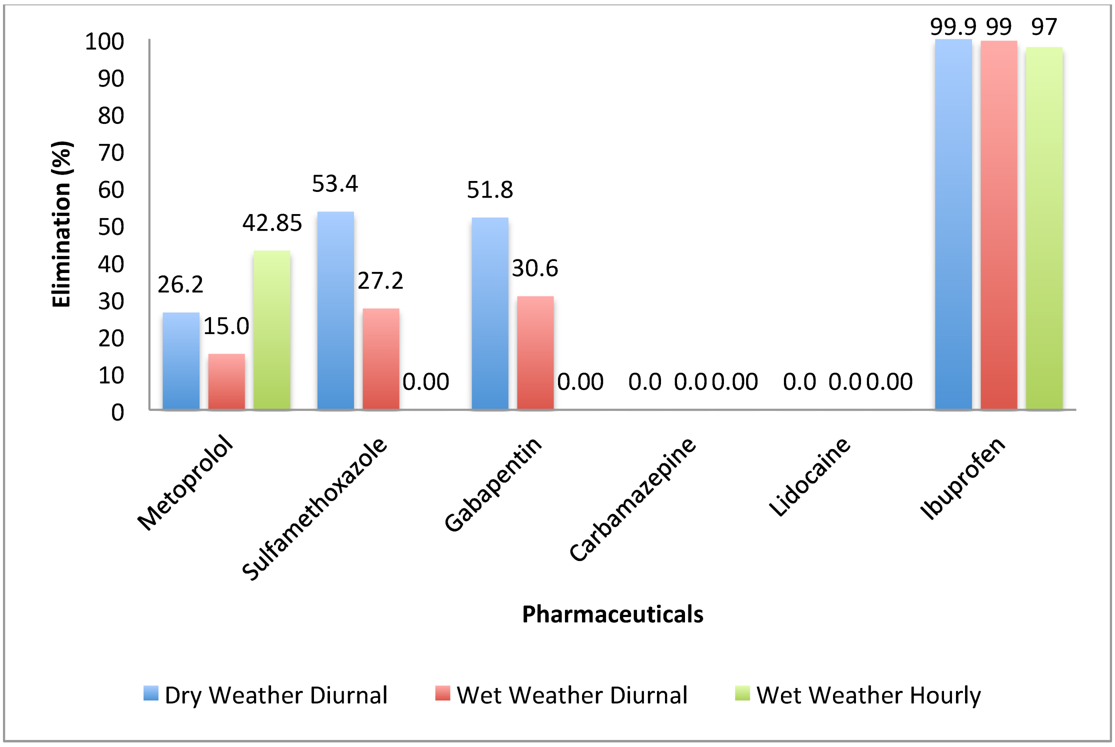


Figure 32: Elimination of pharmaceuticals

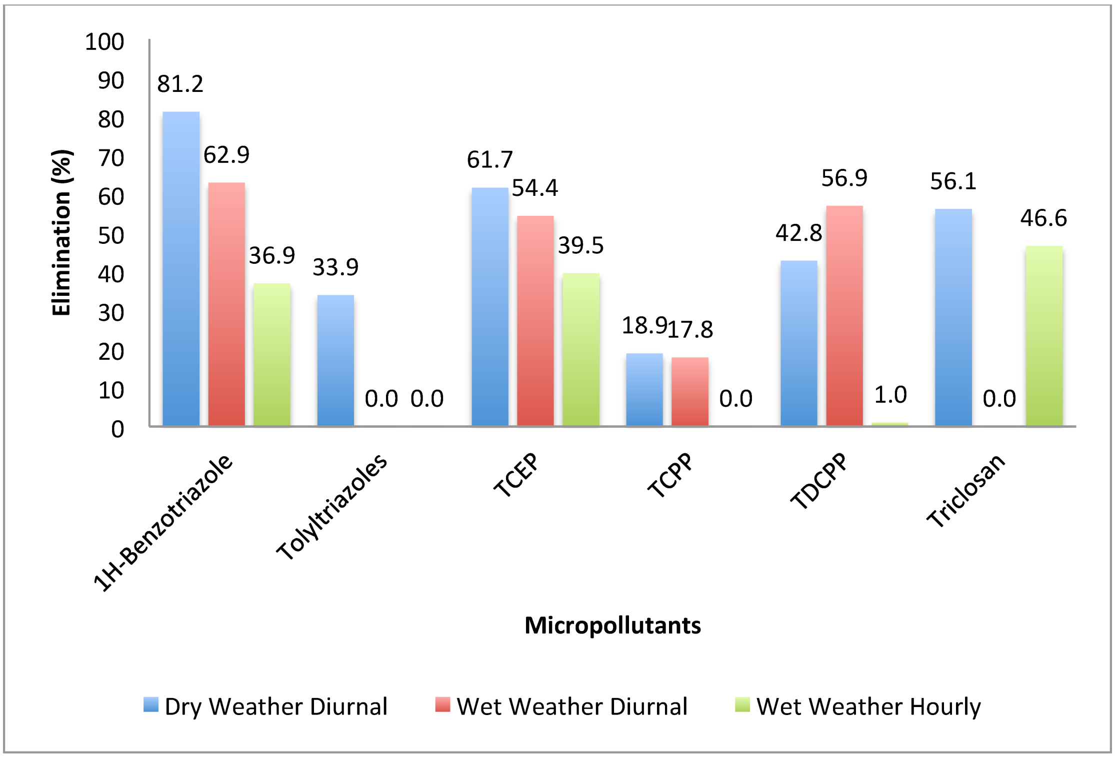


Figure 33: Elimination of other micropollutants

3.3.2. Influent and Effluent of Pharmaceuticals

Metoprolol and Sulfamethoxazole and Gabapentin

Figures 34, 35 and 36 are the comparison of the influent and effluent for the diurnal Metoprolol, hourly Metoprolol and diurnal Sulfamethoxazole respectively. The concentrations seem to decrease by the rain events, indicating the increase of solubility of micropollutants during wet weather conditions. Resembling behavior for the Gabapentin fluctuations can be found in Appendix C. The peak of the Sulfamethoxazole comes almost a day after, implying a very good buffer capacity for the WWTP.

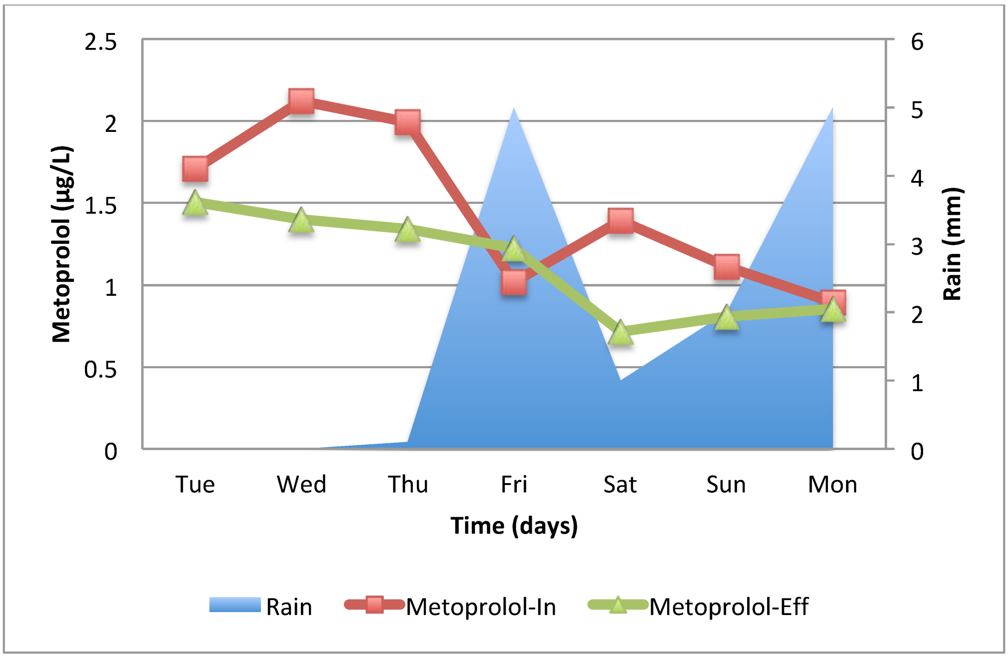


Figure 34: Diurnal influent and effluent concentration of Metoprolol

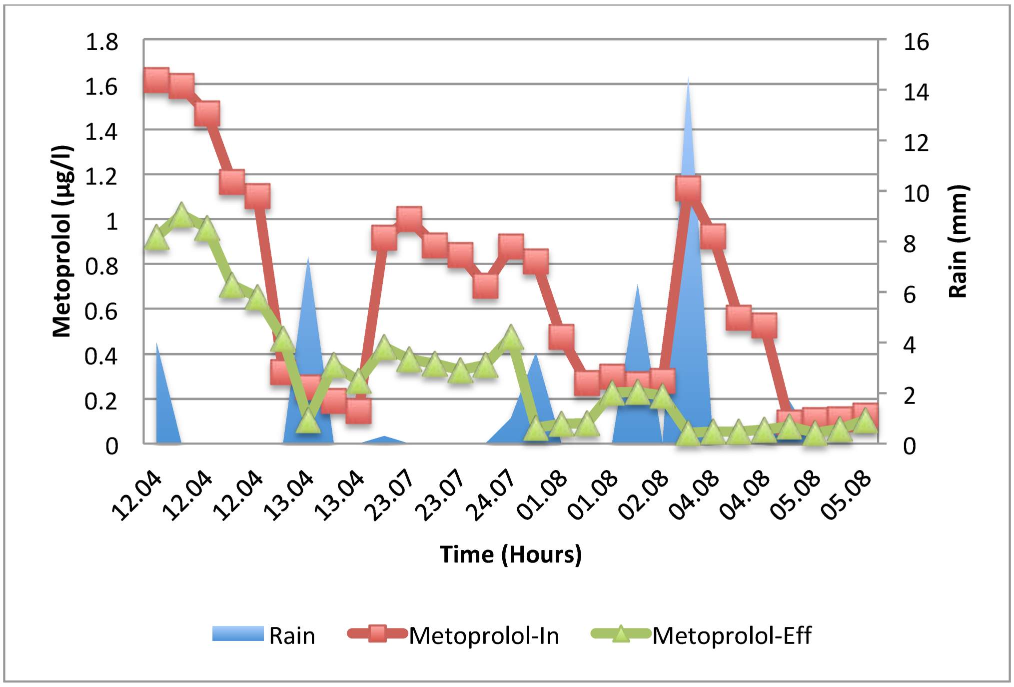


Figure 35: Hourly influent and effluent concentration of Metoprolol

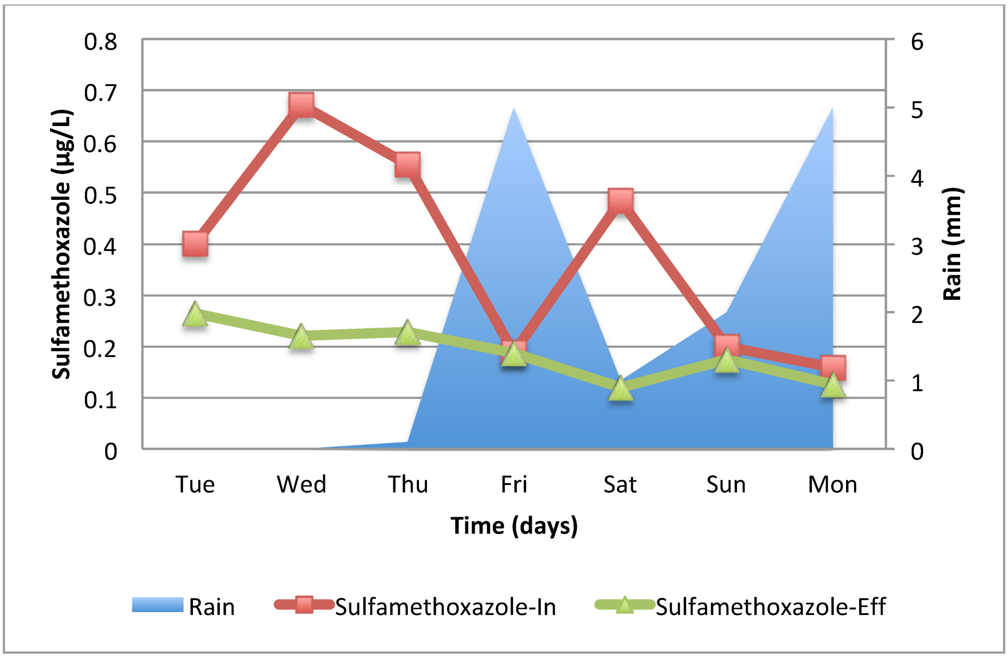


Figure 36: Diurnal influent and effluent concentration of Sulfamethoxazole

Carbamazepine and Lidocaine

Graphs in the Figures 37-39 are illustrating the influent and effluent concentrations for the diurnal Carbamazepine, Lidocaine and the hourly fluctuations of the Lidocaine respectively. In the Figure 37, Carbamazepine seems to have a phase shift over the week, where Lidocaine concentration decreases drastically with the rain event. In some points the concentration of Carbamazepine and Lidocaine have been detected higher than the influent.

There are some compounds (e.g., pharmaceuticals, hormones, drugs of abuse that are excreted by humans and/or animals) that can be found at higher concentrations in the WWTPs effluents than in the respective influents, due to their excretion as conjugates that are broken in the WWTPs. These conjugates are generally metabolized during biological treatment and the parent compound is released, often increasing the concentrations of the parent compounds at the outlet of the WWTPs (Barbosa et al., 2016).

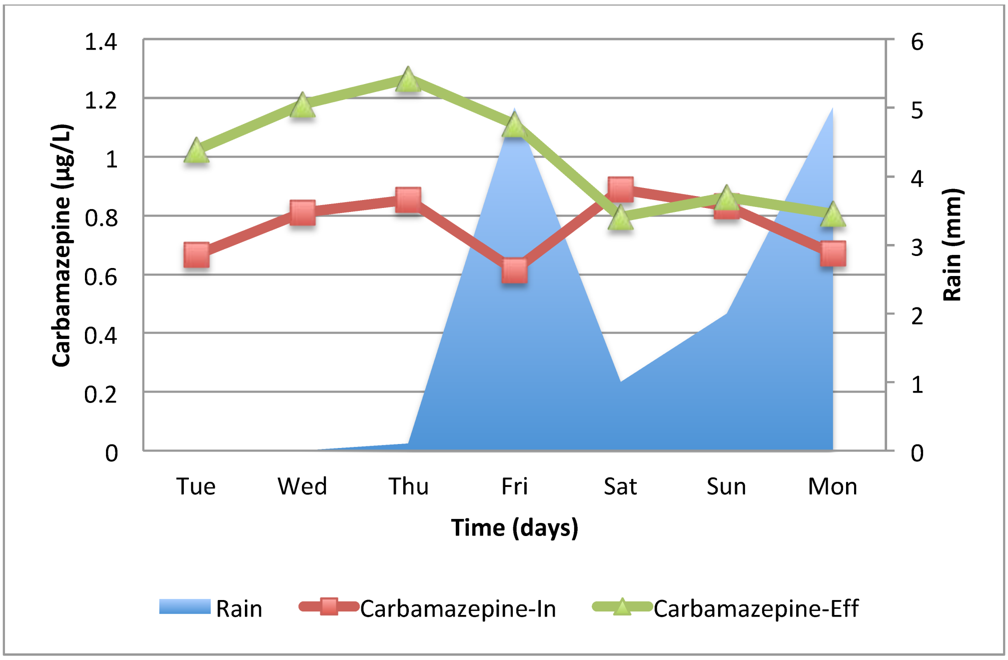


Figure 37: Diurnal influent and effluent concentration of Carbamazepine

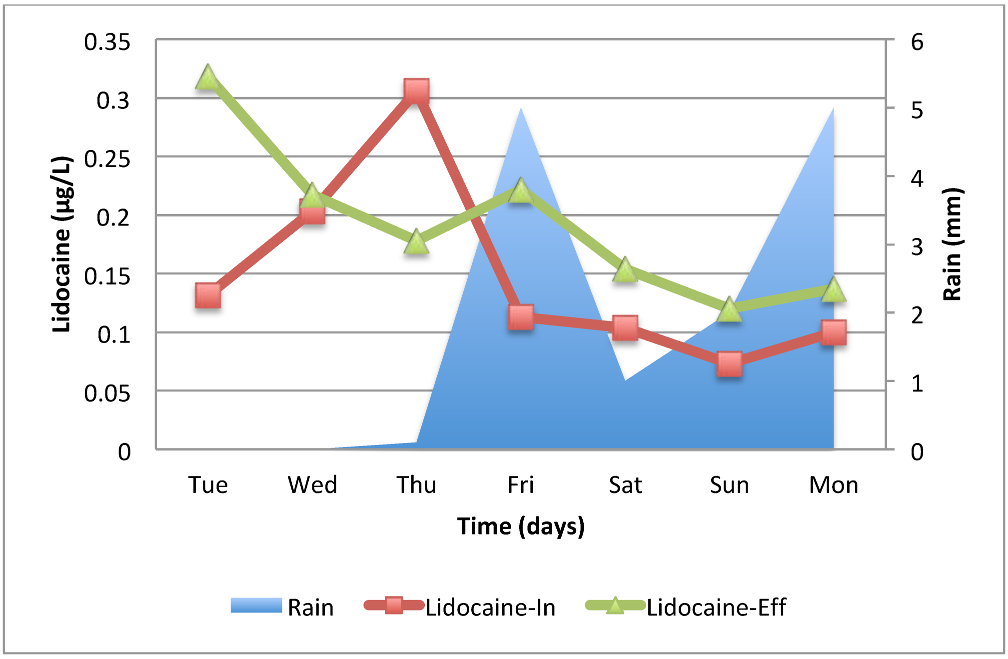


Figure 38: Diurnal influent and effluent concentration of Lidocaine

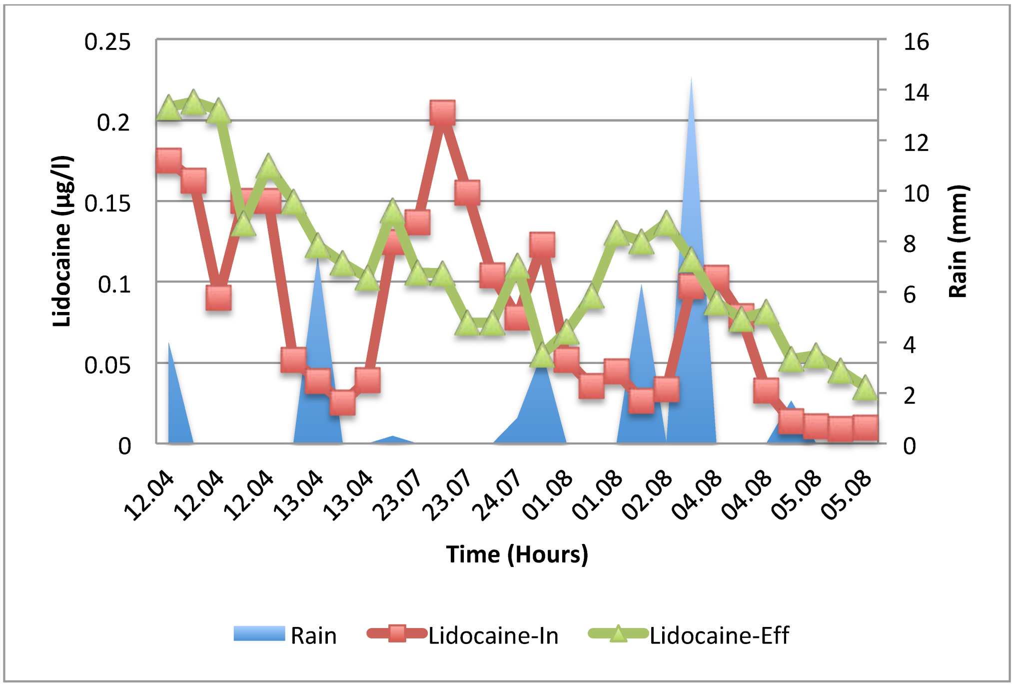


Figure 39: Hourly influent and effluent concentration of Lidocaine

Ibuprofen and Naproxen

Diurnal Ibuprofen and its degradation products Ibuprofen-OH and Ibuprofen-COOH together with the Naproxen hourly influent and effluent are represented in the Figures 40-43. Ibuprofen and its degradation products are nearly almost treated through the activated sludge process. Naproxen influent has been affected by the rain events, however the effluent concentration is in a lower range, indicating an acceptable degree of degradation.

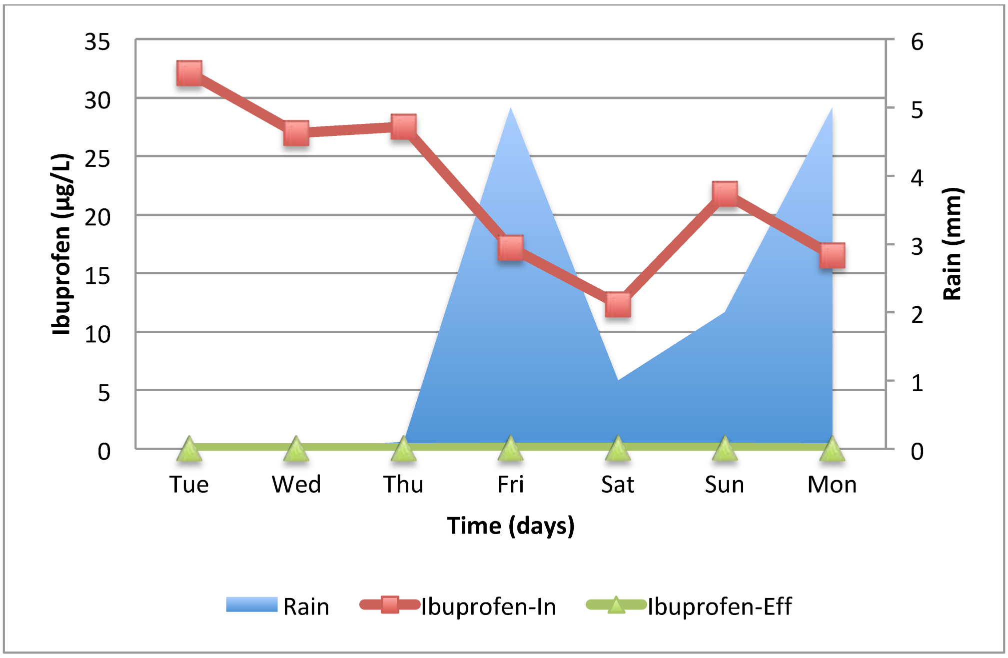


Figure 40: Diurnal influent and effluent concentration of Ibuprofen

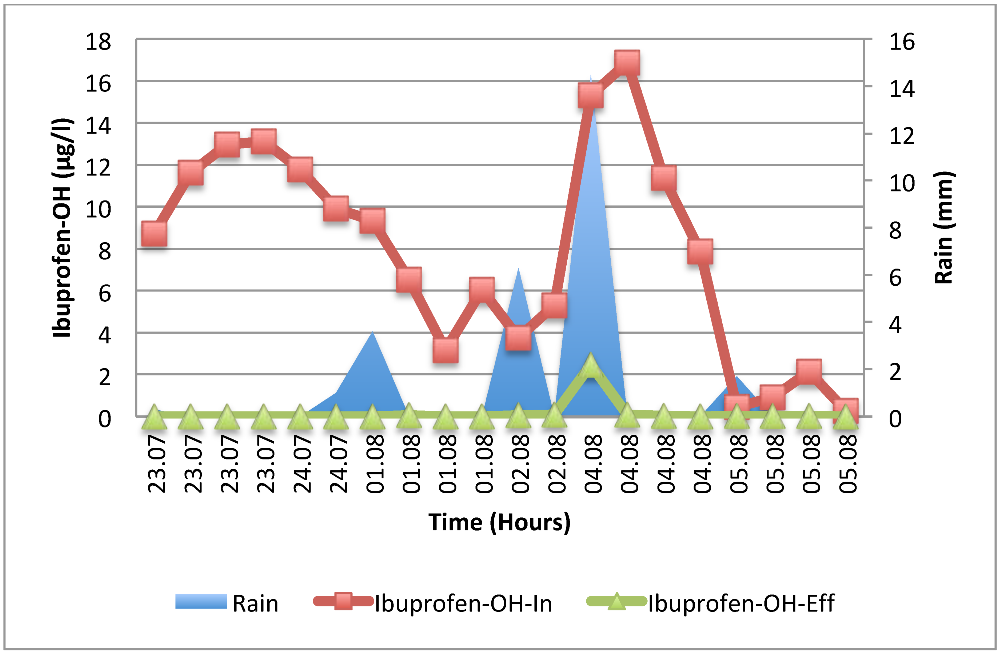


Figure 41: Hourly influent and effluent concentration of Ibuprofen-OH

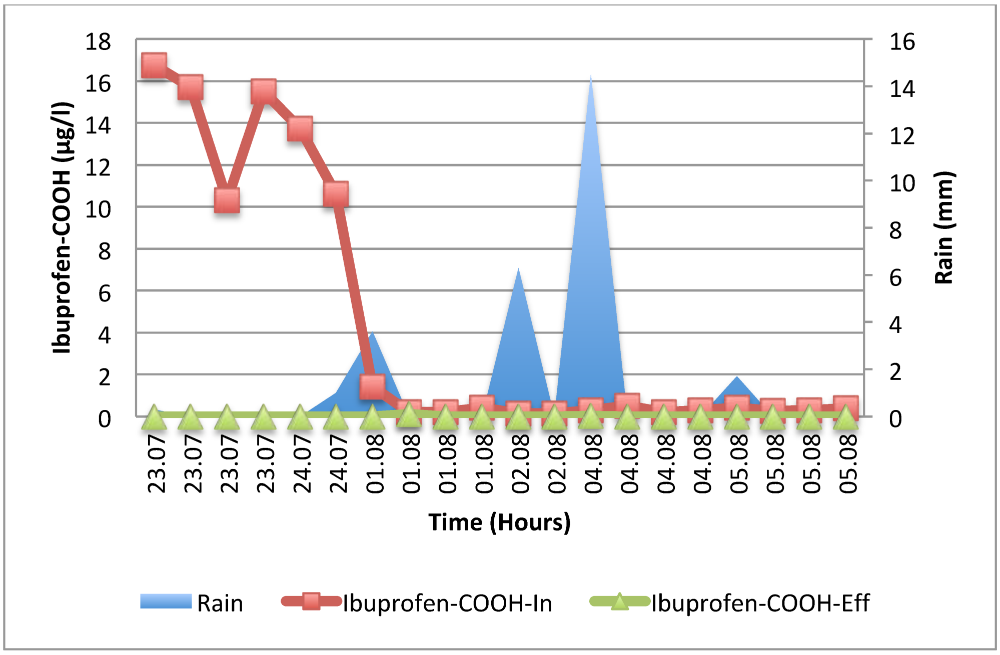


Figure 42: Hourly influent and effluent concentration of Ibuprofen-COOH

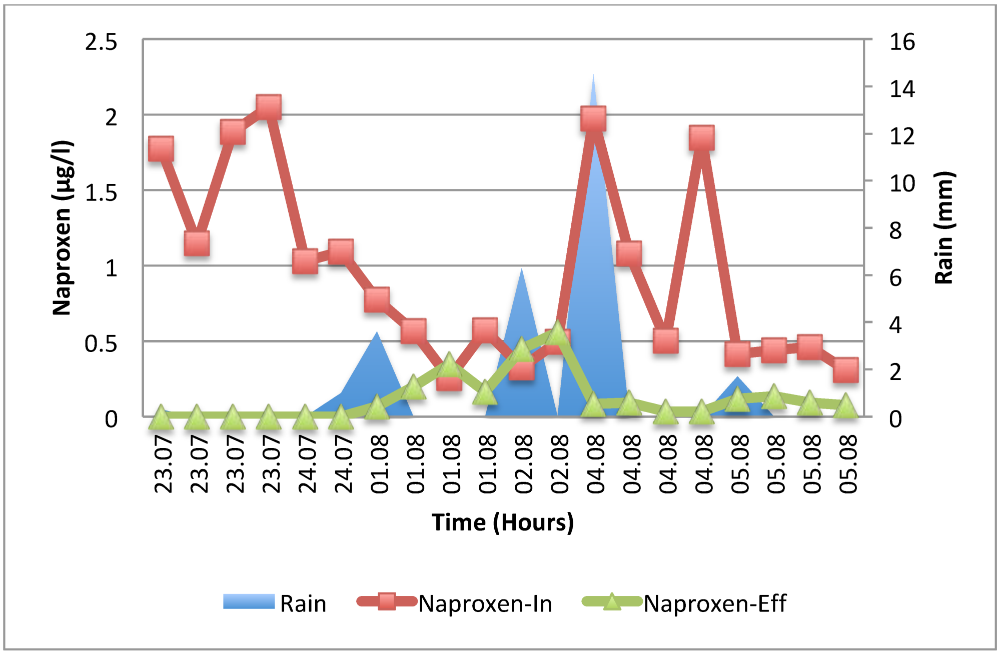


Figure 43: Hourly influent and effluent concentration of Naproxen

3.3.3. Influent and Effluent of Industrial Chemicals

1H-Benzotriazole and Tolytriazoles

Diurnal and hourly influent and effluent concentration of 1H-Benzotriazole and Tolytriazoles are given in the Figures 44-46. As shown in the Figure 44, 1H-Benzotriazole seems to have an effect of dilution during wet weather condition, which implies its solubility in water; its effluent is almost constant, however not necessarily has a very low value of concentration. Tolytriazoles is following the same trend as 1H-Benzotriazole, since both have a similar application as being used in the dishwasher tablets.

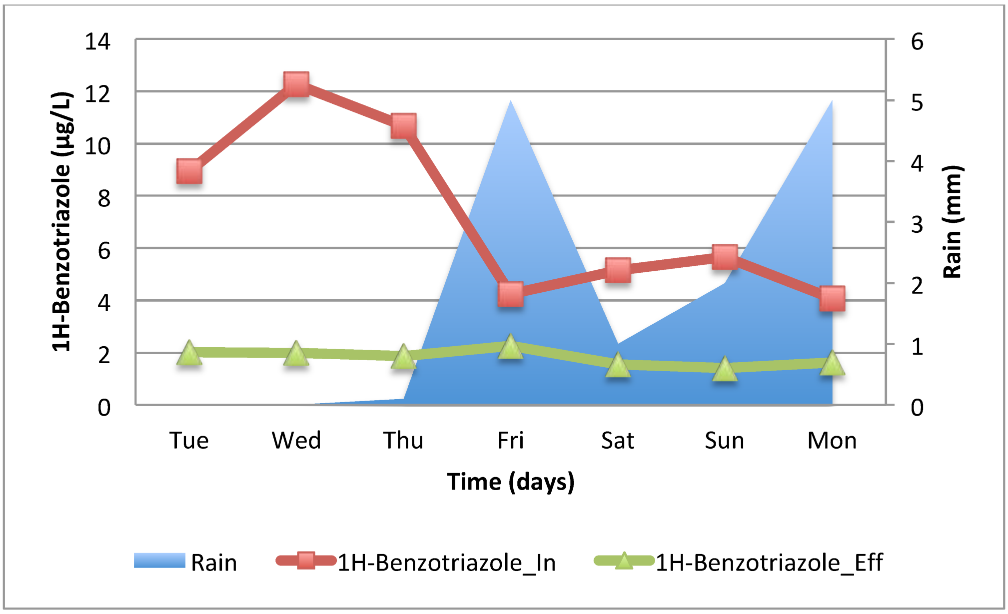


Figure 44: Diurnal influent and effluent concentration of 1H-Benzotriazole

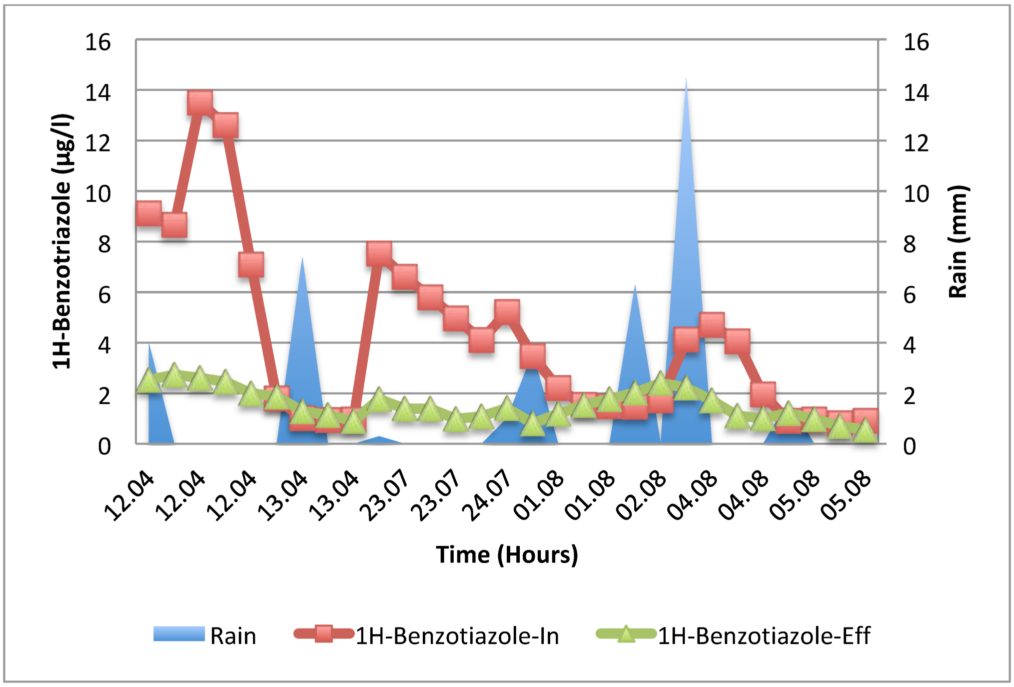


Figure 45: Hourly influent and effluent concentration of 1H-Benzotriazole

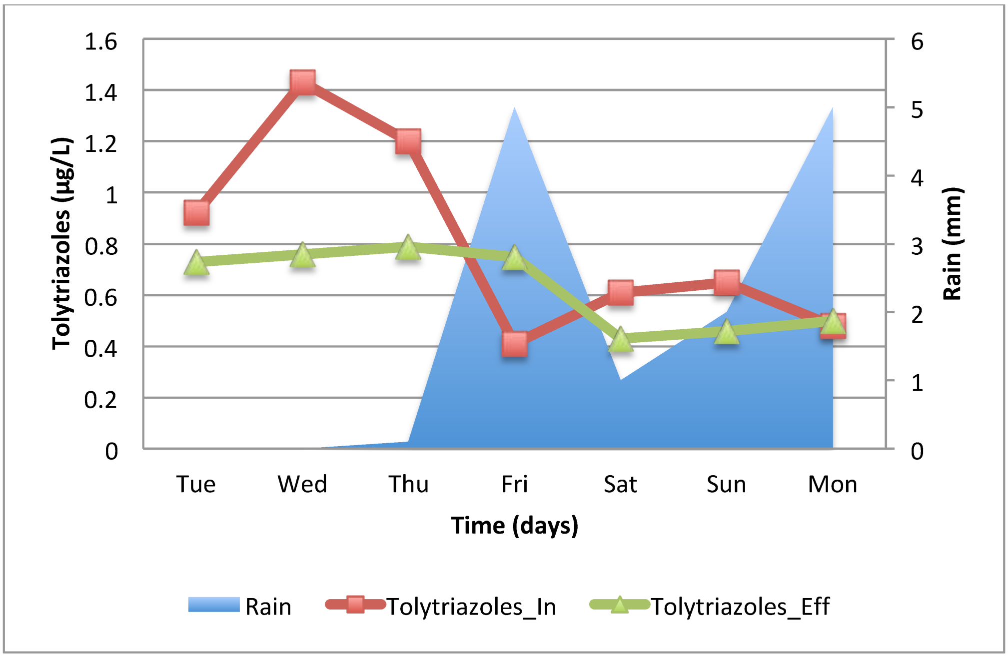


Figure 46: Diurnal influent and effluent concentration of Tolytriazoles

TCEP and TCPP

Figures 47-50 contain the TCEP and TCPP, diurnal and hourly influent and effluent of WWTP. As can be observed, rain events do not have an obvious effect on the influent concentration of the TCEP, implying an independence of its diffuse source from the runoff. However TCPP concentrations shows a contrast to TCEP by decrease of its concentrations after the rain event.

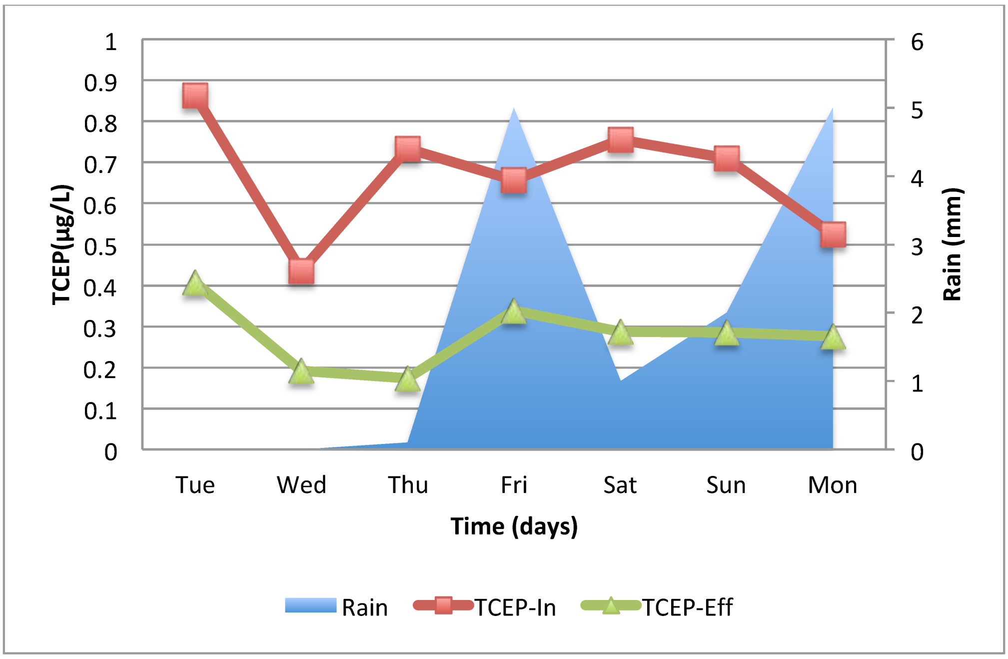


Figure 47: Diurnal influent and effluent concentration of TCEP

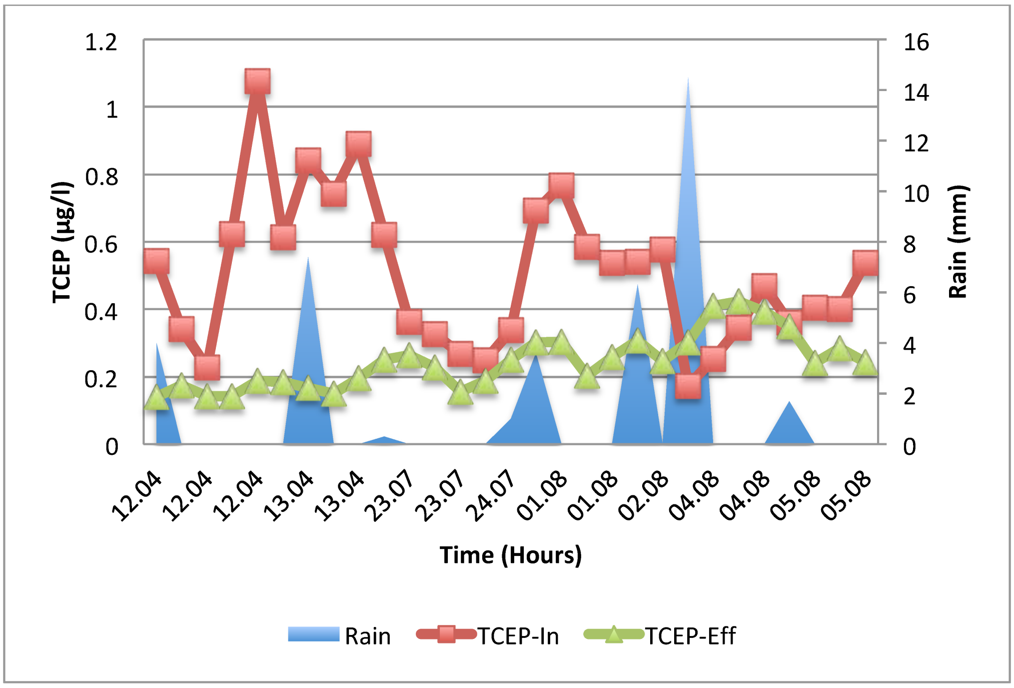


Figure 48: Hourly influent and effluent concentration of TCEP

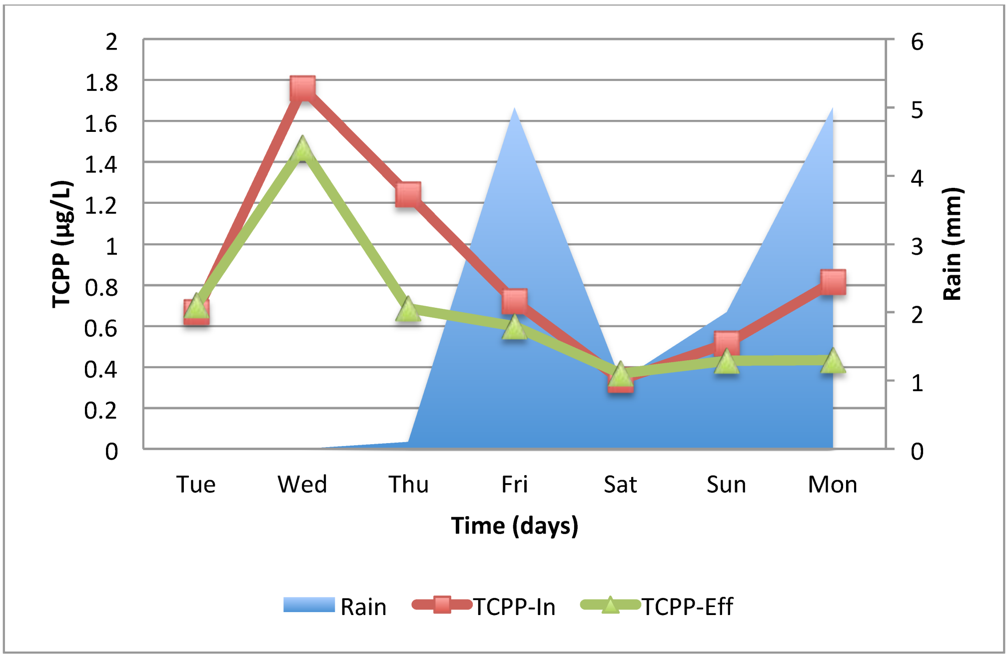


Figure 49: Diurnal influent and effluent concentration of TCPP

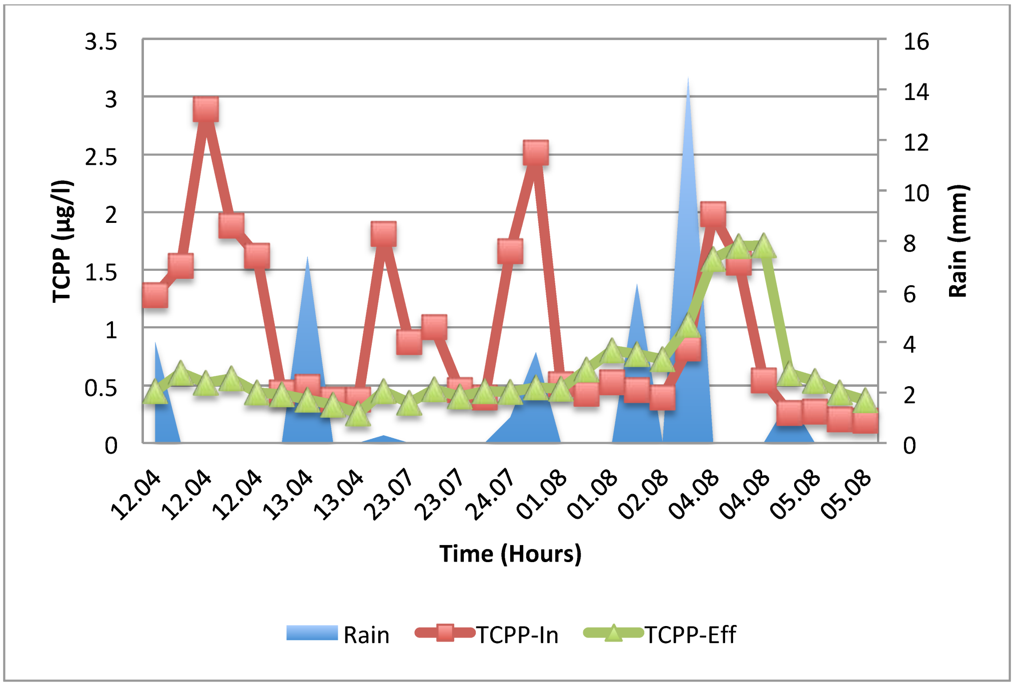


Figure 50: Hourly influent and effluent concentration of TCPP

TDCPP and Bisphenol A

TDCPP is an industrial chemical and it is anticipated that rain has no or minor influence on its concentration. Contrastingly, TDCPP concentration is increasing with rain, behaving in the opposite way than expected as illustrated in the Figure 51. Figures 52 and 53 represent the hourly influent and effluent of TDCPP and Bisphenol A. Even though the influent concentration of the

Bisphenol A rises to very high values, the effluent seems to keep a satisfactory elimination.

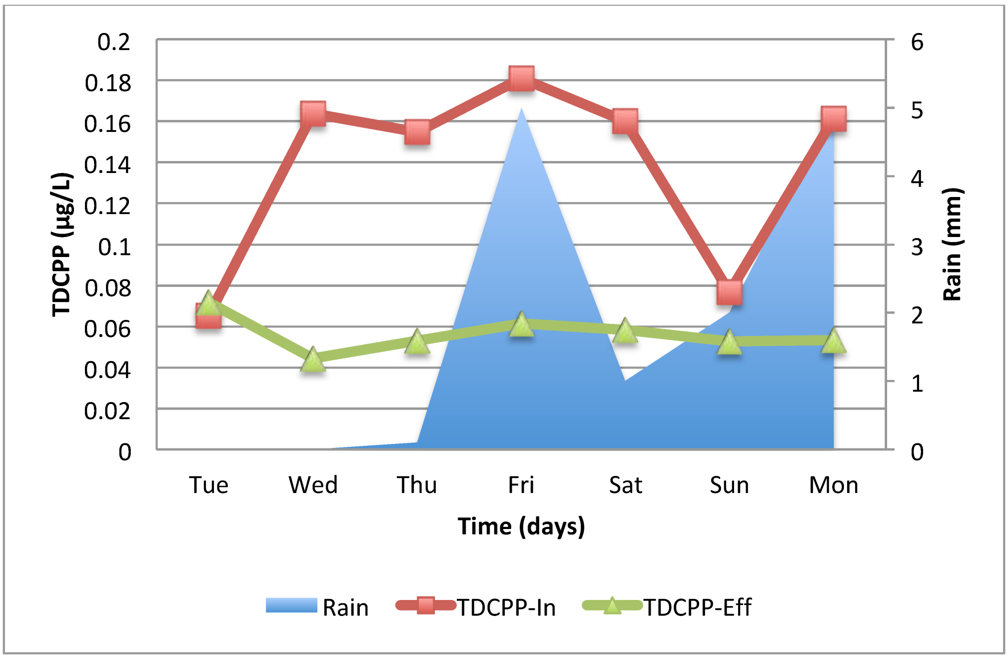


Figure 51: Diurnal influent and effluent concentration of TDCPP

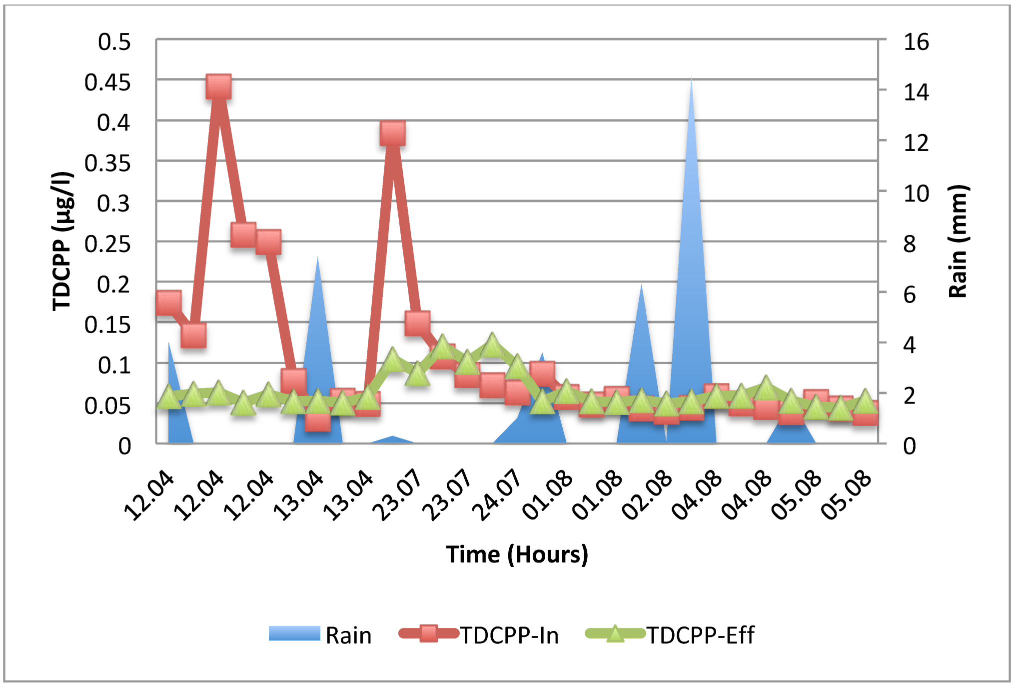


Figure 52: Hourly influent and effluent concentration of TDCPP

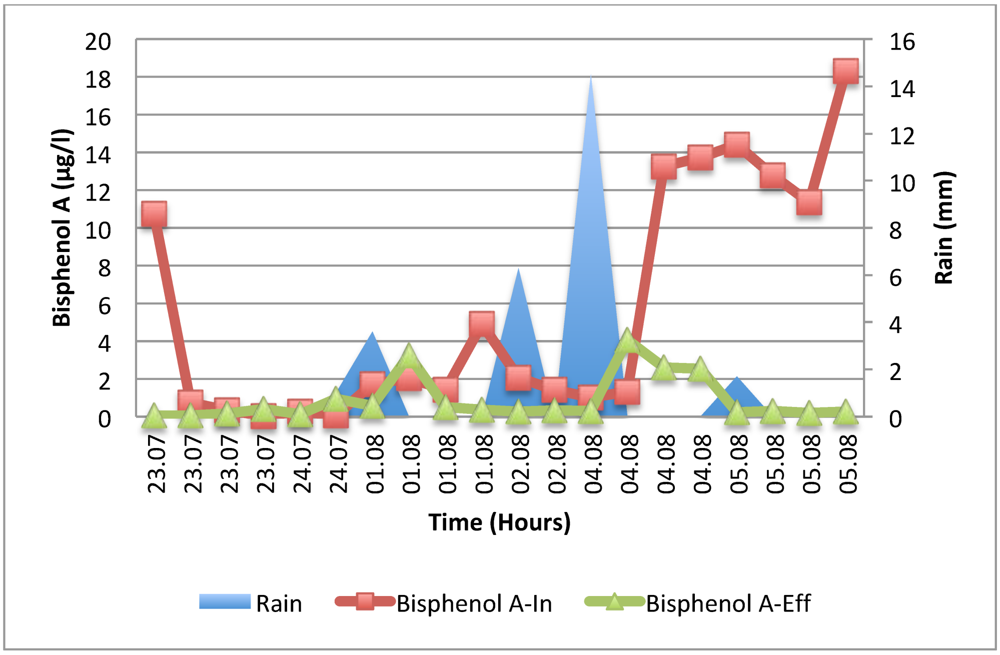


Figure 53: Hourly influent and effluent concentration of Bisphenol A

3.3.4. Influent and Effluent of Personal Care Products

Overall, most studies have been focusing on the parent compounds and little attention has been given to the produced intermediates. It is noteworthy that biological or chemical reactions occurring in the secondary clarifiers might lead to the accumulation of metabolites/by-products (Oulton et al., 2010).

HHCB and its degradation product HHCB-Lactone, besides AHTN hourly influent and effluent are projected in the Figures 54-56. As can be noticed HHCB and AHTN follow a resembling trend, but uniquely the degradation product of HHCB behaves alternatively, especially in the effluent, where it shows an increase over its respective influent. Furthermore the Figure 57 represents the hourly influent and effluent of Triclosan. The concentration has a relative dependency on the rain events, however the effluent concentration seems to fall in to a reasonable range.

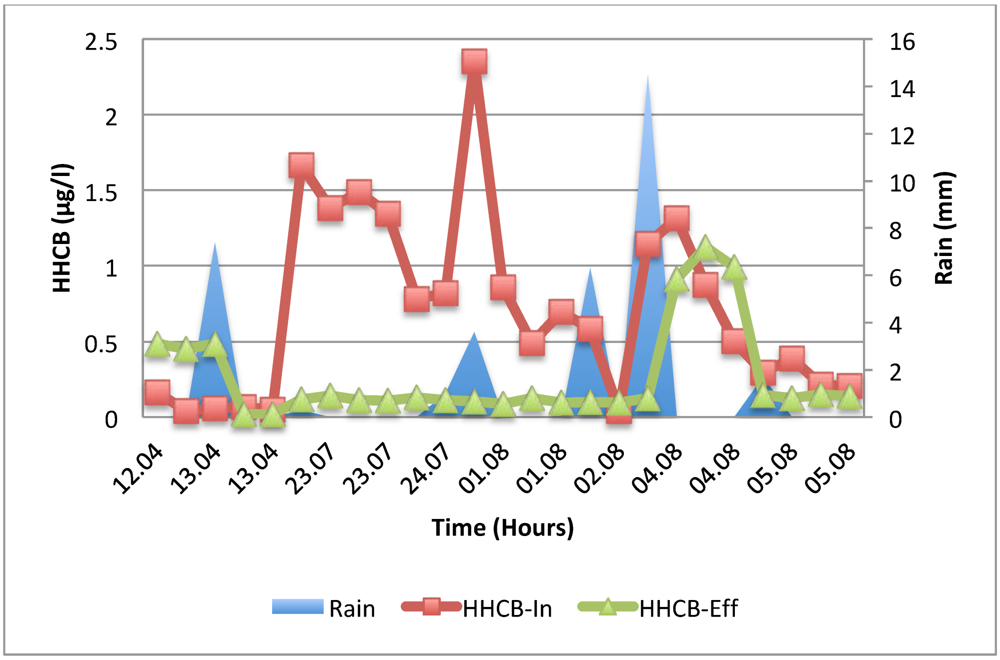


Figure 54: Hourly influent and effluent concentration of HHCB

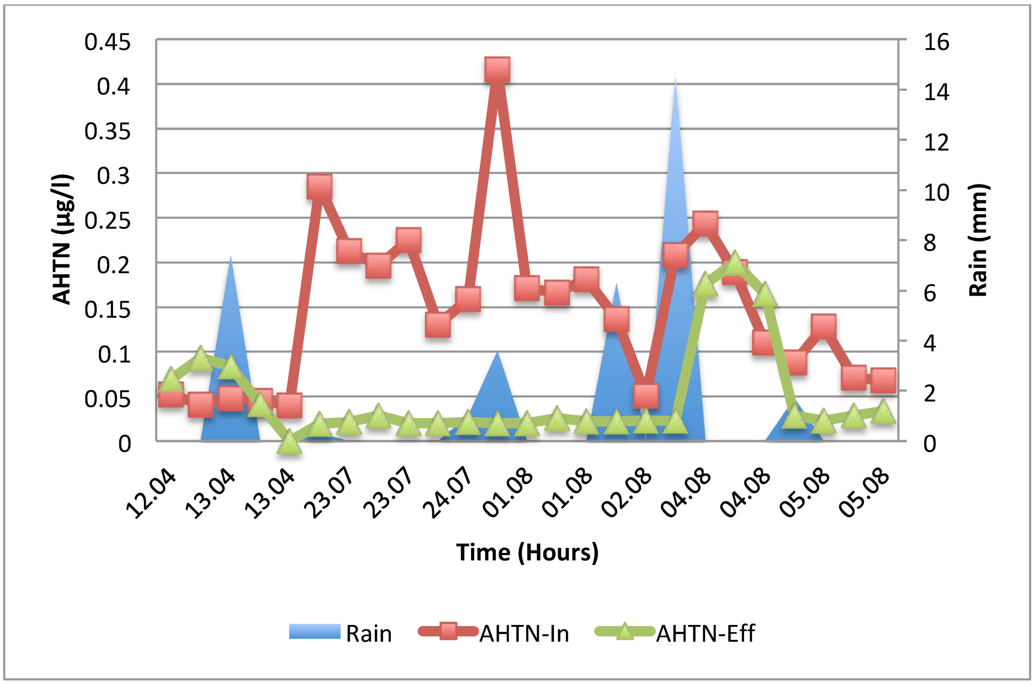


Figure 55: Hourly influent and effluent concentration of AHTN

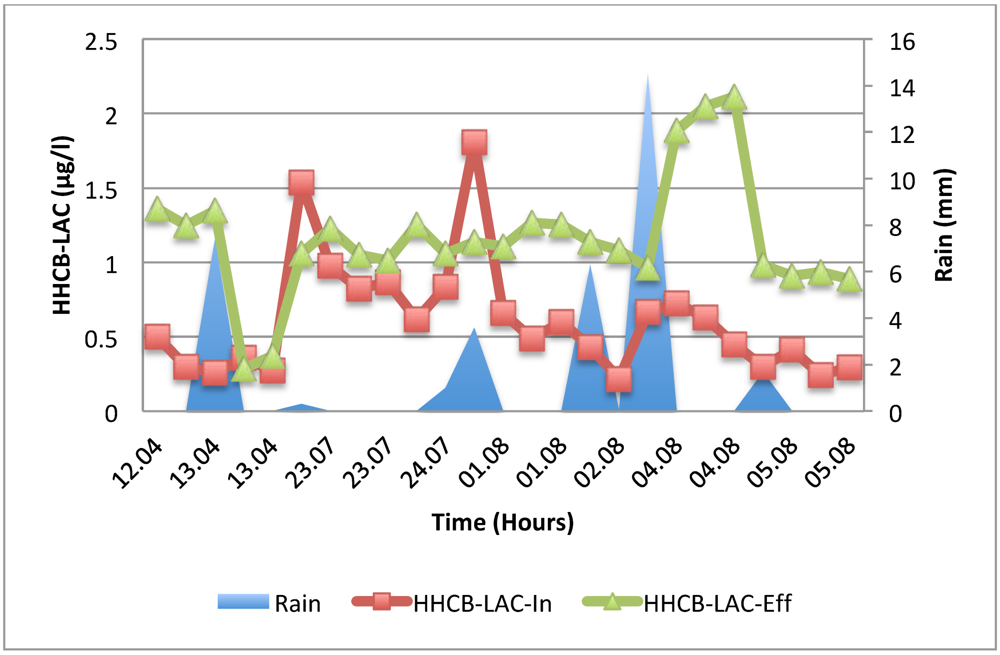


Figure 56: Hourly influent and effluent concentration of HHCB-Lactone

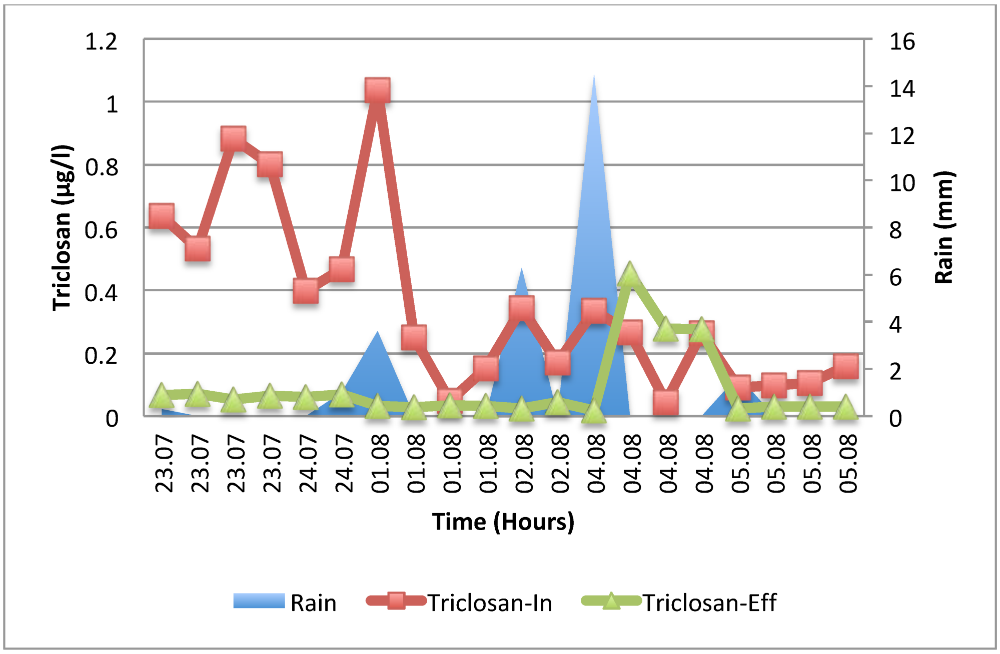


Figure 57: Hourly influent and effluent concentration of Triclosan

3.3.5. Influent and Effluent of Pesticides

Figure 58 is the hourly influent and effluent of the Mecoprop concentration. It seems that the influent and effluent concentration both are drastically low in comparison to the average values over Europe (Loos et al., 2013), which implies either minor usage of pesticides on the farmlands or their runoff is not contributing to the wastewater.

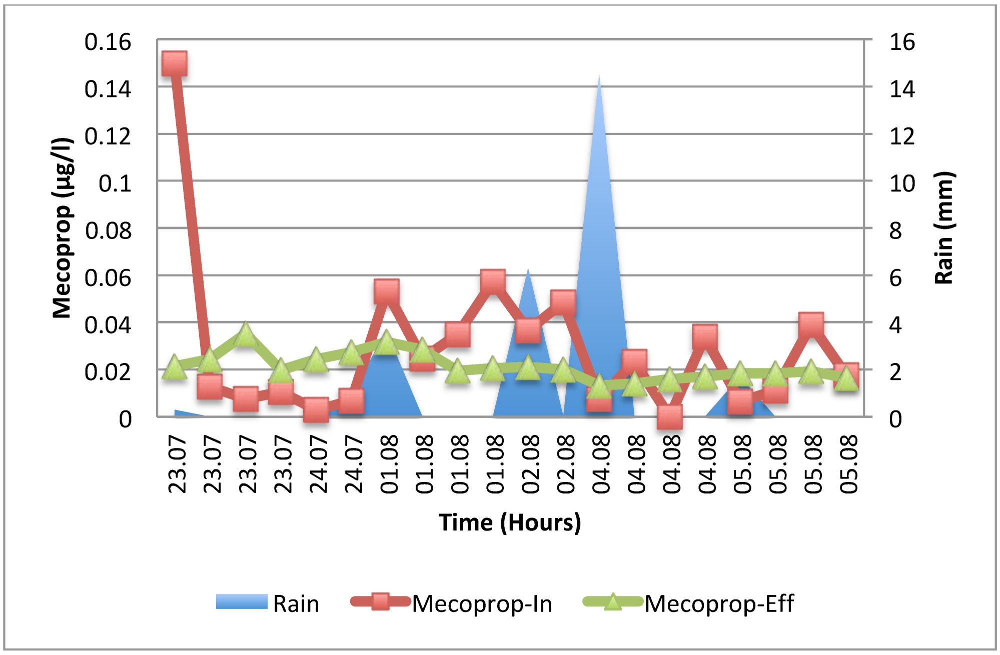


Figure 58: Hourly influent and effluent concentration of Mecoprop

3.4. Correlations

In this section the correlation of the pharmaceuticals with ammonium is investigated, where a close correlation of two different substances with ammonium, conveys a close correlation among them as well. Furthermore the correlations of SAC and pharmaceutical and turbidity with Triclosan have been accomplished. Since the facilities and process for assessing micropollutants are time consuming and expensive, revealing a close correlation and a high regression value among them and conventional parameters, shall ease and comfort the act of prognostication of the micropollutants.

3.4.1. Ammonium and Pharmaceuticals

Metoprolol is a β-Blocker and is excreted from the human body; urine is its diffusing source, which is the same source for ammonium, leading to a very good correlation among each other, Figure 59. Gabapentin follows a similar pattern as Metoprolol and has a very close correlation with the ammonium as shown in Figure 60.

Carbamazepine as can be seen in the Figure 61 does not yield a comprehensive correlation with the ammonium, however the trend still exists and a cloudy correlation with ammonium can be observed. Both Metoprolol and Carbamazepine are from the pharmaceuticals, but comparatively their correlation with ammonium is not similar; this phenomenon can be construed in accordance to the fact that the consumption of pharmaceuticals such as

Metoprolol or Gabapentin are far more frequent than pharmaceuticals like Carbamazepine. Around 10% of the population in Germany ingests Metoprolol in comparison to the Carbamazepine, which only 1 out of 10,000 people consume (Kuch, 2016). Figure 62 contains the correlation of ammonium and Tolytriazoles, which belongs to the industrial chemicals and its poor correlation proves the lack of linkage between industrial chemicals and ammonium.

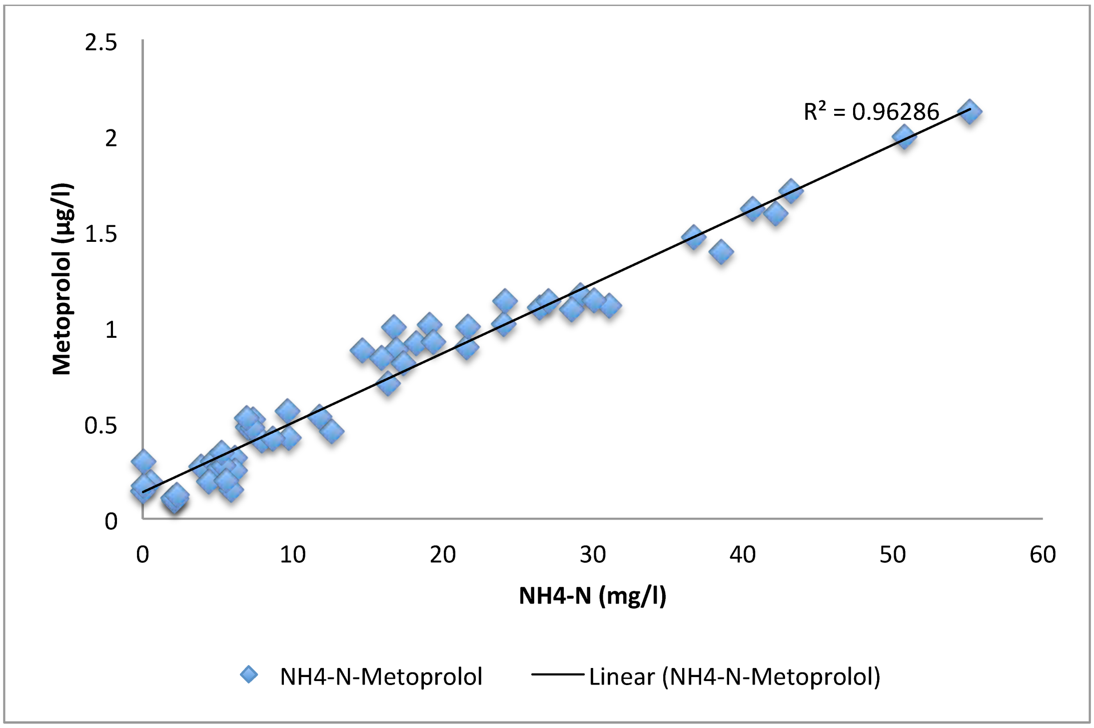


Figure 59: Correlation between ammonium and Metoprolol

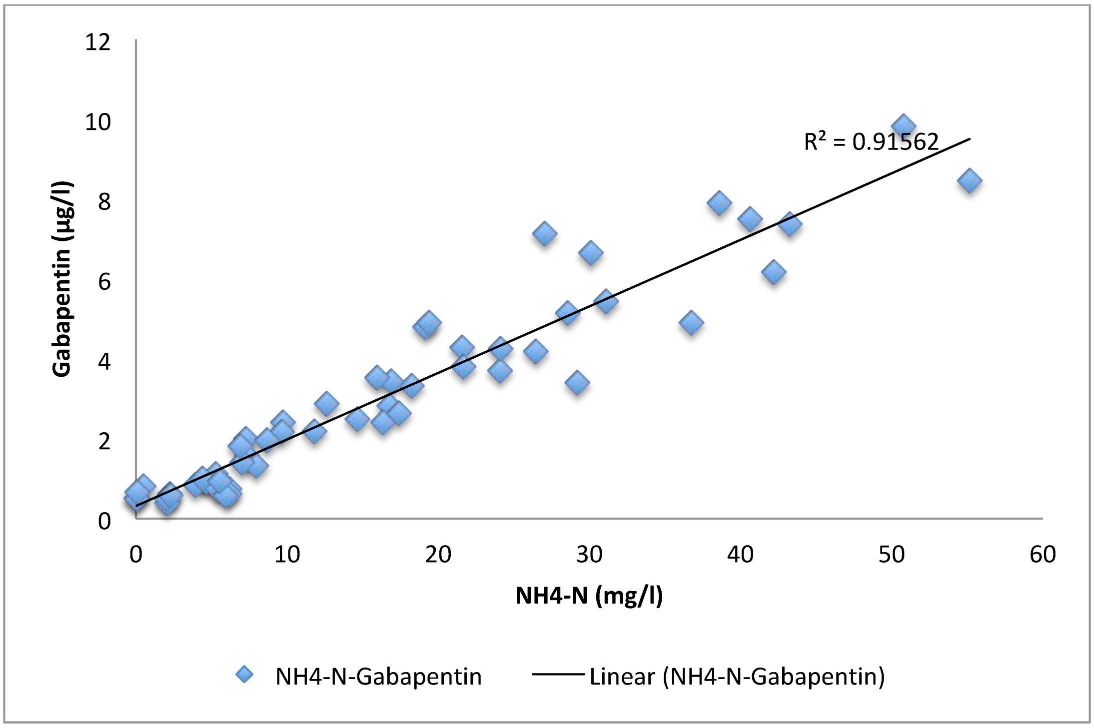


Figure 60: Correlation between ammonium and Gabapentin

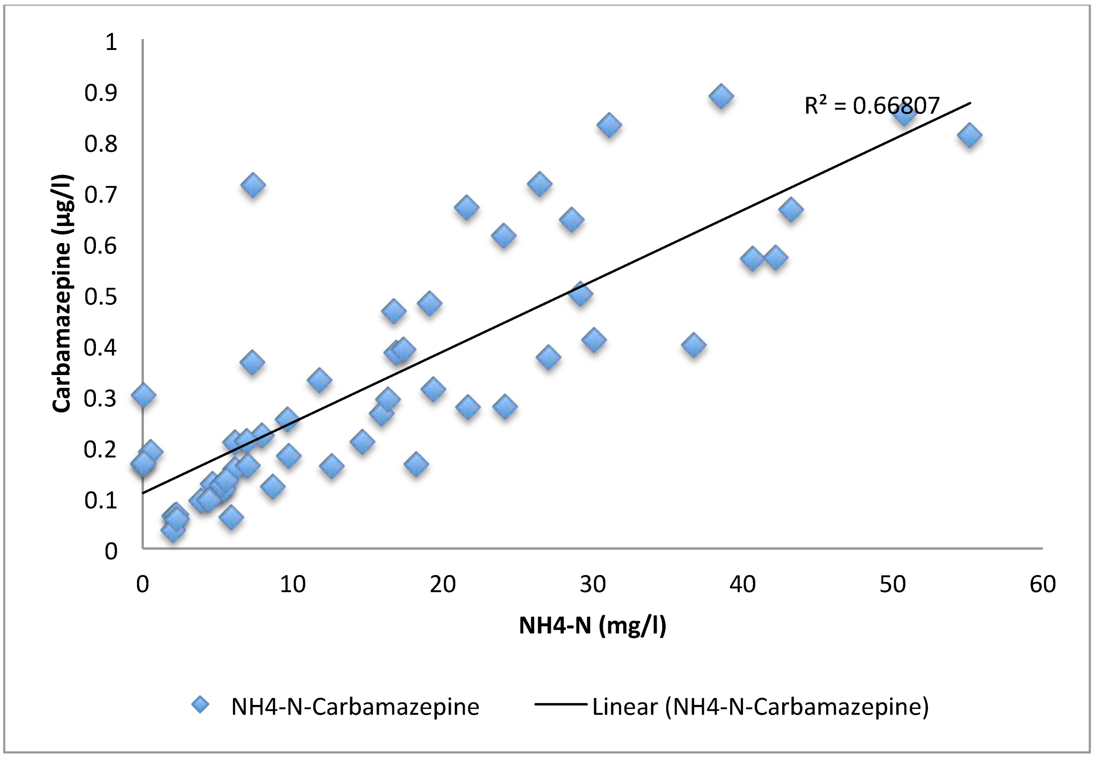


Figure 61: Correlation between ammonium and Carbamazepine

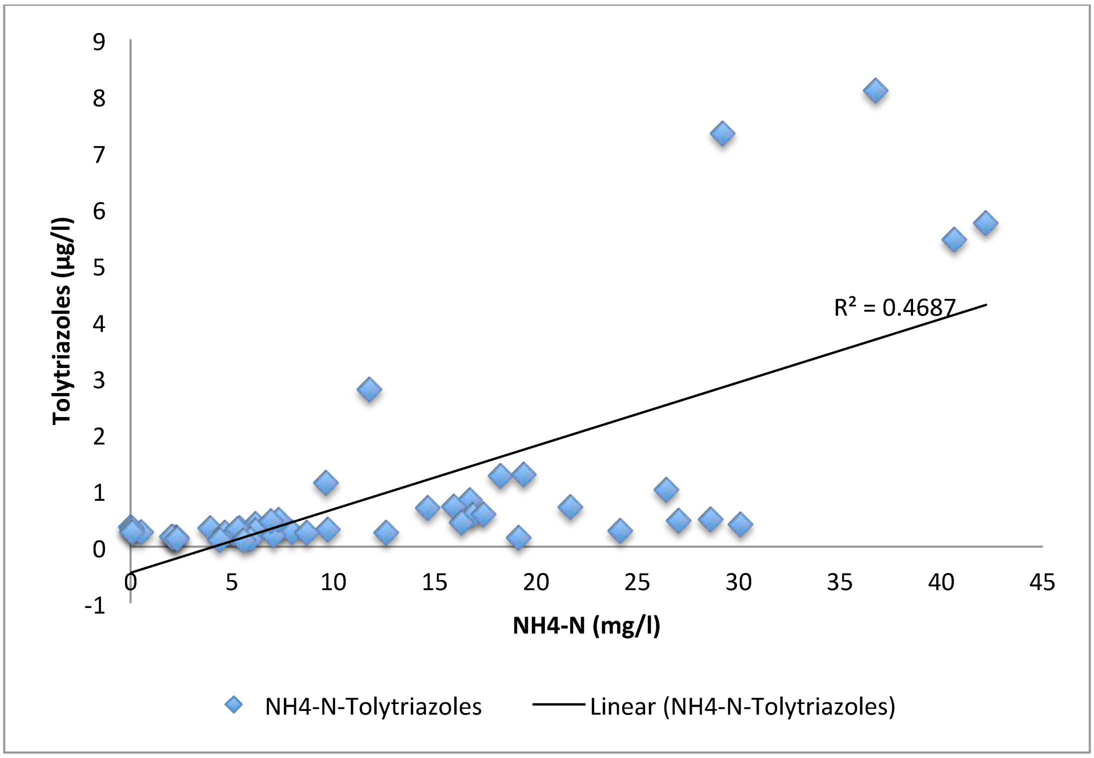


Figure 62: Correlation between ammonium and Tolytriazoles

3.4.2. SAC and Pharmaceuticals

Figure 63 is the correlation of the SAC and Metoprolol. SAC is representative of the yellowish color in the WWTP, matching its source with ammonium to be the urine, and equally important, urine is the path of pharmaceuticals excreted from human body towards the WWTP, hence a satisfactory correlation between SAC and Metoprolol has been obtained. Similar behavior for Gabapentin is captured, and is presented in this regard in the Appendix D.

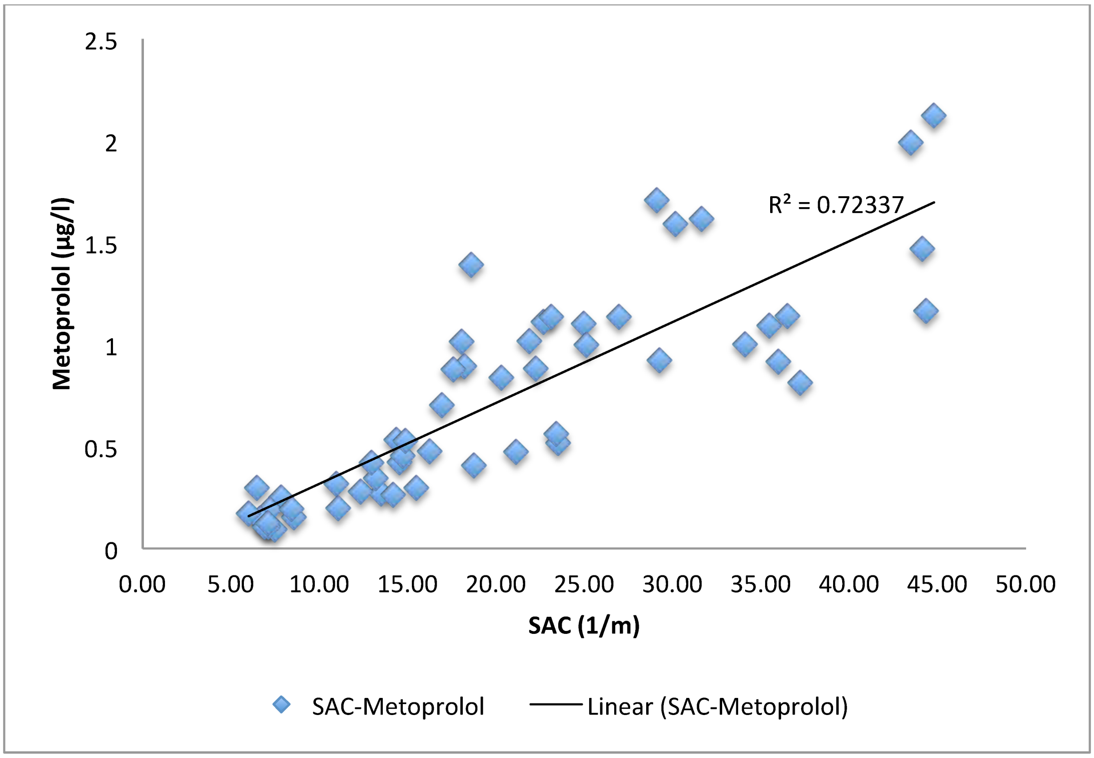


Figure 63: Correlation between SAC and Metoprolol

3.4.3. Turbidity and Triclosan

As have been discussed in the section 3.2.1, the fluctuations of the turbidity and Triclosan follows a similar pattern, this matter can be mistaken by the very direct relation of the parameters. In this regard, correlation of the variables will indicate whether the judgment is superficial or reliable.

Figure 64 exhibits a moderate correlation, however, the study argues the values which have been obtained for the turbidity in a higher range 50-200 NTU, since a second validation of the measurements may lead up to a 25% difference with the first taken values. Therefore, in the interest of accomplishing a further investigation, six values from the mentioned range have been altered with below 25% of alteration; Figure 65 shows this hypothesis and an adequate correlation with the Triclosan, which have been attained. This is essential to note that receiving Triclosan to the WWTP carried out by suspended solid is necessary but not sufficient, meaning there might be suspended solids, which do not carry any Triclosan.

With the purpose of focusing on the correlation of turbidity and Triclosan, this study suggests at least two sets of measurement for turbidity for the influent of the WWTP, so that an average of the multiple values could be obtained from the measurements, leading to more reliable values.

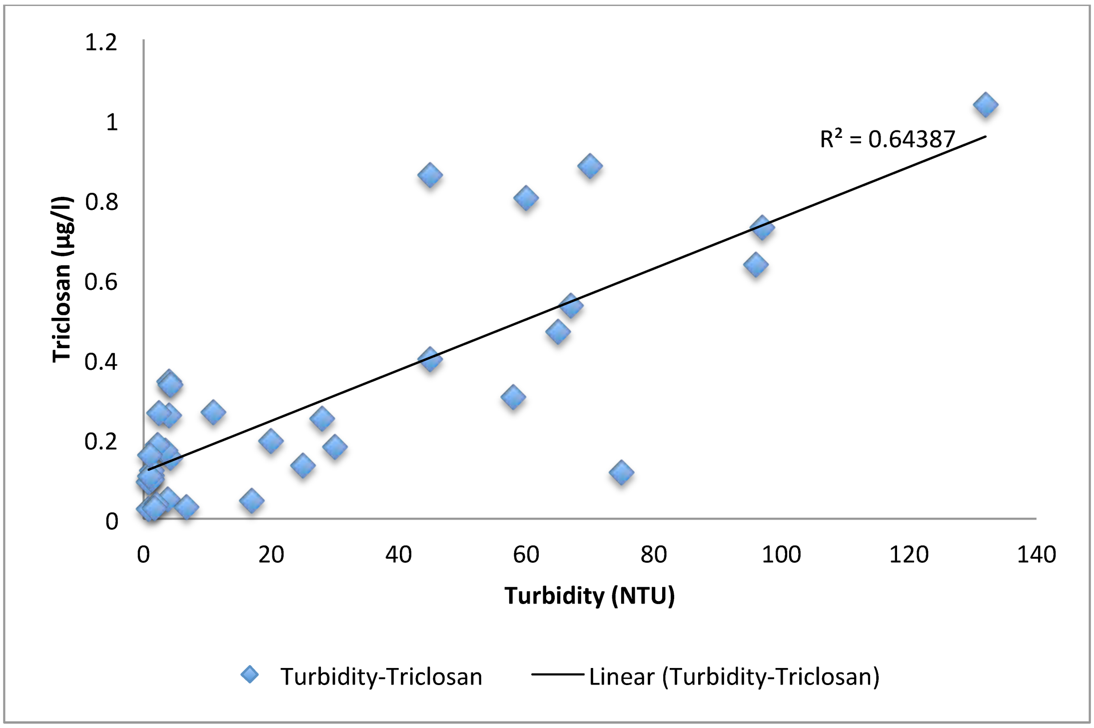


Figure 64: Correlation between turbidity and Triclosan

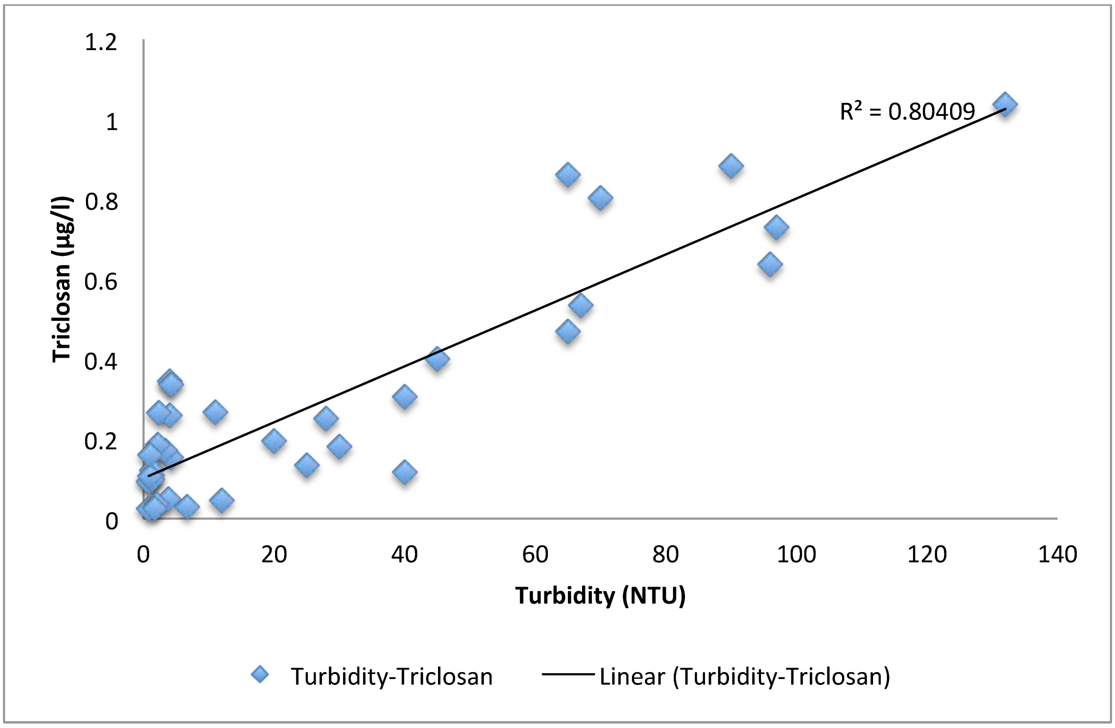


Figure 65: Revision of the correlation between turbidity and Triclosan

3.5. Average Diurnal Loads and Concentrations

In this section average concentrations for the influent as well as effluent has been demonstrated, a comparison of the average effluent concentration for dry weather for 3 WWTPs in Baden-Württemberg along the stream called Sulzbach (Azizi, 2015) as well as the average for 90 WWTPs around Europe (Loos et al., 2013) have been presented. Furthermore, load variations and average values along with an estimation of diurnal load per capita have been reported and compared with the average of 3 WWTPs of Sulzbach catchment area, leading a comprehensive and decent load statistics per capita for the pharmaceuticals together with other micropollutants.

3.5.1. Average Concentrations

Average concentration of the influent and effluent of micropollutants under dry weather and wet weather have been exhibited in the tables 12 and 13. Most of the substances have relatively higher values for dry weather rather than wet weather, except TCEP and Carbamazepine, which could be explained by their lack of solubility in water.

Figures 66-68 are the average effluent concentrations and comparison with 3 WWTPs along Sulzbach and 90 WWTPs along Europe. Bisphenol A and Carbamazepine have very high values for the effluent compared to the other WWTPs, contrarily the concentration of Mecoprop and Ibuprofen is inferior in comparison with the other European average values, implying a very low influent from the diffuse source and a proper degradation along the treatment process respectively.

Table 12: Average of the influent and effluent concentration of pharmaceuticals under dry and wet weather conditions

Micropollutant	**Ave-Influent (μg/l)**		**Ave-Effluent (μg/l)**	
	Dry Weather	Wet Weather	Dry Weather	Wet Weather
Metoprolol	1.94	1.10	1.42	0.90
Sulfamethoxazole	0.54	0.26	0.24	0.15
Gabapentin	8.56	5.33	4.09	3.28
Carbamazepine	0.78	0.75	1.16	0.89
Lidocaine	0.21	0.10	0.24	0.16
Ibuprofen	28.87	16.97	0.04	0.08
Ibu-OH	68.91	40.19	0.03	0.11
Ibu-COOH	98.68	55.84	0.28	0.72

Table 13: Average of the influent and effluent concentration of other micropollutants under dry and wet weather conditions

Micropollutant	Ave-Influent (μg/l)		Ave-Effluent (μg/l)	
	Dry Weather	Wet Weather	Dry Weather	Wet Weather
1H-Benzotriazole	10.63	4.78	1.96	1.71
Tolytriazoles	1.18	0.54	0.76	0.54
HHCB	0.19	0.00	0.11	0.12
AHTN	-	-	0.12	0.13
HHCB-Lac	-	-	2.02	1.44
TCEP	0.68	066	0.26	0.30
TCPP	1.22	0.60	0.95	0.46
TDCPP	0.13	0.14	0.06	0.06
Mecoprop	0.00	0.00	0.01	0.02
Triclosan	0.15	0.12	0.06	0.20
Bisphenol A	-	-	0.31	-

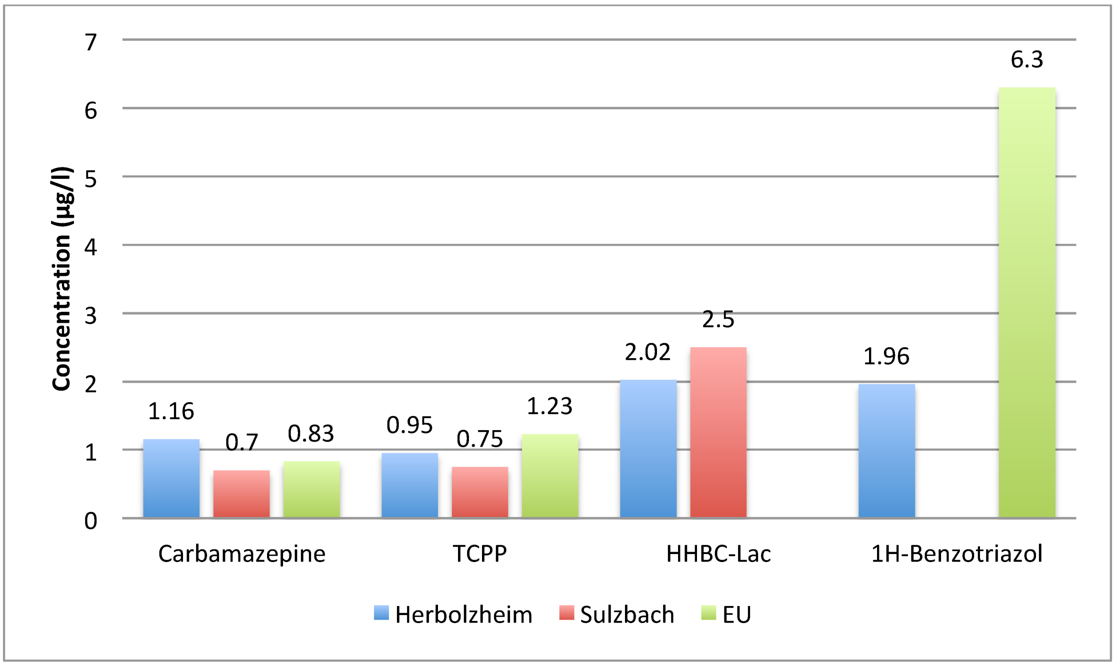


Figure 66: Average effluent concentrations and comparison under dry weather conditions

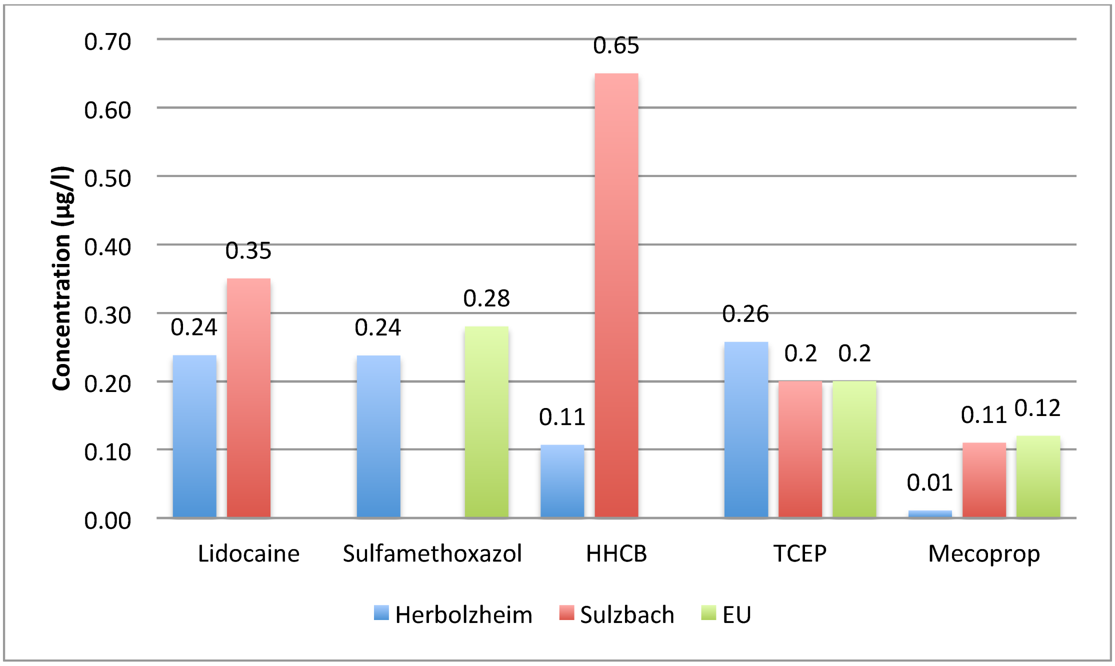


Figure 67: Average effluent concentrations and comparison under dry weather conditions

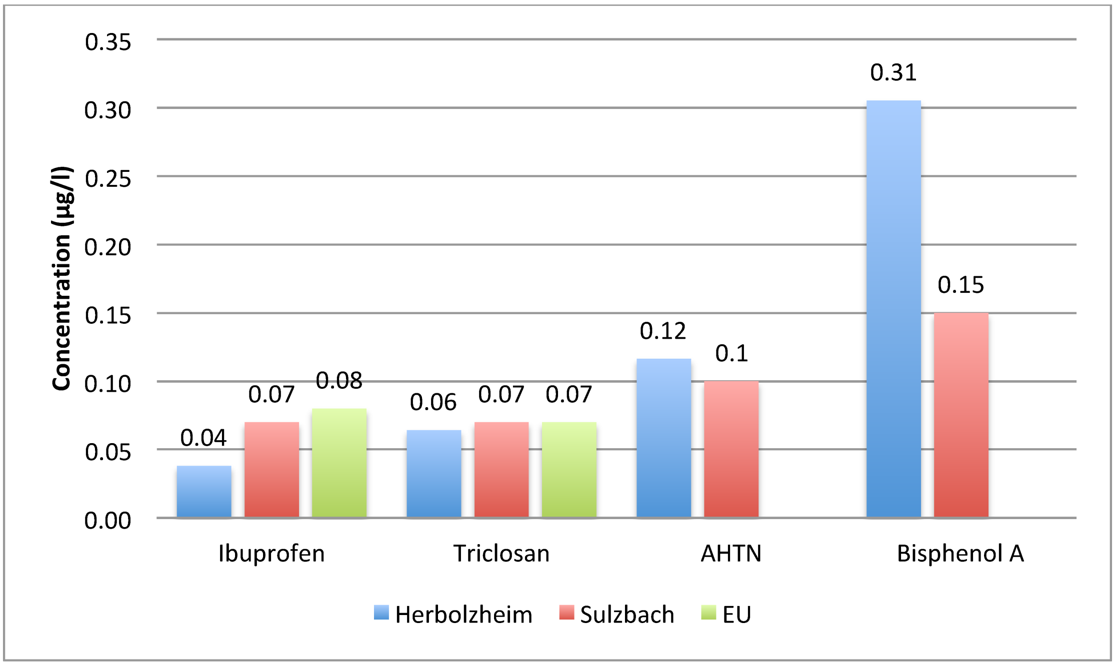


Figure 68: Average effluent concentrations and comparison under dry weather conditions

3.5.2. Load Variations

Tables 14 and 15 are containing the diurnal minimum and maximum values for loads of pharmaceuticals and rest of the micropollutants respectively. Increase of the loads of Carbamazepine and Lidocaine in effluents, compared to influent is visible, such an increase also happened for TCPP.

Figures 69-72 are the load variations of the Gabapentin, Carbamazepine, Lidocaine and TCEP. Gabapentin seems to have almost a constant introduction of load to in the influent. Metoprolol, Carbamazepine and Lidocaine have very similar behavior; related graphs are available in Appendix E. Additionally, Lidocaine is hypothesized to experience a decrease in the amount of its load during the weekend, which might be explained by the close dentist clinics as the major diffusers of Lidocaine.

Despite of the pharmaceuticals, TCEP and other industrial chemicals tend to have a peak in their influent load by the rain events, as well as effluents. TCPP and TDCPP graphs are available in the Appendix E.

Table 14: Diurnal minimum and maximum loads of pharmaceuticals

Micropollutant	Influent (g)		Effluent (g)	
	Min	Max	Min	Max
Metoprolol	3.53	5.11	1.82	6.16
Sulfamethoxazole	0.64	1.29	0.30	0.94
Gabapentin	15.51	20.06	6.60	18.99
Carbamazepine	1.40	3.09	2.02	5.58
Lidocaine	0.23	0.57	0.32	1.11
Ibuprofen	31.35	86.37	0.06	0.42
Ibu-OH	121.35	201.93	0.05	0.62
Ibu-COOH	180.35	280.59	0.53	2.91

Table 15: Diurnal minimum and maximum loads of other micropollutants

Micropollutant	Influent (g)		Effluent (g)	
	Min	Max	Min	Max
1H-Benzotriazole	13.08	23.67	336	11.36
Tolytriazoles	1.55	2.76	1.09	3.77
HHCB	0.41	041	0.19	0.61
AHTN	-	-	0.20	0.63
HHCB-Lac	-	-	2.46	7.61
TCEP	0.84	3.30	0.31	1.70
TCPP	0.86	3.69	0.93	3.02
TDCPP	0.14	0.91	0.09	0.31
Mecoprop	0.00	-	0.02	0.10
Triclosan	0.20	1.12	0.06	1.09
Bisphenol A	-	-	0.53	0.61

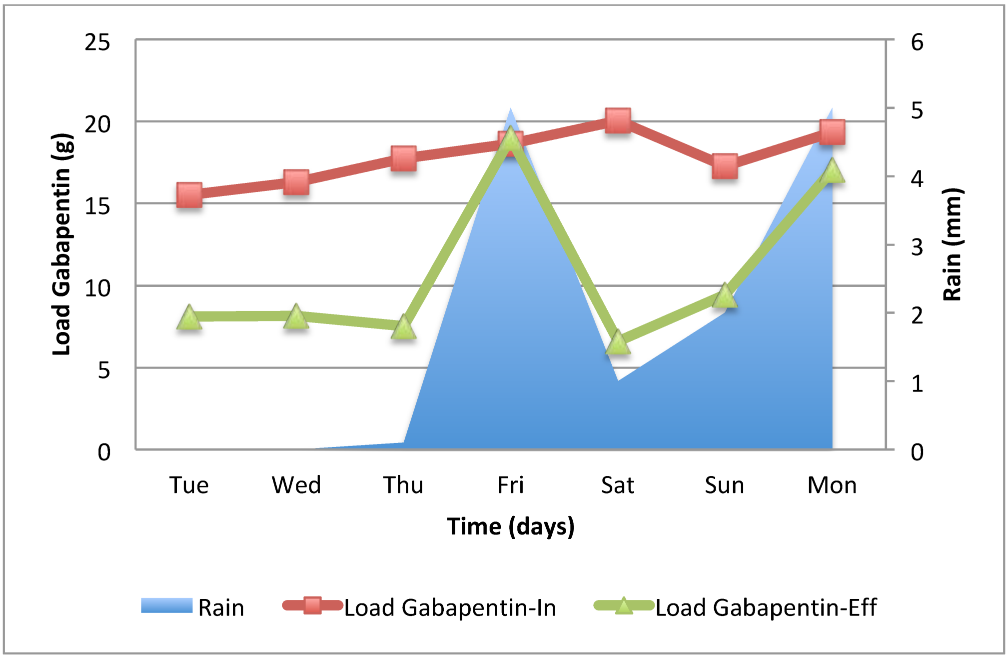


Figure 69: Diurnal influent and effluent load of the Gabapentin

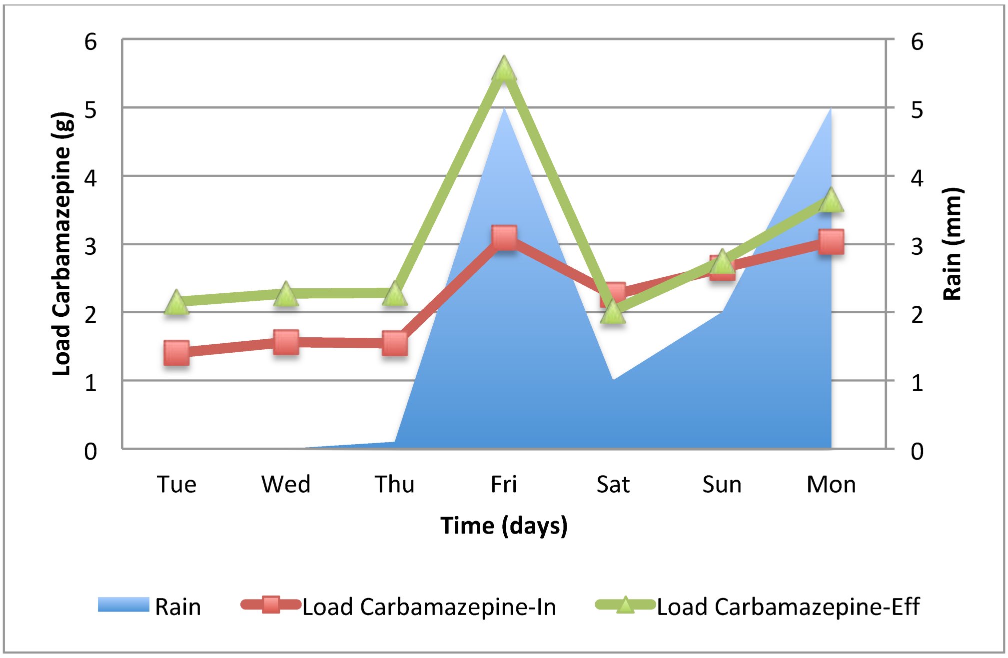


Figure 70: Diurnal influent and effluent load of the Carbamazepine

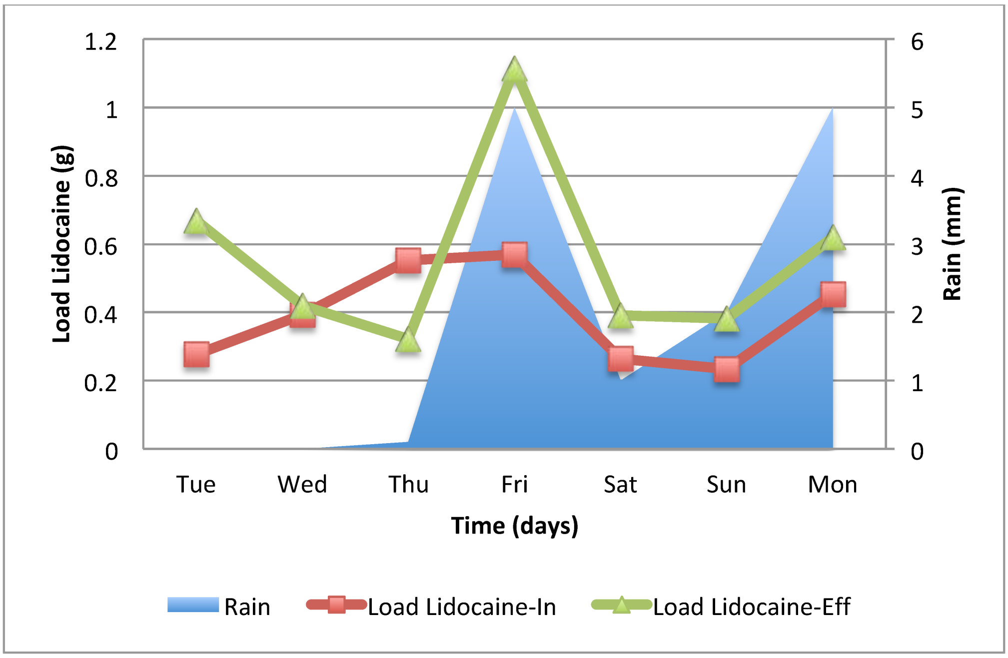


Figure 71: Diurnal influent and effluent load of the Lidocaine

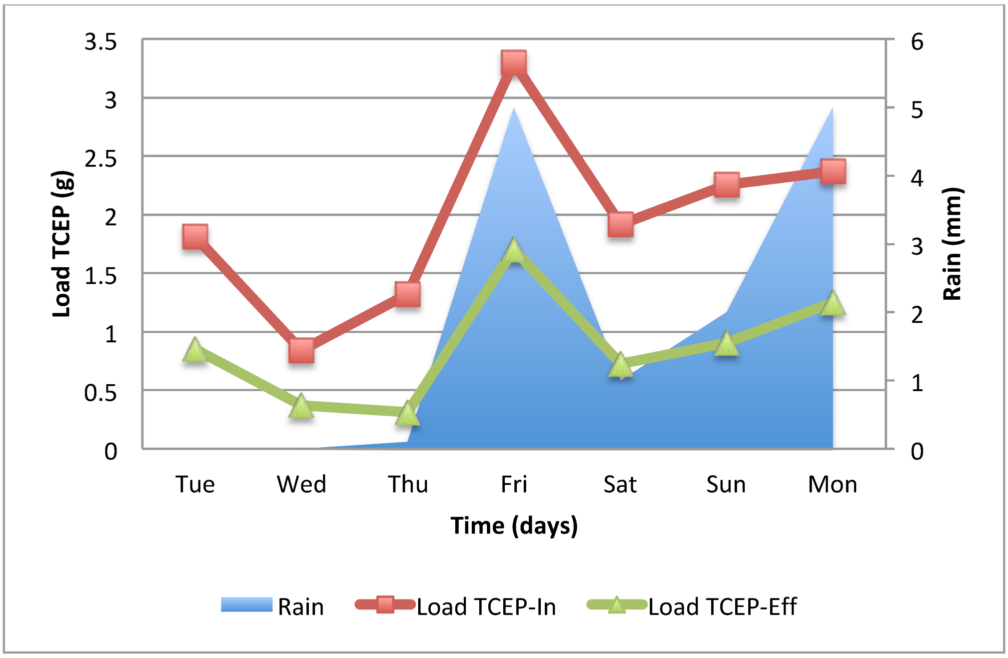


Figure 72: Diurnal influent and effluent load of the TCEP

3.5.3. Diurnal Average Load and Estimation Per Capita

Tables 16 and 17 are representing the average value for loads of influent and effluent for pharmaceuticals and the rest of the micropollutants respectively. These numbers are base for the calculation of estimation of the load per capita. The load of the pharmaceuticals, industrial chemicals, personal care products and pesticides produced per population equivalent have been carried out using the following formula:

L = (C*Q)/P.E

L: Diurnal average load (mg/C.d)

C: Diurnal concentration of the substance (μg/l)

Q: Discharge of the respective influent (m^3/d)

P.E: Population equivalent of the WWTP

These values are presented for dry and wet weather and have been compared to the average values from 3 WWTPs of the Sulzbach catchment, producing a rough estimation of loads in the influent of the WWTPs in the area of southeastern Germany, Figures 73 and 74. Apart from the mutual micropollutants from this study and (Azizi, 2015), the rest of the available estimation of loads have been illustrated in the Figures 75 and 76.

Table 16: Average diurnal loads of influent and effluent of pharmaceuticals

Micropollutant	Ave-Influent (g)		Ave-Effluent (g)	
	Dry Weather	Wet Weather	Dry Weather	Wet Weather
Metoprolol	3.76	3.97	2.76	2.85
Sulfamethoxazole	1.05	1.08	0.46	0.81
Gabapentin	16.52	17.40	7.93	12.35
Carbamazepine	1.50	2.27	2.23	2.83
Lidocaine	0.41	0.42	0.47	0.67
Ibuprofen	56.39	47.24	0.07	0.88
Ibu-OH	134.79	130.38	0.06	1.01
Ibu-COOH	192.48	149.47	0.54	1.25
Naproxen	-	6.78	-	1.13

Table 17: Average diurnal loads of influent and effluent of other micropollutants

Micropollutant	Ave-Influent (g)		Ave-Effluent (g)	
	Dry Weather	Wet Weather	Dry Weather	Wet Weather
1H-Benzotriazole	20.57	18.75	3.82	8.32
Tolytriazoles	2.29	3.59	1.47	2.64
HHCB	0.41	3.95	0.21	0.88
AHTN	-	0.86	0.23	0.37
HHCB-Lac	-	3.81	3.92	6.25
TCEP	1.33	3.30	0.51	1.35
TCPP	2.35	3.76	1.85	2.68
TDCPP	0.24	0.55	0.11	0.32
Mecoprop	0.00	0.15	0.02	0.18
Triclosan	0.30	1.15	0.13	0.50
Bisphenol A	-	31.41	0.57	1.80

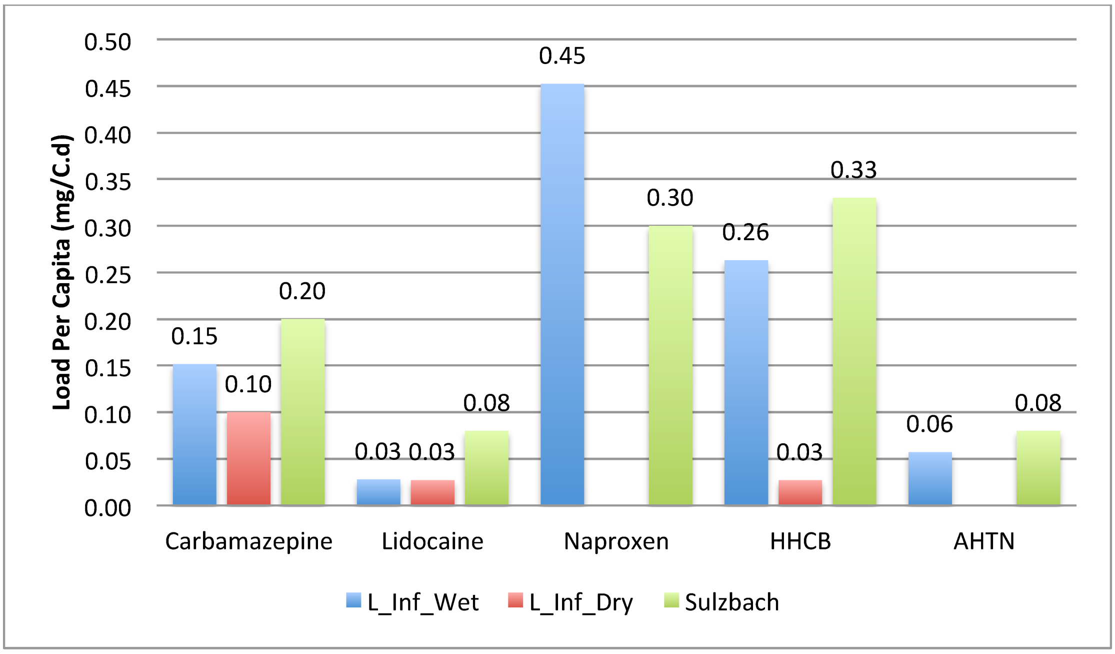


Figure 73: Average diurnal influent load per capita and comparison

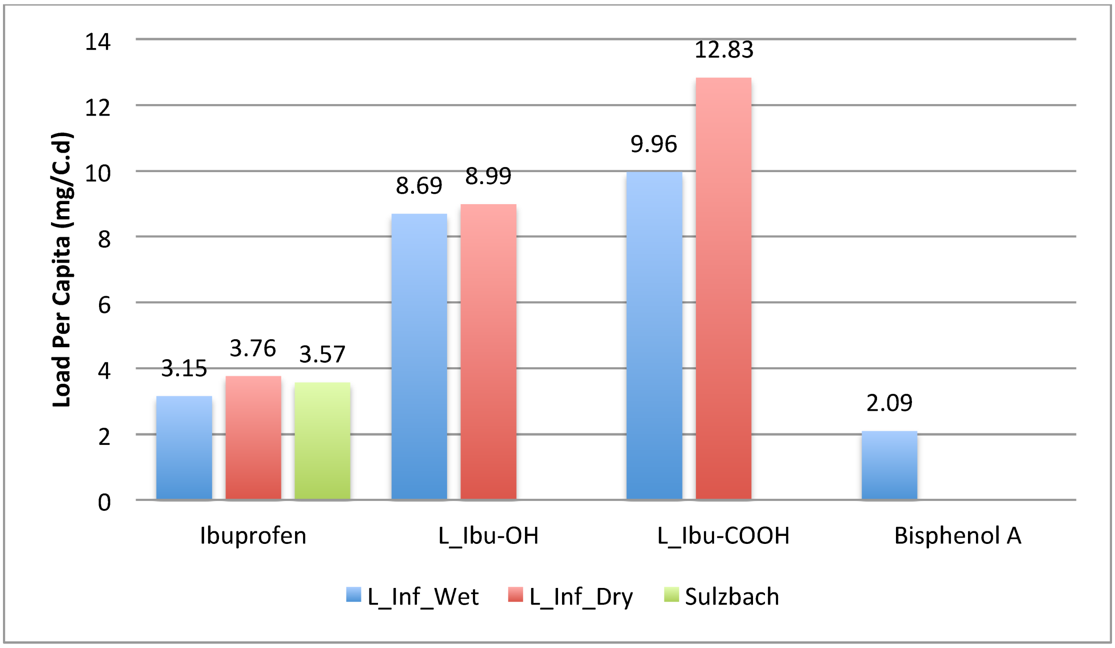


Figure 74: Average diurnal influent load per capita and comparison

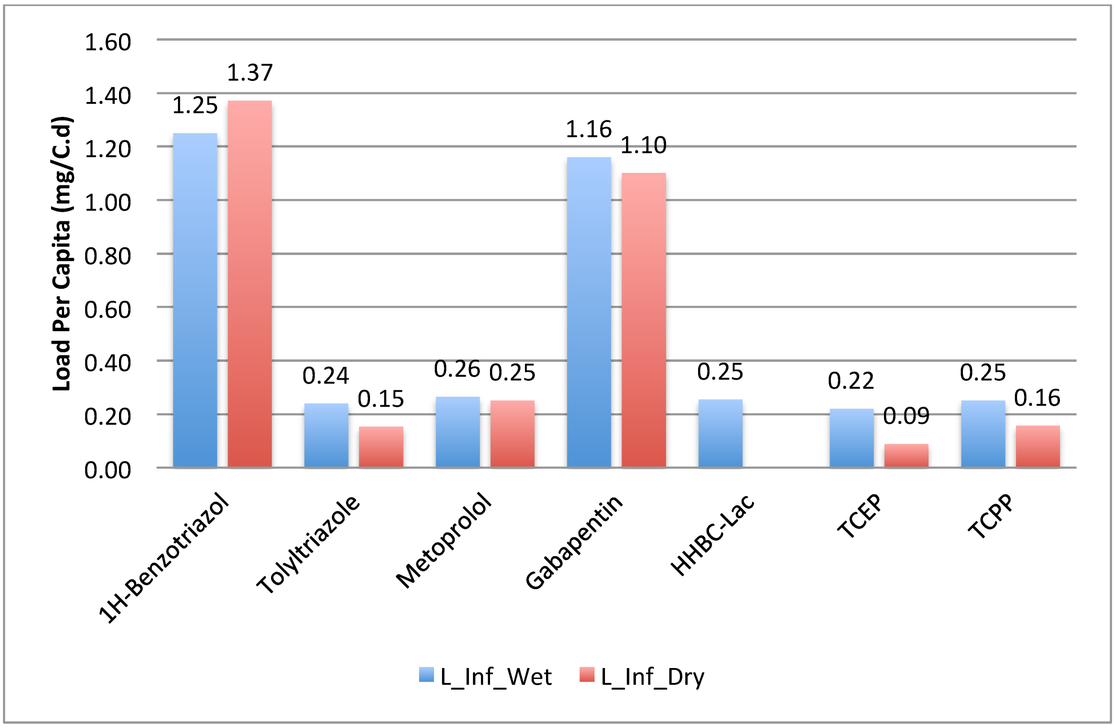


Figure 75: Average diurnal influent load per capita under dry weather and wet weather conditions

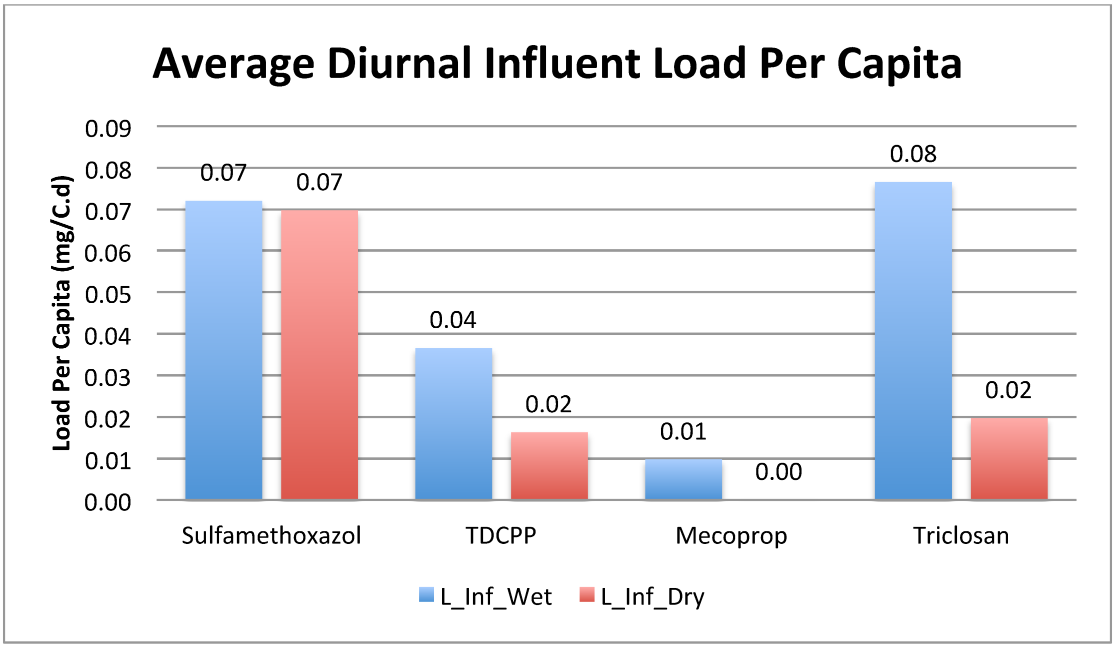


Figure 76: Average diurnal influent load per capita under dry weather and wet weather conditions

3.6. Heavy Metals

Consideration of heavy metals as an indicator for the occurrence of micropollutants has been carried out in this section. Figures 77 and 78 contain the diurnal and hourly influent and effluent of potassium, indicate almost similar concentrations between the influent and effluent, which can be argued based on the lack of degradation process and sorption for the potassium. Additionally, the retention time of the WWTP can be observed in the weekly fluctuations. Potassium is from the urine, as discussed later in the section 3.4.1 and 3.2.2; the correlation of the potassium is expected to match with ammonium and pharmaceuticals. Figures 79 and 80 contain the correlation between potassium and ammonium and Metoprolol respectively. A satisfactory correlation with ammonium and relatively good correlation with Metoprolol have been obtained. Except Gabapentin, there is no further acceptable correlation among other pharmaceuticals in the influent with potassium. However, a weak correlation exists with Gabapentin and Carbamazepine for the effluent.

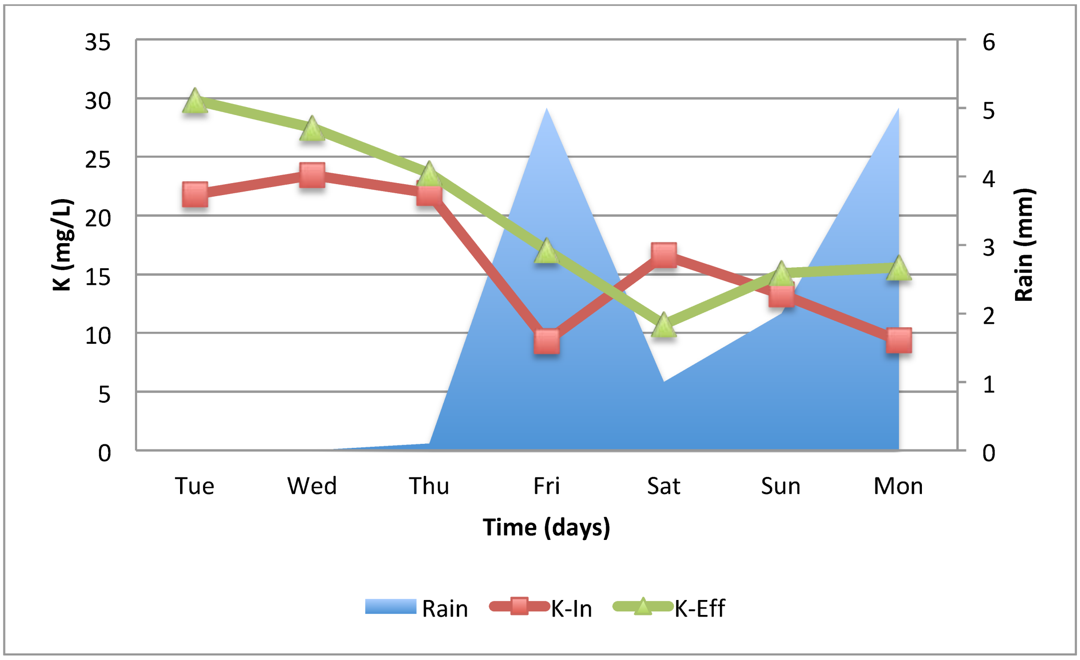


Figure 77: Diurnal influent and effluent concentration of Potassium

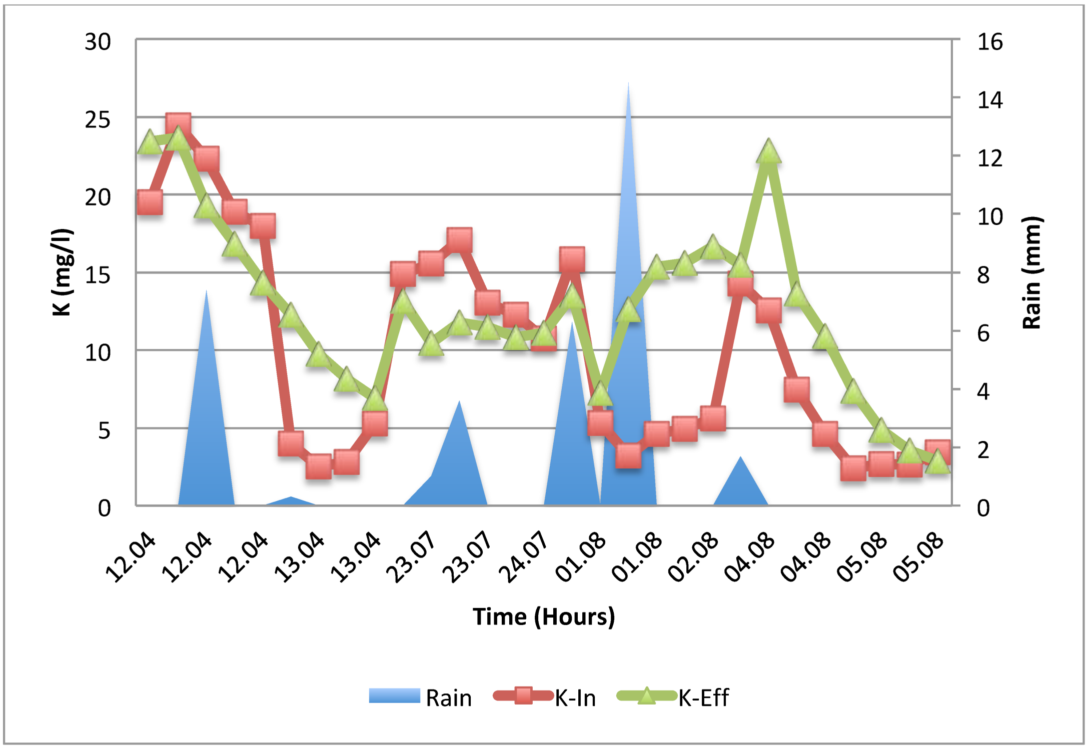


Figure 78: Hourly influent and effluent concentration of Potassium

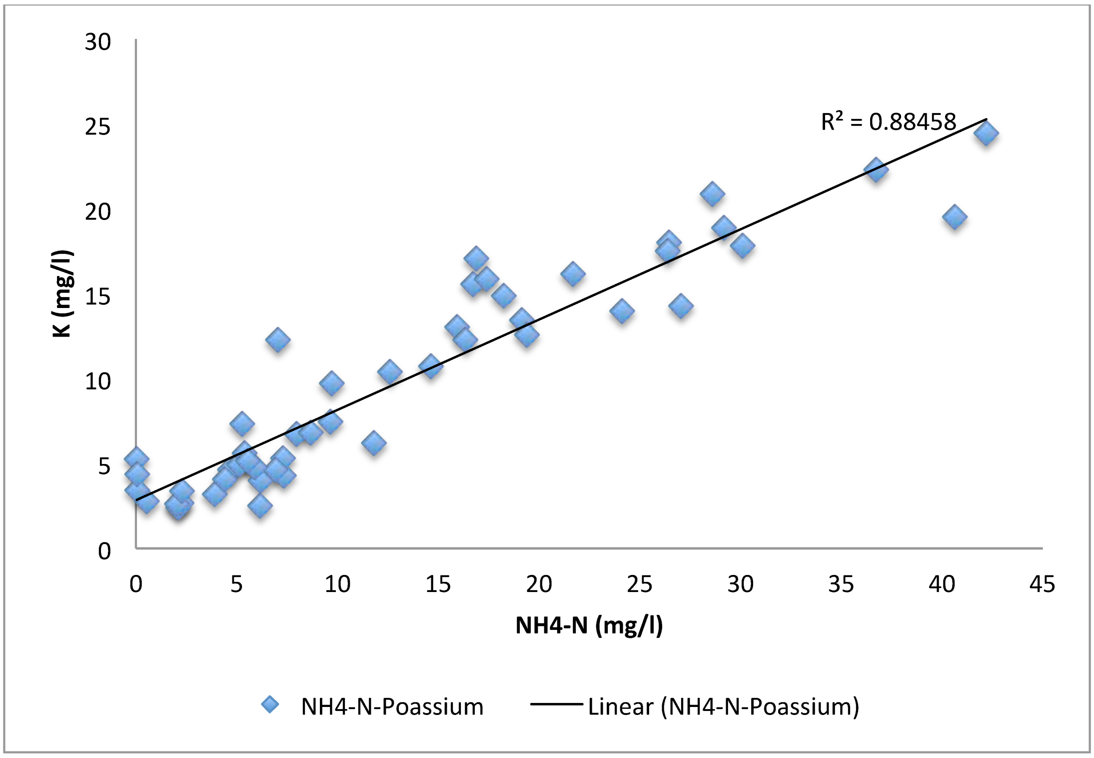


Figure 79: Correlation between ammonium and Potassium

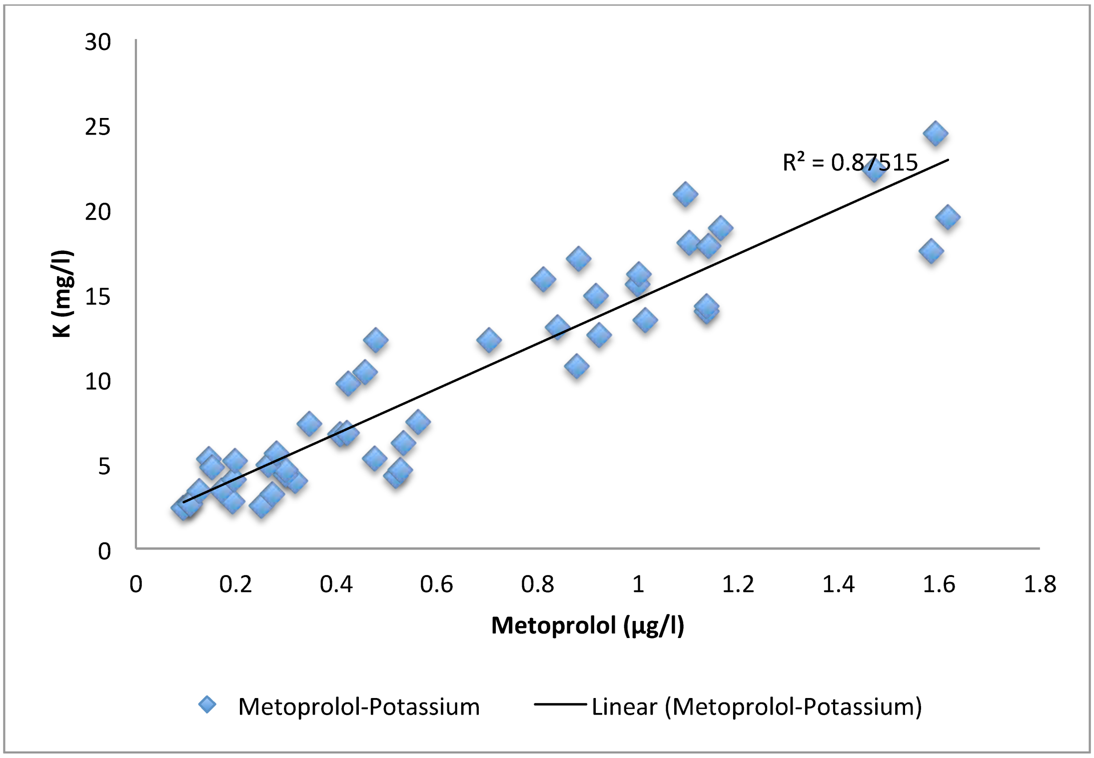


Figure 80: Correlation between Metoprolol and Potassium

3.7. Micropollutants in CSOs

Along the catchment area of Herbolzheim multiple CSOs with various capacities are featured in the sewer system. Unfortunately none of dates for the respective samples from CSOs are matching the influent and effluent data for the WWTP; nevertheless numerous amounts of data enable a decent average over the time for multiple CSOs. This section is dedicated to the existence of micropollutants in the CSOs, focusing on the concentrations and loads from 3 different CSOs located along the sewer system of the catchment area Herbolzheim, named: Wagenstadt, Herbolzheim and Bleichheim, as a reference they are named CSO1, 2 and 3 respectively.

3.7.1. Concentration of Micropollutants in CSOs

The range and the average concentration of different micropollutants in various CSOs shall be compared with the range and the average of the influent and effluent of the respective substance in the WWTP, Figures 81-84 are indicating the range and the average values for multiple substances. As it is assumed, in case of the discharge of higher than the design discharge of WWTP, the CSOs will be short cut without treatment into the receiving water bodies, it is essential to assess whether the load and the concentrations of the micropollutants exceed the effluent values or not.

Metoprolol shows a reliable range and average in regards to the effluent of the WWTP. Likewise, the average of 1H-Benzotriazole stays below the average of effluent; however, the range for CSO1 and 2 exceed the range and average of the effluent. The case for Lidocaine and TCPP is critical where the values of range and average both surpasses not only the effluent but also the influent concentrations of the WWTP.

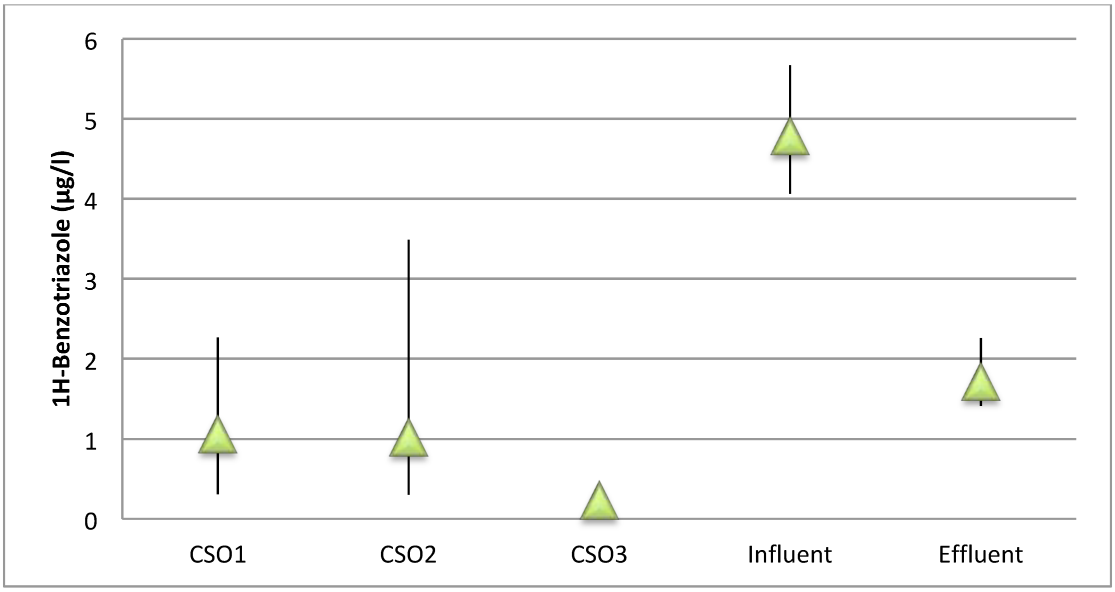


Figure 81: Minimum, maximum and average concentration of 1H-Benzotriazole for CSOs, influent and effluent

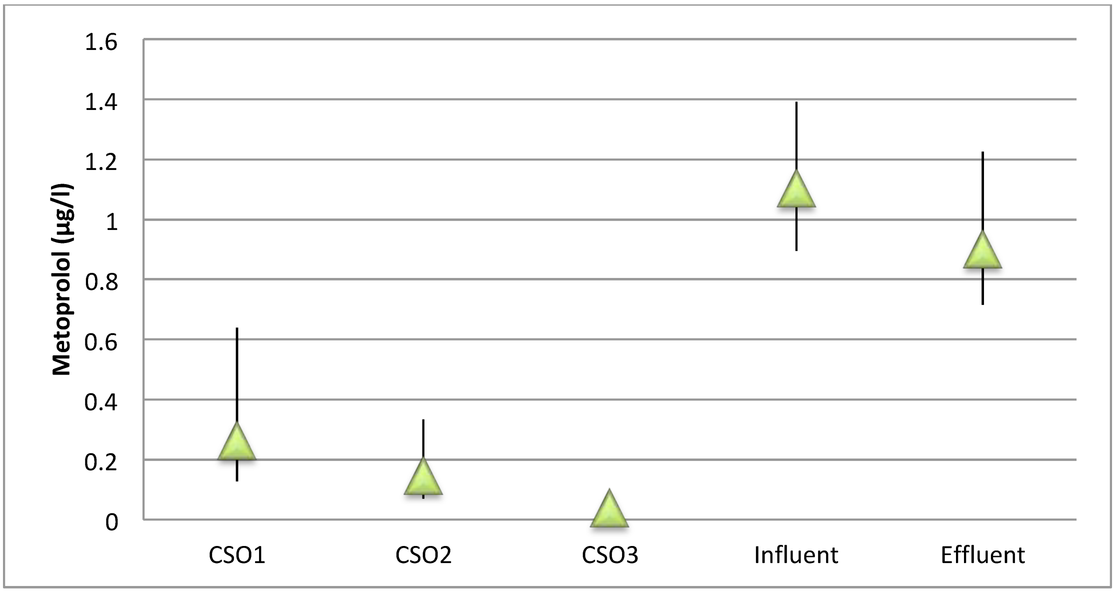


Figure 82: Minimum, maximum and average concentration of Metoprolol for CSOs, influent and effluent

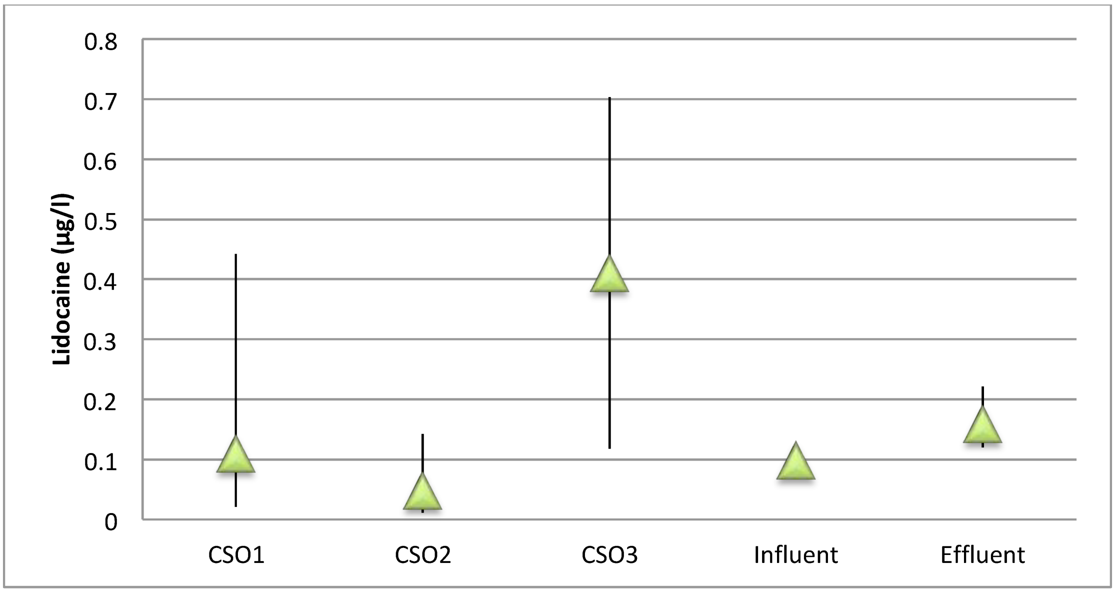


Figure 83: Minimum, maximum and average concentration of Lidocaine for CSOs, influent and effluent

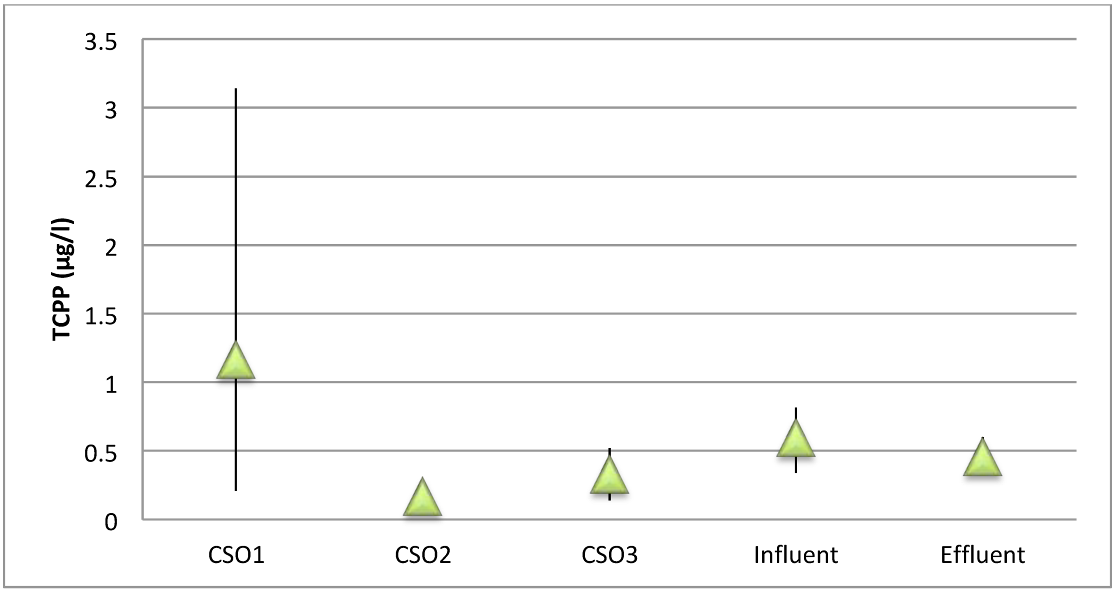


Figure 84: Minimum, maximum and average concentration of TCPP for CSOs, influent and effluent

3.7.2. Load of Micropollutants in CSOs

Figure 85 is illustrating the diurnal load of the CSOs. Despite of the alarming concentrations of Lidocaine and TCPP, the load of the respecting substances are not magnificent; however in the events of intense rains these presented load of g/d may happen within a few minutes. Figure 86 is the correlation of ammonium and Metoprolol in the CSOs, which indicates a relatively strong correlation, and it is noteworthy to point out that such a correlation was not established for the most of the pharmaceuticals in CSOs.

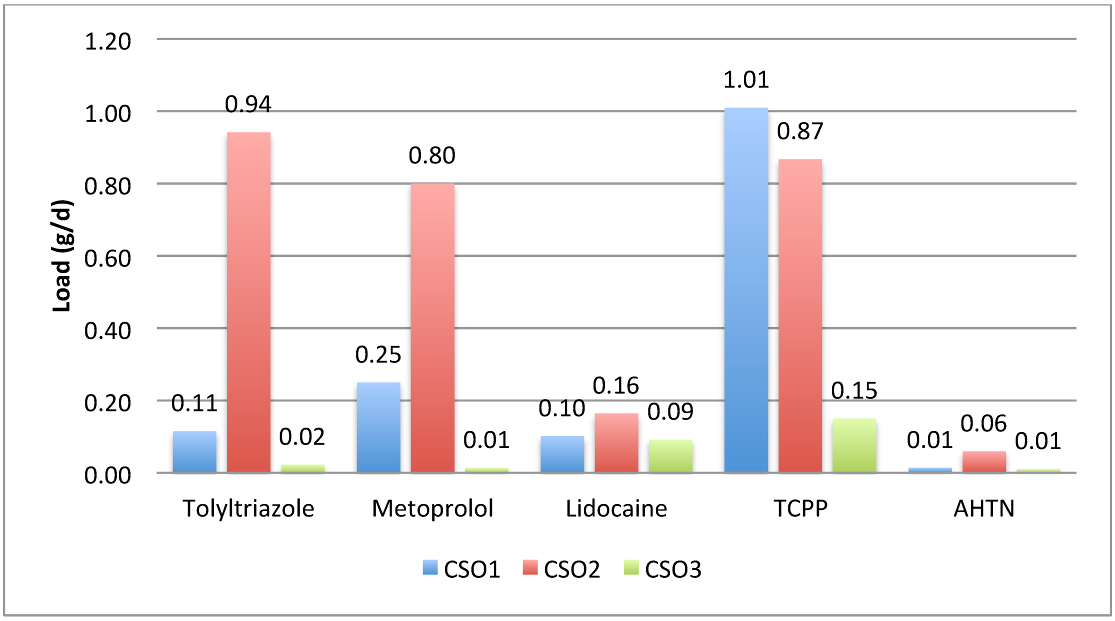


Figure 85: Diurnal load of the micropollutants in CSOs

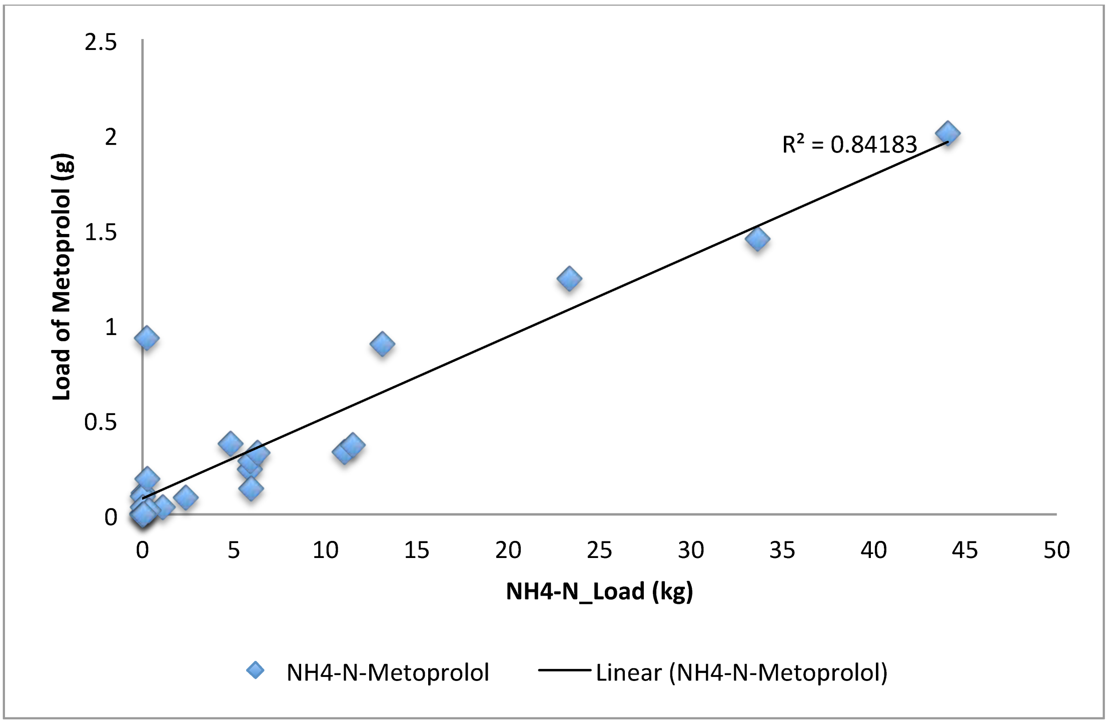


Figure 86: Correlation of the ammonium and Metoprolol in CSOs

With consideration of the results and discussions carried out in this chapter, a comprehensive relevancy among the conventional parameters and micropollutants is revealed, as a matter of fact, the strong correlations among pharmaceuticals and ammonium and SAC as well as between turbidity and Triclosan gives a notion about that. The summary of observations and inferences executed on this chapter will be presented in the chapter Conclusion.

Chapter 4. Conclusion

As shown by this study, the importance of a comprehensive evaluation of the adverse effects of micropollutants is revealed. Furthermore, the concrete objectives over the engrossing aspects of inspection and multiple paths for uncovering of the existence of micropollutants have been decided. Additionally, a selection of micropollutants from various diffuse sources has been chosen for further investigation. Samples from influent and effluent of the WWTP Herbolzheim, its receiving water body and existing CSOs in the catchment area have been collected, processed, and polar substances with HPLC and non-polar substances with GC-MS have been investigated.

In order to fulfill the study's objectives, further investigation of the correlation and codependence of the samples, as well as their fluctuations have been recognized by quantification of the concentration of different micropollutants. An analysis of the mutual behavior of conventional parameters has been accomplished in order to vouch whether the application of them in contrast to micropollutants concentration is persuasive. An expected behavior of ammonium and SAC has been observed, whereas the COD and TOC values and their ratio for influent show very high values, indicating a poorly oxidized mixture. Contrastingly, the ratio of effluent appears to fall in the degraded range. Rain events have an immediate influence on the load of the NH4-N arriving to the WWTP, despite of the fact that the peak for the ratio of COD/TOC happens with a delay because it takes more time for rain to wash the settled sludge in the sewer, which is the origin of COD and TOC and flushes it to the WWTP.

Attachment of Triclosan to the suspended particles in the wastewater results in the resemblance of fluctuations for the concentration of turbidity and Triclosan. In the same fashion, fluctuations of the ammonium and most of the pharmaceuticals have a similar trend since the source of diffuse for both of them is urine. Pharmaceuticals such as Lidocaine with different application forms do not have a similar trend with ammonium.

In the existence of policies for conventional parameters, regulated effluent concentrations are evident, whereas, the lack of regulations for micropollutants is leading to privation of adjusted or mitigated effluent concentrations. In spite of the fact that the average elimination for conventional parameters such as COD, TOC are 93% and 84% respectively, and parameters such as NH4-N are up to 99% degraded, elimination of the micropollutants does not follow a decent pattern. Different compounds with various elimination rates exist among the list of micropollutants investigated in this study. Substances with the medium elimination range around 50% include Gabapentin and Sulfamethoxazole, whereas substances like Ibuprofen have shown an impressive elimination of 99%, and contrastingly, Carbamazepine and Lidocaine are almost persistent in the conventional treatment. Lastly, Tolytriazoles with the elimination of 34% during dry weather conditions demonstrates no elimination under wet weather conditions.

The effect of rain is evident in substances such as Metoprolol, Sulfamethoxazole and Gabapentin due to their solubility, resulting a decrease in their influent concentrations. On the other hand, rain events do not play an important role in introducing the industrial chemicals such as TCEP, implying its independence from the diffuse source. Contrastingly, TDCPP has demonstrated an opposite of the anticipations by increasing of its concentration under the wet weather conditions. Moreover, the excellent buffer capacity of WWTP could be recognized by observation of the peak for Sulfamethoxazole.

Diffuse of conjugates that are broken in the wastewater, may lead to the increase of concentration for some compounds in a way that the concentration detected in the effluent surpasses the influent concentrations. Ibuprofen and its degradation products as well as Naproxen and Bisphenol A are almost degraded through the activated sludge process. Comparatively, the effluent concentration of degradation product of HHCB, HHCB-Lactone does not follow the same pattern as its parent compound and surpasses its respective influent, indicating almost no elimination.

Despite of the fact that Tolytriazoles and 1H-Benzotriazole experience a moderately good elimination, the effluent concentration value is still appearing in a high range of 1.5 to 2.5 μg/l for 1H-Benzotriazole, with the consideration that the origin source of the mentioned micropollutants are dishwasher tablets, and the increasing utilization of dishwashers will rise the concentration and adverse effect of them on the aquatic life. However, the effluent concentration of 1H-Benzoriazole is remarkably lower than the average of Europe with 6.3 μg/l, which implies the minor application of dishwashers in the area. With the same fashion, Mecoprop effluent as well as influent concentrations values are significantly inferior to the average Europe, which can be elucidated by either the lower application of pesticides for agriculture, or a disconnection between the farmland run off and the sewage.

According to the substantial cost and time-consuming methods existing for the assessment of micropollutants, revealing a close relation and strong correlation between specific conventional parameters and some micropollutants could shed a light on the projection and prediction of the attained concentration of micropollutants. The strength of the correlation of pharmaceuticals and ammonium is relevant to the mutual diffuse source and is dependence on the frequency of the consumed medicine. Pharmaceuticals, which are not ingested will not be introduced to the wastewater by urine, hence the correlation of such pharmaceuticals like Lidocaine has no relation with ammonium. On the other hand, medicines like Metoprolol and Gabapentin, whose their consumptions are more common among the patients, have a very strong correlation, while Carbamazepine exhibits a weaker correlation to the ammonium.

The strong correlation of SAC and ammonium implies a close correlation among SAC and pharmaceuticals, since SAC is representative of yellow color in the wastewater and its source matches with ammonium. The similar fluctuations for turbidity and Triclosan may not be reliable as the correlation is moderate. However the values for turbidity in the range of 50 to 200 NTU requires a second set for validation, since the second read may vary about 25%. This study highly recommends at least two sets of measurements for the value of turbidity for the influent in order to reduce the uncertainties.

Average effluent concentrations for dry weather in comparison to the values from other studies across the Europe and the state of Baden-Württemberg depicts a very similar range for most of the micropollutants such as Triclosan and TCEP. Nevertheless, substances such as Mecoprop, HHCB and Bisphenol A seem to be distinct compared to the other studies. Influent load to the WWTP is almost constant throughout the week for many of the micropollutants or trace a unique pattern, leading to an estimation of the average diurnal influent per capita. Almost identical values from this study compared to the other study in the Baden-Württemberg elucidate the resembling behavior of the input sources discharged into the wastewater.

The use of correlation for ammonium and pharmaceuticals, especially for the ones which are only in the water phase, is promising, since there is no sorption for those pharmaceuticals and their behavior is similar to heavy metals. Potassium has a close correlation with Metoprolol and Gabapentin, regarding the source of urine as its origin, whereas no further correlation with other pharmaceuticals is obtained, a weak correlation with Gabapentin and Carbamazepine is evident. The average and range for concentration of several micropollutants surpasses the average and range of effluent concentration of respective micropollutants, indicating the act of discharging the CSO into the surface water body without any treatment will diminish the significant role of WWTPs as the barrier for the safety of water resources. Furthermore, in some substances such as Lidocaine and TCPP, concentration in the CSOs can be even greater than the influent concentration of the WWTPs, which will threaten the aquatic environment with the hazardous aspects of micropollutants.

In conclusion, CSOs could have an effect on the WWTP influent, when the overflow is directed for treatment into the WWTP. Furthermore, the effect of rain events on the influent and effluent concentrations as well as loads of the WWTP is inevitable, and it is certainly dependent on the duration, intensity and frequency of the rain. Furthermore, combined with the necessity of micropollutants elimination, implementation of source control has to be carried out. Additionally, in case of enforcement of regulations on micropollutants concentrations, still the lack of feasible and inexpensive measuring devices for monitoring the WWTPs efficiencies is apparent. Therefore, further studies and research with the focus on the prognostication of the micropollutants based on the conventional parameters are found worthy.

References

Andersen H, Siegrist H, Halling-Sørensen B, Ternes TA. Fate of estrogens in a municipal sewage treatment plant. Environmental Science and Technology 2003; 37: 4021–6.

ASHP “The American Society of Health-System Pharmacists”. Retrieved 28 Mar 2015.

ASHP “The American Society of Health-System Pharmacists”. Retrieved Apr 21, 2014.

Attal N, Cruccu G, Baron R, et al. (September 2010). "EFNS guidelines on the pharmacological treatment of neuropathic pain: 2010 revision". Eur. J. Neurol. 17 (9): 1113–e88. doi:10.1111/j.1468-1331.2010.02999.x. PMID 20402746.

Barber L.B., Murphy S.F., Verplanck P.L., Sandstrom M.W., Taylor H.E., Furlong E.T. (2006). Chemical loading into surface water along a hydrological, biogeochemical, and land use gradient: A holistic watershed approach. Environmental Science and Technology 40: 475-486.

Barbosa, Marta O., Nuno F.f. Moreira, Ana R. Ribeiro, Manuel F.r. Pereira, and AdriÃ¡n M.t. Silva. "Occurrence and Removal of Organic Micropollutants: An Overview of the Watch List of EU Decision 2015/495." Water Research 94 (2016): 257-79. Elsevier. Web. Dec. 2016. <http://www.sciencedirect.com/science/article/pii/S0043135416301063>.

Cirja M, Ivashechkin P, Schäffer A, Corvini PF. Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR). Reviews in Environmental Science and Bio/Technology 2008; 7: 6178.

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ. Health Perspect. 107 (Suppl. 6), 907e938.

Deegan A.M., Shaik B., Nolan K., Urell K., Oelgemöller M., Tobin J., Morrissey A. (2001). Treatment options for wastewater effluents from pharmaceutical Companies. Environmental Science and Technology 8(3): 649-666.

DWA Landesverband Baden-Württemberg, Stuttgart (2013). Kläranlagen und Kanal- Nachbarschaften; Ergebnisse des kommunalen Leistungsvergleichs 2012. 200-202.

EEA, Copenhagen (2009). Water resources across Europe-confronting water scarcity and drought. EEA Report No 2/2009.

EPA. "Ibuprofen." EPA.gov. Environmental Protection Agency, 2009. Web. <https://iaspub.epa.gov/tdb/pages/contaminant/contaminantOverview.do?contaminantId=10022>.

EPA. "What Are Pesticides and How Do They Work?" Http://www.epa.nsw.gov.au. N.p., n.d. Web. 2016. <http://www.epa.nsw.gov.au/pesticides/pestwhatrhow.htm>.

European Communities (2011). Common implementation strategy for Water Framework Directive (2000/60/EC), Guidance document No. 27; Technical guidance for deriving environmental quality standards.

European Parliament and The Council. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the eld of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. Off J EU 2008; L348: 84–97.

FDA "US Food and Drug Administration". http://www.fda.gov.

Kidd, K.A., Blanchfield, P.J., Mills, K.H., Palace, V.P., Evans, R.E., Lazorchak, J.M., Flick, R.W., 2007. Collapse of a fish population after exposure to a synthetic estrogen. Proc. Natl. Acad. Sci. 104 (21), 8897e8901.

Kuch, Bertram. "Assessing Micropollutants." Personal interview. 2016.

Kuch, Bertram. "Practical Class." Sanitary Engineering. Stuttgart University, Stuttgart. 2015. Lecture.

Leo-BW.de. "Bevölkerungsentwicklung Und Ausländeranzahl Herbolzheim." N.p., n.d. Web. Jan. 2017. <http://www.leo-bw.de>.

Loos, Robert, Raquel Carvalho, Diana C. AntÃ³nio, Sara Comero, Giovanni Locoro, Simona Tavazzi, Bruno Paracchini, Michela Ghiani, Teresa Lettieri, Ludek Blaha, Barbora Jarosova, Stefan Voorspoels, Kelly Servaes, Peter Haglund, Jerker Fick, Richard H. Lindberg, David Schwesig, and Bernd M. Gawlik. "EU-wide Monitoring Survey on Emerging Polar Organic Contaminants in Wastewater Treatment Plant Effluents." Water Research 47.17 (2013): 6475-487. Elsevier. Web. Dec. 2016. <http://www.sciencedirect.com/science/article/pii/S0043135413006647>.

Martin C., Möder M., Daniel X., Krauss G., Schlosser D. (2007). Biotransformation of the polycyclic musks HHCB and AHTN and metabolite formation by fungi occurring in freshwater environments. Environmental Science and Technology 41: 5395-5402.

Metzger, Jörg W. "Organic Chemistry." Chemistry and Microbiology. Stuttgart University, Stuttgart. 2015. Lecture.

Mitchell, Greg B., Mati Kahru, John Wieland, and Malgorzata Stramska. Chapter 4. San Diego: UCSD, 2000. Scripps Institution of Oceanography, University of California San Diego, California. Web. 2016. <https://spg.ucsd.edu/People/Greg/Publications/005379_MItchell_NASA%20Report.pdf>.

Müller B, Scheytt T, Asbrand M, de Casas AM. Pharmaceuticals as indictors of sewage-influenced groundwater. Hydrogeology Journal 2012; 20: 111729.

OEHHA, CA. "Evidence on the Carcinogenicity of Tris(1,3-Dichloro-2-Propyl) Phosphate." OEHHA.CA.gov (2011): n. pag. Web. 2016. <http://oehha.ca.gov/media/downloads/proposition-65/presentation/tdcpp_jflma101211.pdf>.

Oulton, R.L., Kohn, T., Cwiertny, D.M., 2010. Pharmaceuticals and personal care products in effluent matrices: a survey of transformation and removal during wastewater treatment and implications for wastewater management. J. Environ. Monit. 12 (11), 1956e1978.

Phillips P.J., Chalmers A.T., Gray J.L., Kolpin D.W., Foreman W.T., Wall G.R. (2012). Combined sewer overflows: An environmental source of hormones and wastewater micropollutants. Environmental Science and Technology 46(10): 5336–5343.

Renge V.C., Khedkar S.V., Bhoyar K.S. (2012), Micropollutant removal from waste water treatment plant-A review. International Journal of Advanced Engineering Technology 3(4): 27-30.

Rossi, S, ed. (2013). Australian Medicines Handbook (2013 ed.). Adelaide: The Australian Medicines Handbook Unit Trust. ISBN 978-0-9805790-9-3.

Ruegg, U.T & Rudinger, J. (1977). "Reductive cleavage of cystine disulfides with tributylphosphine". Methods Enzymol. Methods in Enzymology. 47: 111–116. ISBN 978-0-12-181947-7. doi:10.1016/0076-6879(77)47012-5. PMID 927167

Santos, L.H., Araujo, A.N., Fachini, A., Pena, A., Delerue-Matos, C., Montenegro, M.C., 2010. Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. J. Hazard. Mater. 175 (1e3), 45e95.

Schwarzenbach R.P., Escher B.I., Fenner K., Hofstetter T.B., Johnson C.A., von Gunten U., Wehrli B. (2006). The challenge of micropollutants in aquatic systems. Science 313: 1072- 1077.

Siegrist, Hansruedi, Adriano Joss, and Thomas A. Ternes. "Chapter 7. Micro-Pollutant Removal." Activated Sludge - 100 Years and Counting. London: IWA Publ., 2014. N. pag. Print.

Steinmetz, Heidrun. "Wastewater Technology." Sanitary Engineering. Stuttgart University, Stuttgart. 2014. Lecture.

UCLA. "Drying Agents." Chem.ucla.edu. N.p., 21 Mar. 2016. Web. <http://www.chem.ucla.edu/~bacher/Specialtopics/Drying%20Agents.html>.

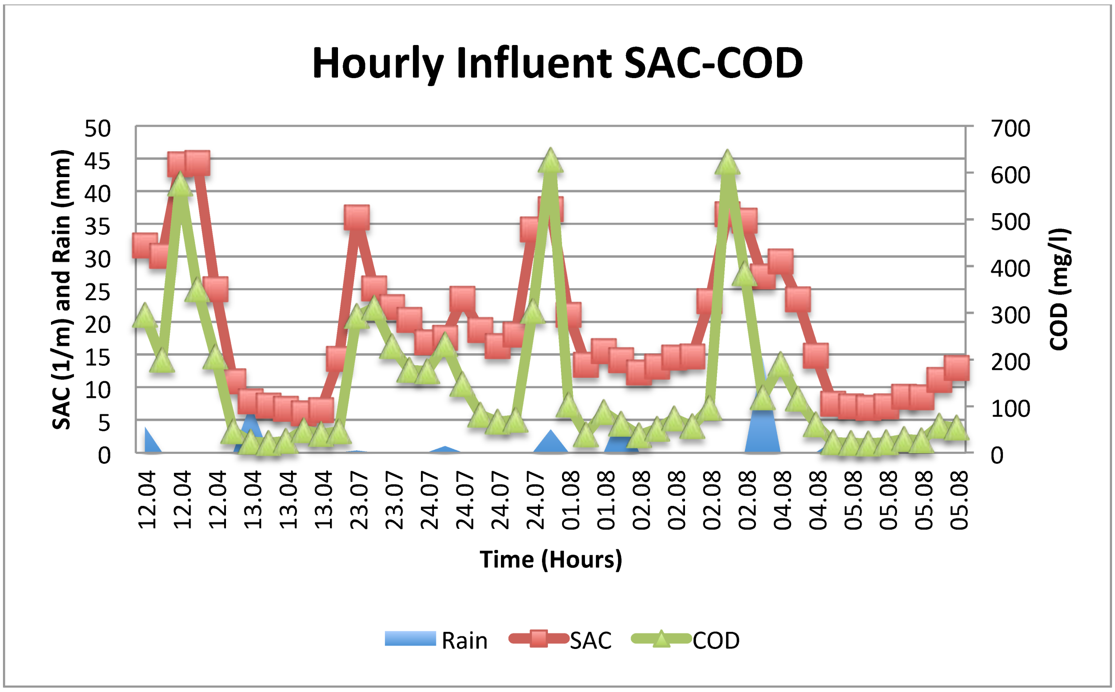
UNEP. "An Overview of the State of the World's Fresh and Marine Waters." Unep.org. N.p., 2002. Web. <http://www.unep.org/training/programmes/Instructor%20Version/Part_2/Activities/Economics_of_Ecosystems/Water/Supplemental/Global_Water_Resources.pdf>.

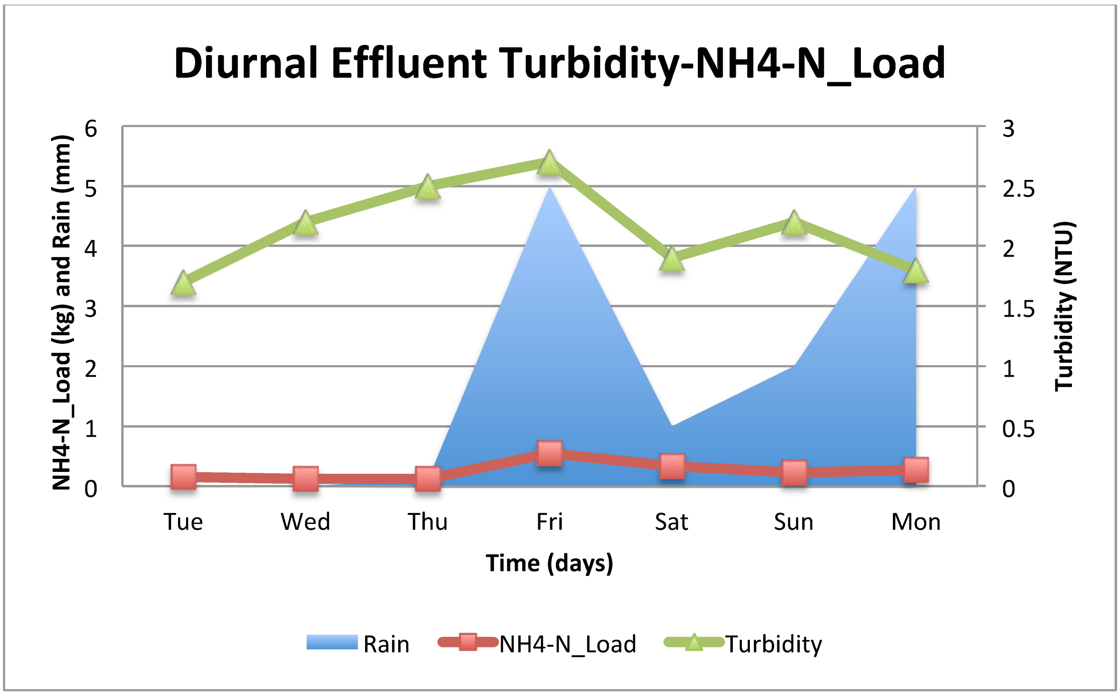
UNESCO. "New Report Highlights Crucial Role of Water in Development | United Nations Educational, Scientific and Cultural Organization." Unesco.org. N.p., 2009. Web. Dec. 2016. <http://www.unesco.org/new/en/media-services/single-view/news/new_report_highlights_crucial_role_of_water_in_development/>.

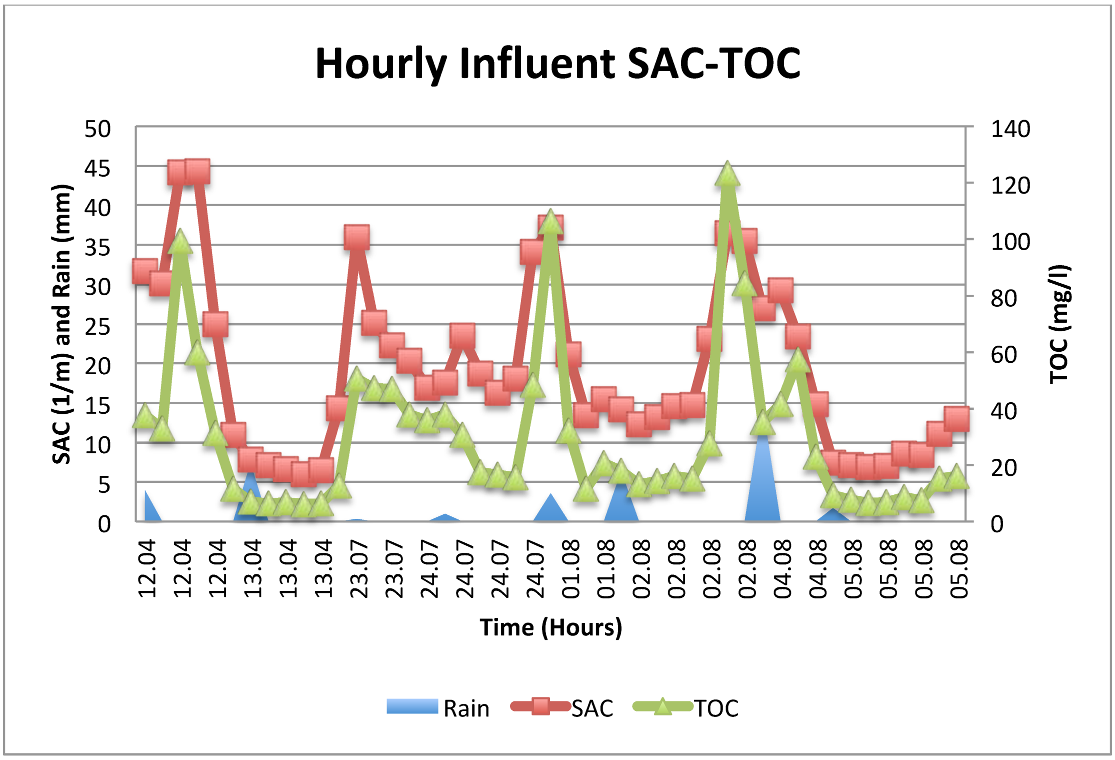
WBCSD. "WaterIntroduction." World Business Council for Sustainable Development (n.d.): n. pag. Unwater.org. 2005. Web. 2016. <http://www.unwater.org/downloads/Water_facts_and_trends.pdf>.

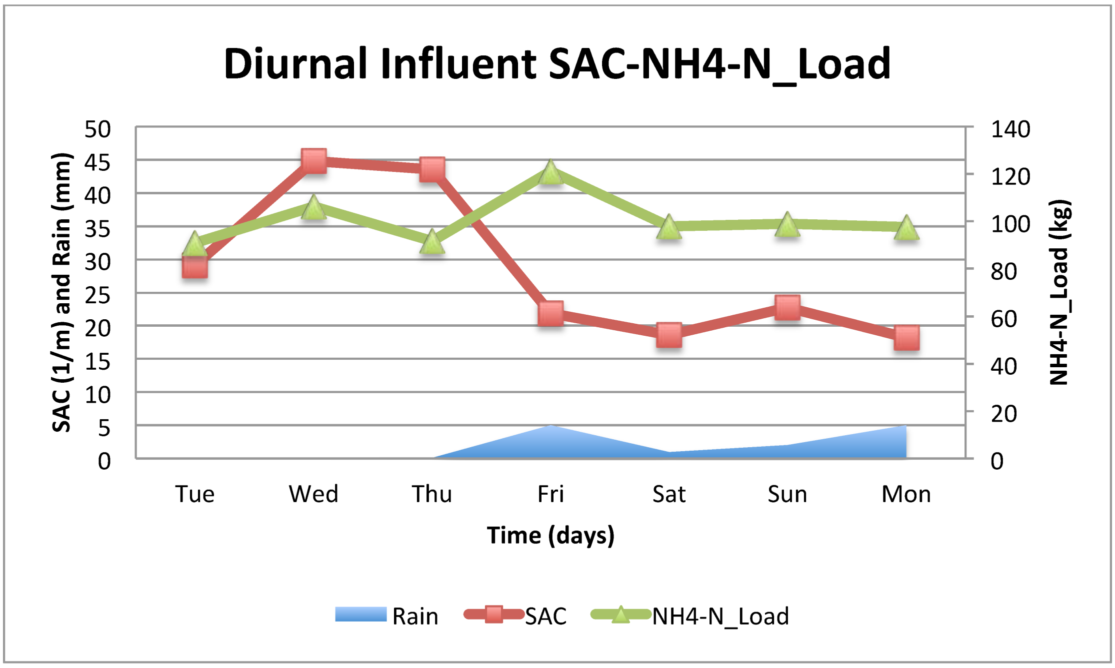
Appendices

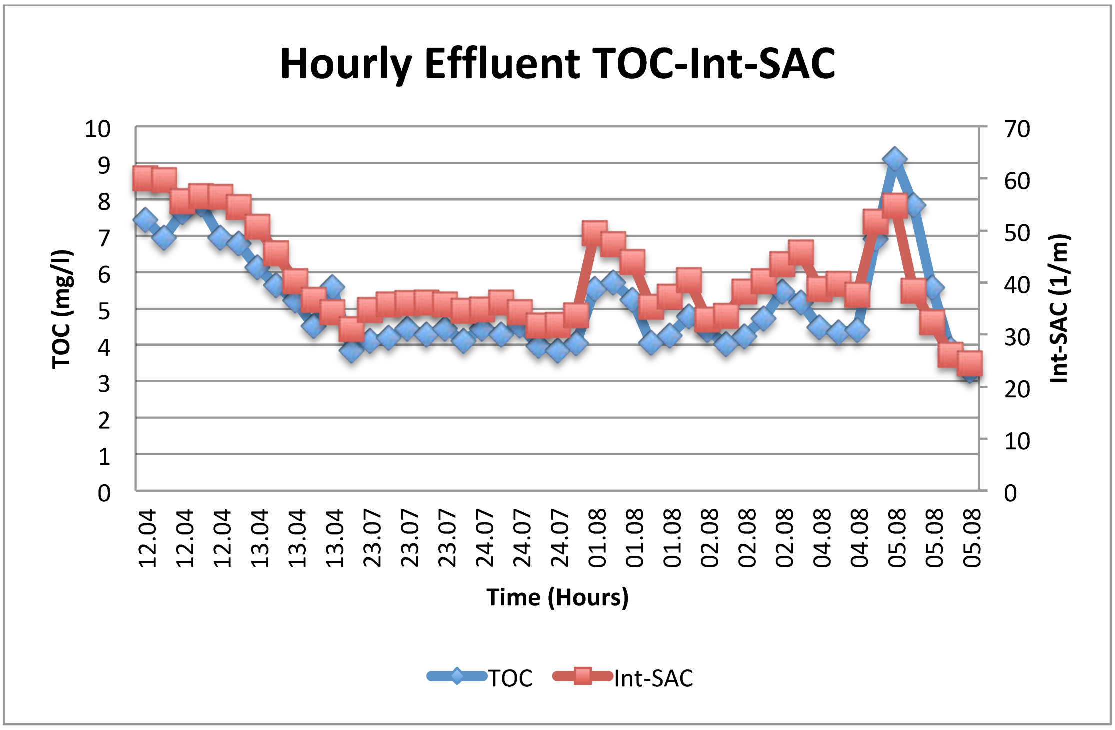
Appendix A



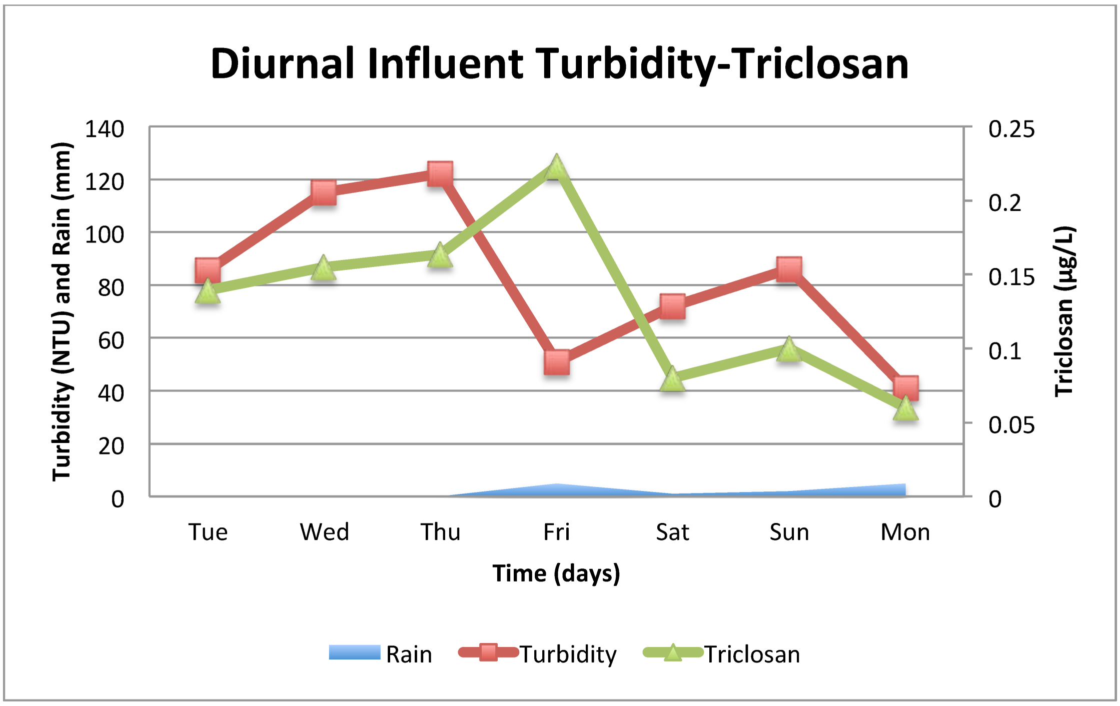


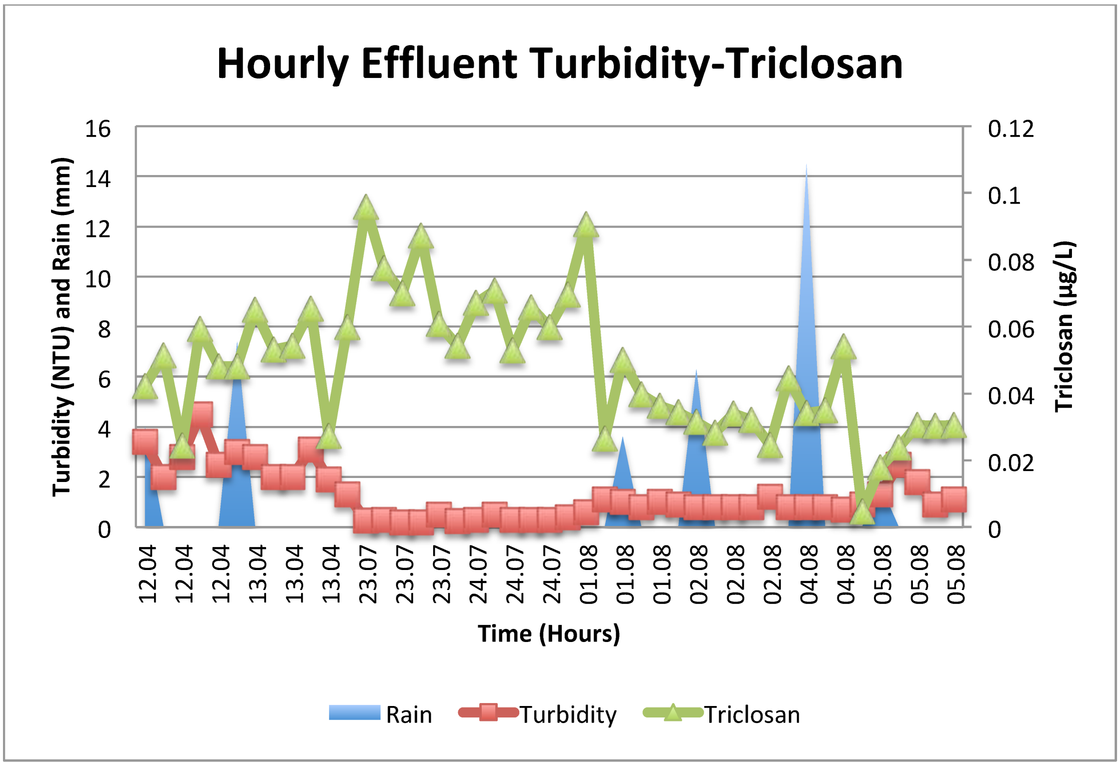

Hourly Influent SAC-TOC
SAC (1/m) and Rain (mm)
50
45
40
35
30
25
20
15
10
5
0
140
120
100
80
60
40
20
0
TOC (mg/l)
12.04
12.04
12.04
13.04
13.04
13.04
23.07
23.07
24.07
24.07
24.07
24.07
01.08
01.08
02.08
02.08
02.08
02.08
04.08
04.08
05.08
05.08
05.08
05.08
Time (Hours)
Rain
SAC
TOC

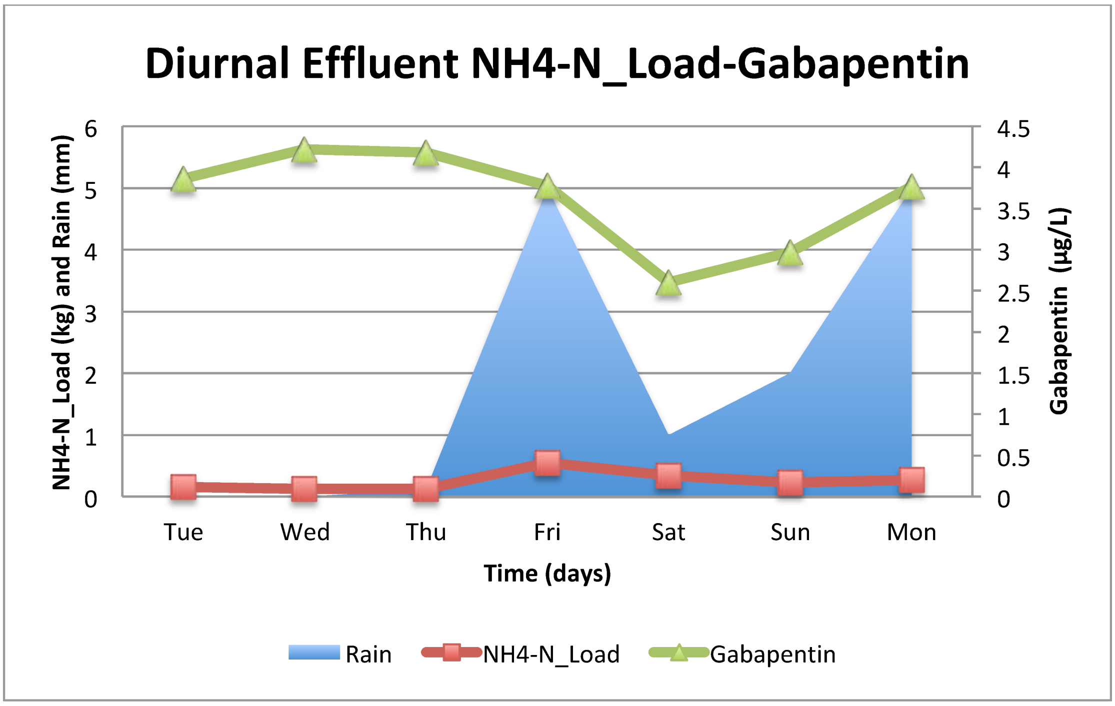

Diurnal Influent SAC-NH4-N_Load
SAC (1/m) and Rain (mm)
50
45
40
35
30
25
20
15
10
5
0
140
120
100
80
60
40
20
0
NH4-N_Load (kg)
Tue
Wed
Thu
Fri
Sat
Sun
Mon
Time (days)
Rain
SAC
NH4-N_Load

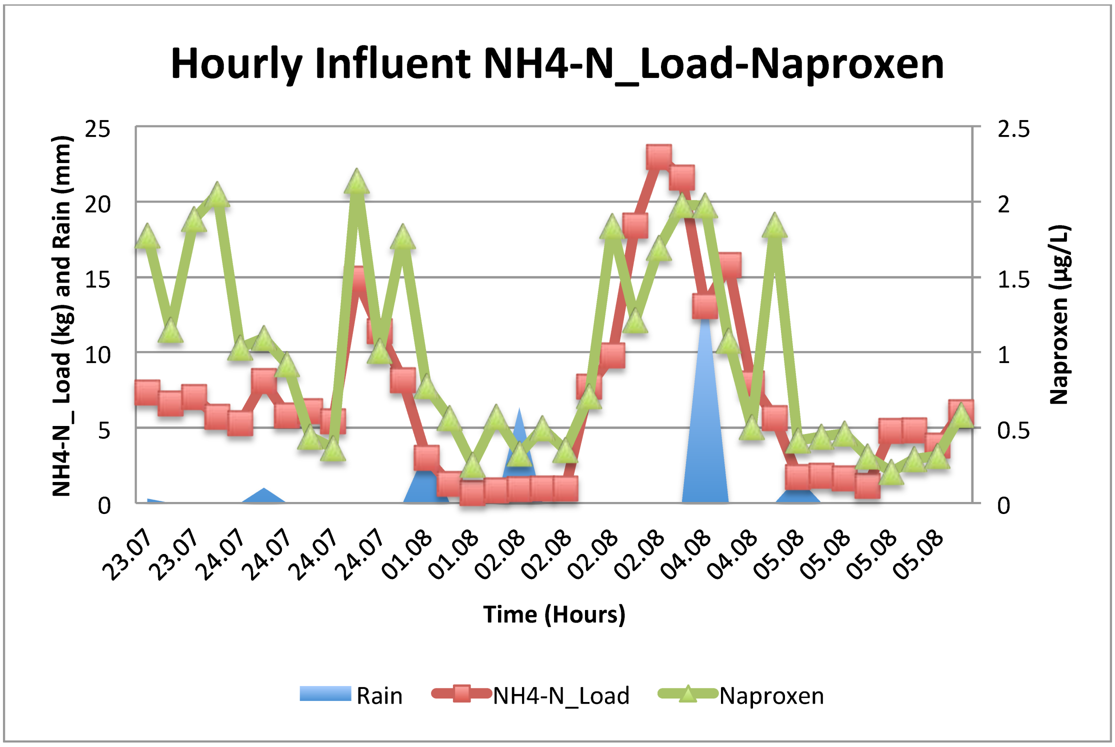

Hourly Effluent TOC-Int-SAC
TOC (mg/l)
Int-SAC (1/m)
10
9
8
7
6
5
4
3
2
1
0
70
60
50
40
30
20
10
0
12.04
12.04
12.04
13.04
13.04
13.04
23.07
23.07
23.07
24.07
24.07
24.07
01.08
01.08
01.08
02.08
02.08
02.08
04.08
04.08
05.08
05.08
05.08
Time (Hours)
TOC
Int-SAC

Appendix B

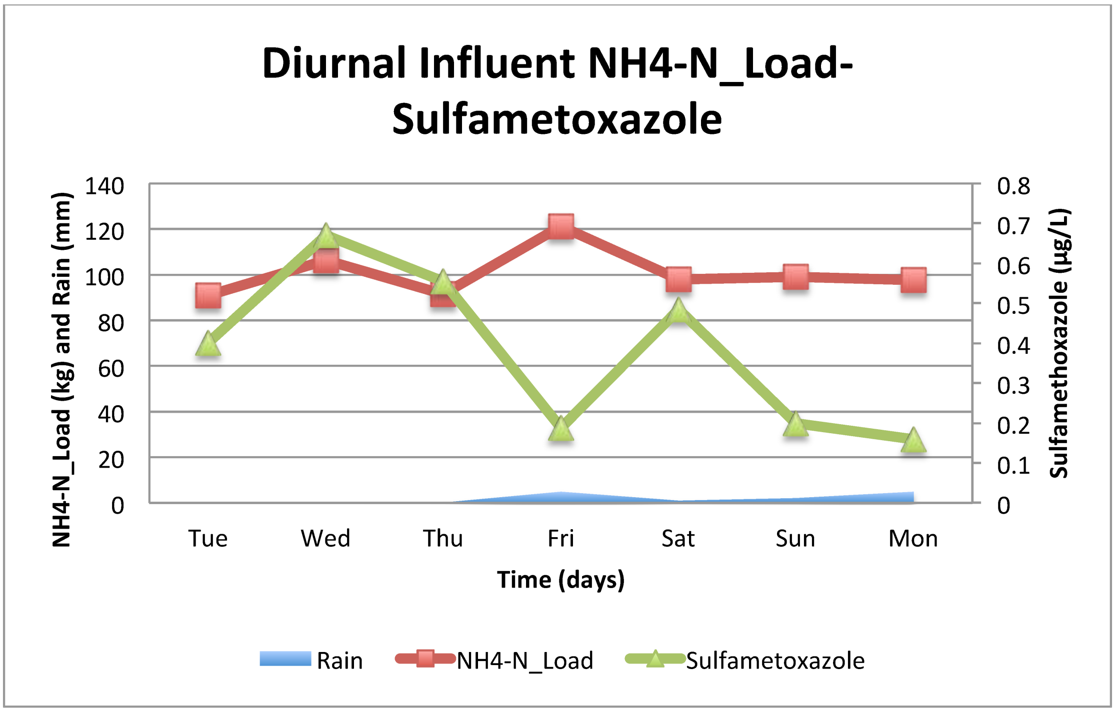

Diurnal Influent Turbidity-Triclosan
Turbidity (NTU) and Rain (mm)
Triclosan (µg/L)
140
120
100
80
60
40
20
0
0.25
0.2
0.15
0.1
0.05
0
Tue
Wed
Thu
Fri
Sat
Sun
Mon
Time (days)
Rain
Turbidity
Triclosan


Hourly Effluent Turbidity-Triclosan
Turbidity (NTU) and Rain (mm)
Triclosan (µg/L)
16
14
12
10
8
6
4
2
0
0.12
0.1
0.08
0.06
0.04
0.02
0
12.04
12.04
12.04
13.04
13.04
13.04
23.07
23.07
23.07
24.07
24.07
24.07
01.08
01.08
01.08
02.08
02.08
02.08
04.08
04.08
05.08
05.08
05.08
Time (Hours)
Rain
Turbidity
Triclosan


Diurnal Effluent NH4-N_Load-Gabapentin
NH4-N_Load (kg) and Rain (mm)
Gabapentin (µg/L)
6
5
4
3
2
1
0
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Tue
Wed
Thu
Fri
Sat
Sun
Mon
Time (days)
Rain
NH4-N_Load
Gabapentin

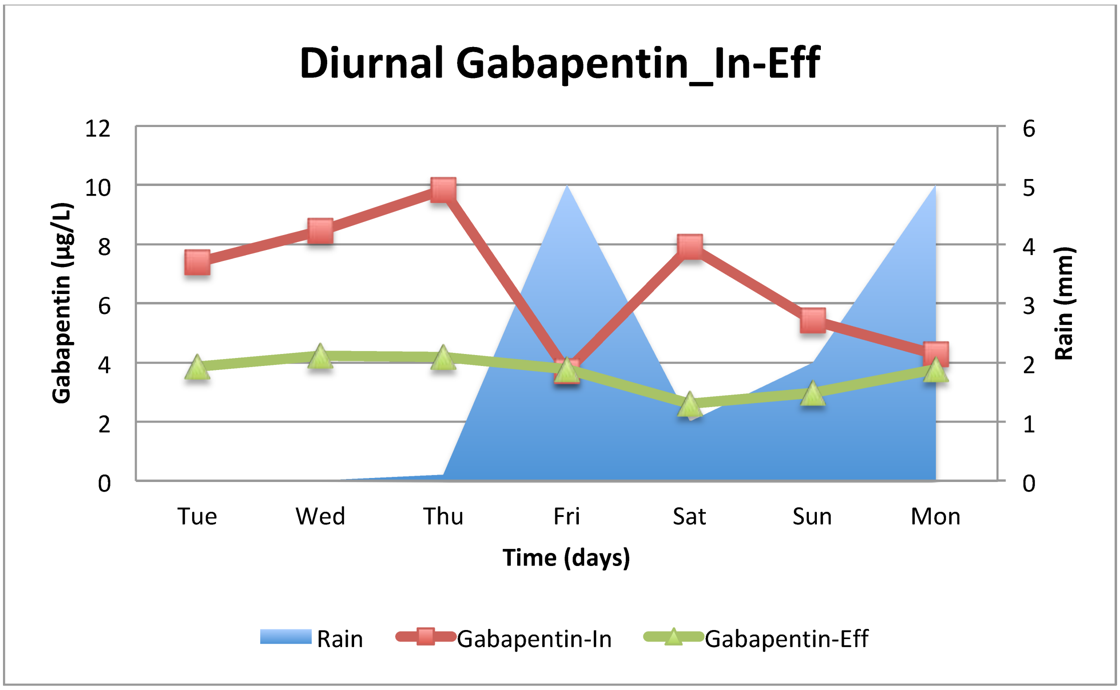


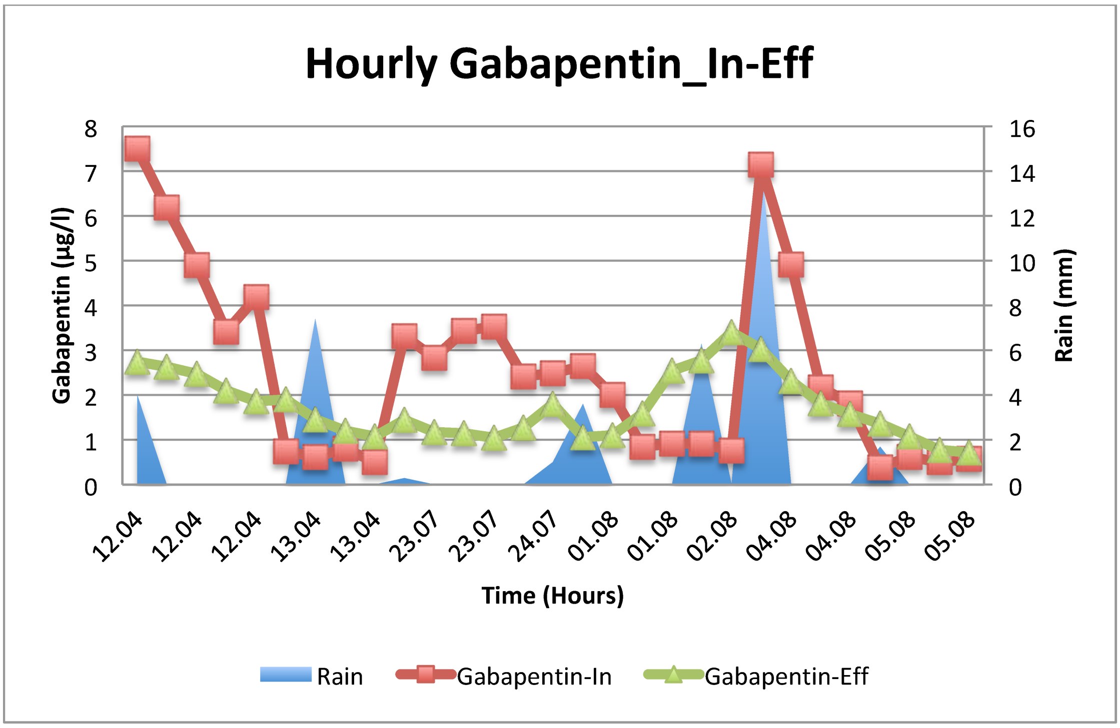
Hourly Influent NH4-N_Load-Naproxen
NH4-N_ Load (kg) and Rain (mm)
0
5
10
15
20
25
Naproxen (µg/L)
0
0.5
1
1.5
2
2.5
23.07
23.07
24.07
24.07
24.07
24.07
01.08
01.08
02.08
02.08
02.08
02.08
04.08
04.08
05.08
05.08
05.08
05.08
Time (Hours)
Rain
NH4-N_Load
Naproxen

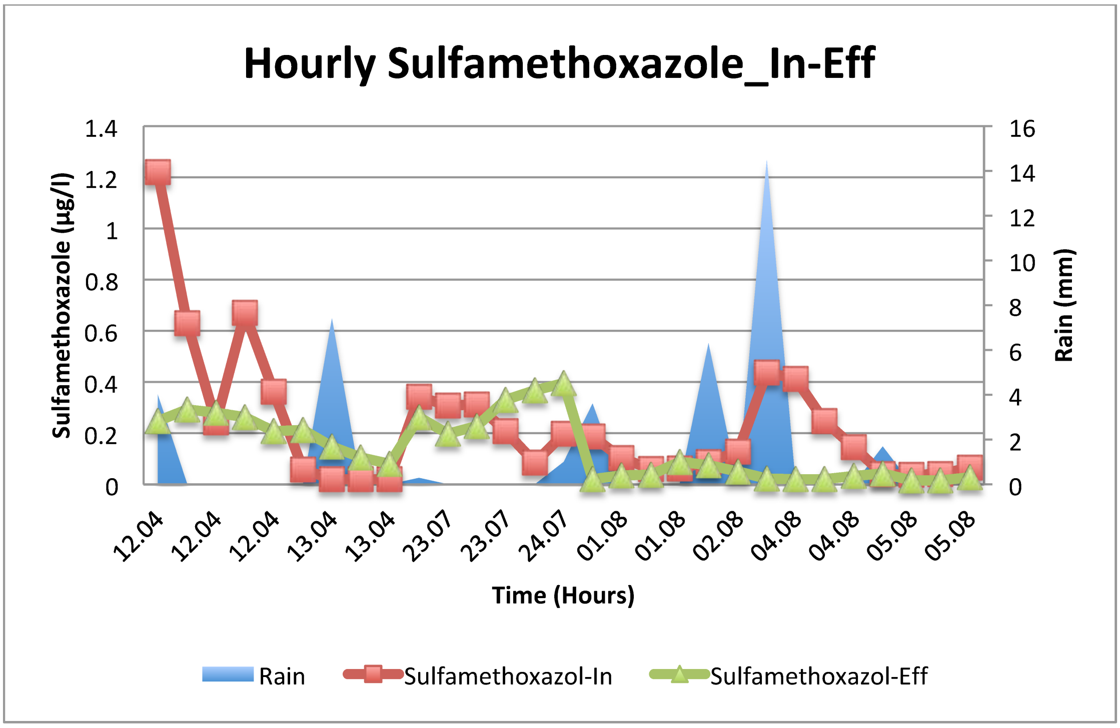


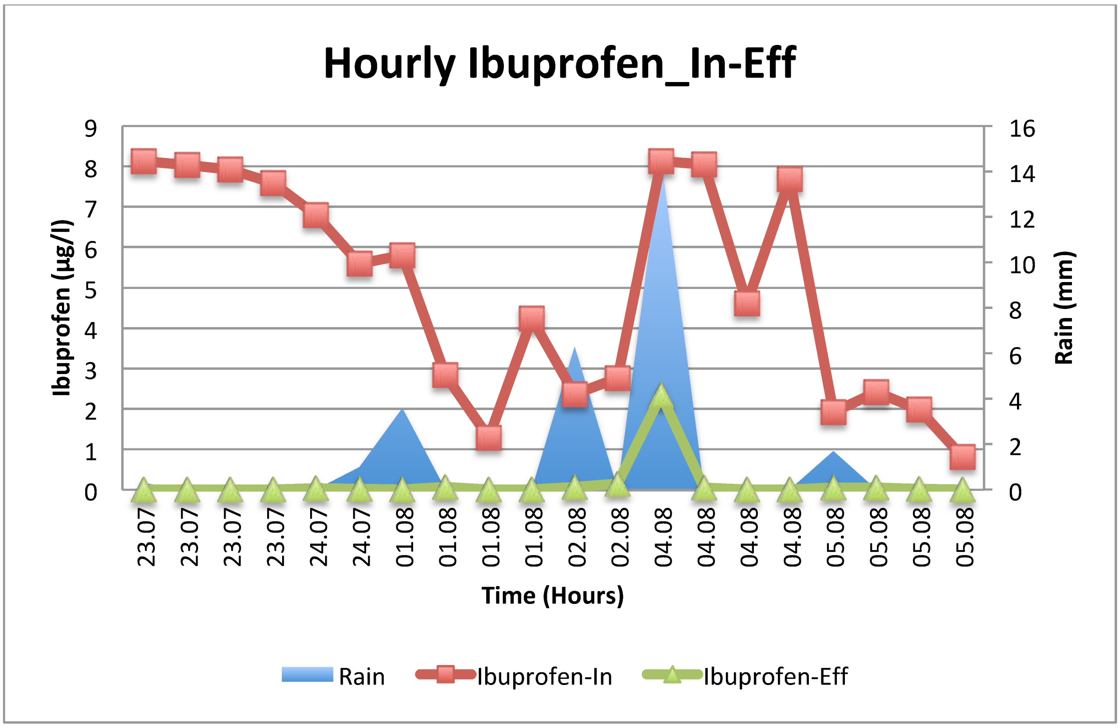
Diurnal Influent NH4-N_Load-Sulfametoxazole
NH4-N_Load (kg) and Rain (mm)
0
20
40
60
80
100
120
140
Sulfamethoxazole (µg/L)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Tue
Wed
Thu
Fri
Sat
Sun
Mon
Time (days)
Rain
NH4-N_Load
Sulfametoxazole

Appendix C

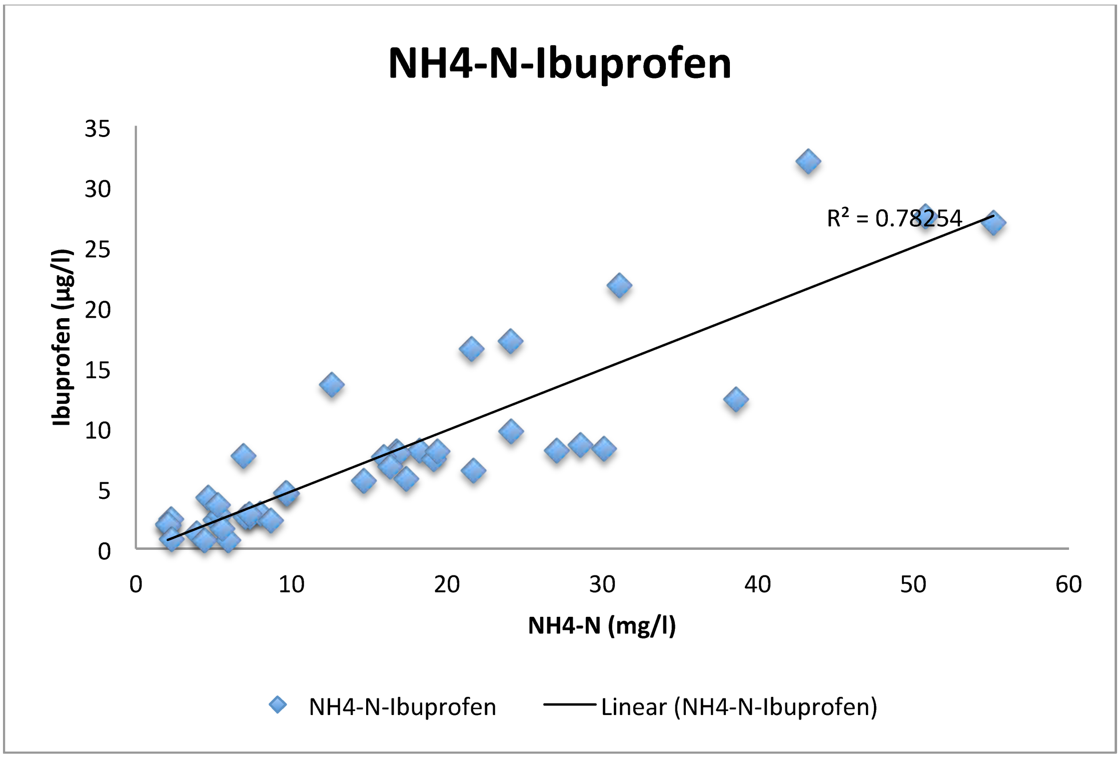

Diurnal Gabapentin_In-Eff
Gabapentin (µg/L)
Rain (mm)
12
10
8
6
4
2
0
6
5
4
3
2
1
0
Tue
Wed
Thu
Fri
Sat
Sun
Mon
Time (days)
Rain
Gabapentin-In
Gabapentin-Eff

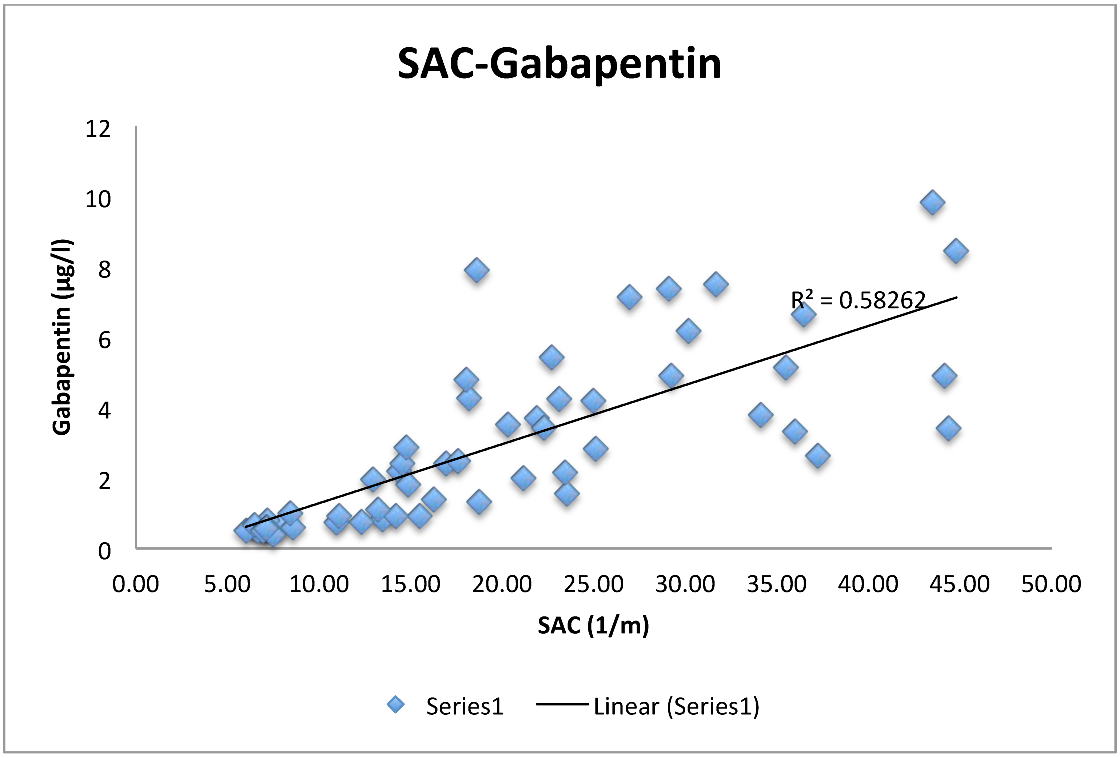

Hourly Gabapentin_In-Eff
Gabapentin (µg/l)
Rain (mm)
8
7
6
5
4
3
2
1
0
16
14
12
10
8
6
4
2
0
12.04
12.04
12.04
13.04
13.04
23.07
23.07
24.07
01.08
01.08
02.08
04.08
04.08
05.08
05.08
Time (Hours)
Rain
Gabapentin-In
Gabapentin-Eff


Hourly Sulfamethoxazole_In-Eff
Sulfamethoxazole (µg/l)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
16
14
12
10
8
6
4
2
0
Rain (mm)
12.04
12.04
12.04
13.04
13.04
23.07
23.07
24.07
01.08
01.08
02.08
04.08
04.08
05.08
05.08
Time (Hours)
Rain
Sulfamethoxazol-In
Sulfamethoxazol-Eff

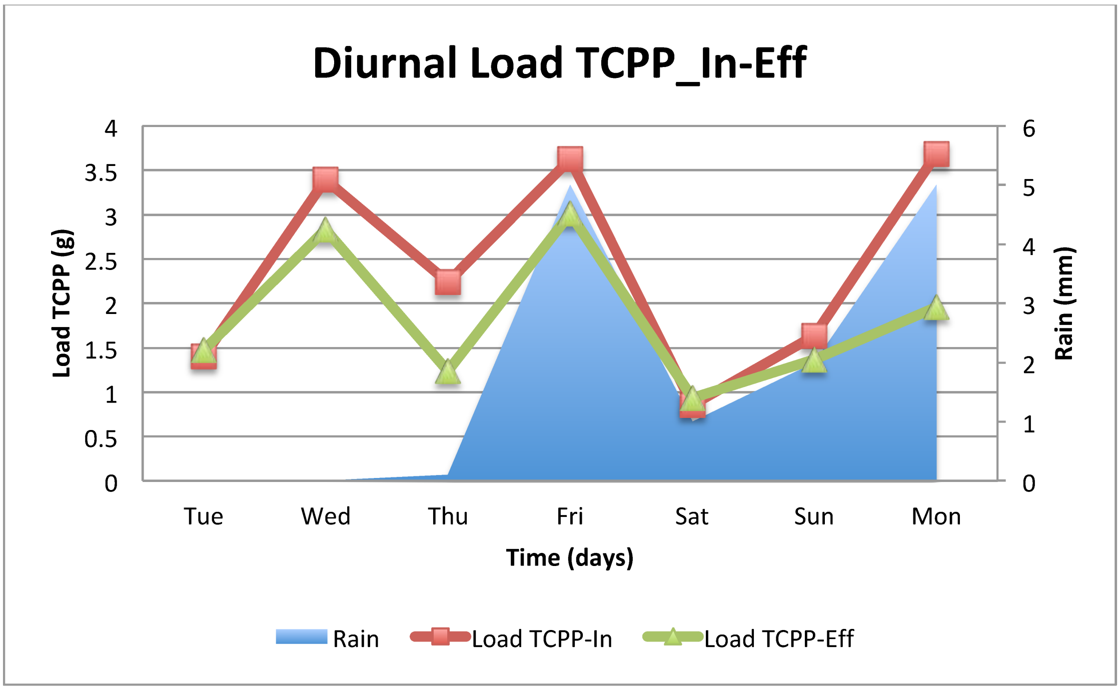

Hourly Ibuprofen_In-Eff
Ibuprofen (µg/l)
9
8
7
6
5
4
3
2
1
0
16
14
12
10
8
6
4
2
0
Rain (mm)
23.07
23.07
23.07
23.07
24.07
24.07
01.08
01.08
01.08
01.08
02.08
02.08
04.08
04.08
04.08
04.08
05.08
05.08
05.08
05.08
Time (Hours)
Rain
Ibuprofen-In
Ibuprofen-Eff

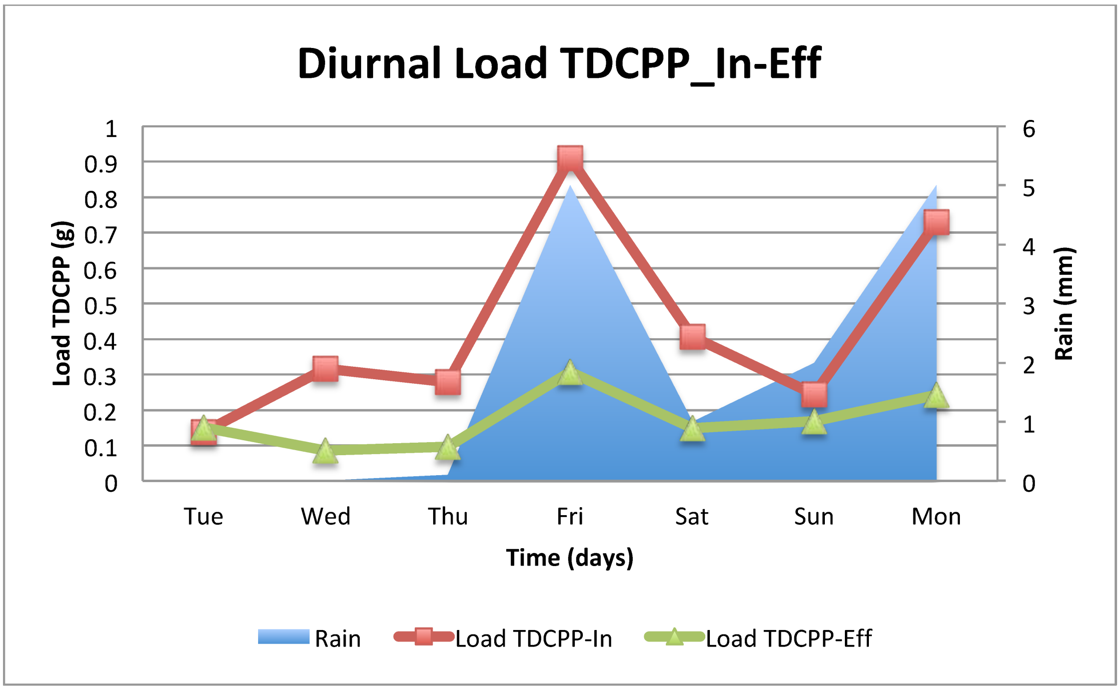
Appendix D


NH4-N-Ibuprofen
Ibuprofen (µg/l)
35
30
25
20
15
10
5
0
0
10
20
30
40
50
60
NH4-N (mg/l)
R² = 0.78254
NH4-N-Ibuprofen
Linear (NH4-N-Ibuprofen)


SAC-Gabapentin
Gabapentin (µg/l)
12
10
8
6
4
2
0
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
SAC (1/m)
R² = 0.58262
Series1
Linear (Series1)

Appendix E


Diurnal Load TCPP_In-Eff
Load TCPP (g)
4
3.5
3
2.5
2
1.5
1
0.5
0
Rain (mm)
6
5
4
3
2
1
0
Tue
Wed
Thu
Fri
Sat
Sun
Mon
Time (days)
Rain
Load TCPP-In
Load TCPP-Eff


Diurnal Load TDCPP_In-Eff
Load TDCPP (g)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Rain (mm)
6
5
4
3
2
1
0
Tue
Wed
Thu
Fri
Sat
Sun
Mon
Time (days)
Rain
Load TDCPP-In
Load TDCPP-Eff