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KONYA TECHNICAL UNIVERSITY  
INSTITUTE OF GRADUATE STUDIES**



**REMOVING OF ORGANIC MATTER,  
NUTRIENTS AND MICRO POLLUTANTS  
FROM WASTEWATER BY A SUBSURFACE-  
FLOW CONSTRUCTED WETLANDS**

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**Ph.D. THESIS**

**DEPARTMENT OF ENVIRONMENTAL  
ENGINEERING**

**May-2019  
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## TEZ KABUL VE ONAYI

Godfrey Fremeau TAHINDRAZANA tarafından hazırlanan “YÜZEYALTI AKIŞLI YAPAY SULAK ALANLAR İLE ATIKSULARDAN ORGANİK MADDE, NÜTRİYENT VE MİKROKİRLİTİCİLERİN GİDERİMİ” adlı tez çalışması 31/05/2019 tarihinde aşağıdaki jüri tarafından oy birliği / oy çokluğu ile Konya Teknik Üniversitesi Lisansüstü Eğitim Enstitüsü ÇEVRE MÜHENDİSLİĞİ Anabilim Dalı’nda DOKTORA TEZİ olarak kabul edilmiştir.

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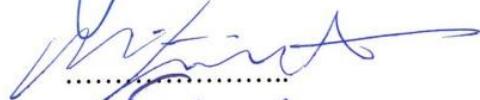
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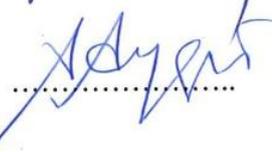
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Godfrey Fremeau TAHINDRAZANA

Tarih: 31.05.2019

**ÖZET****DOKTORA TEZİ****YÜZEYALTI AKIŞLI YAPAY SULAK ALANLAR İLE ATIKSULARDAN ORGANİK MADDE, NÜTRİENT VE MİKROKİRLETİCİLERİN GİDERİMİ****Godfrey Fremeau TAHINDRAZANA****Konya Teknik Üniversitesi  
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Türkiye’de küçük yerleşim yerlerinin atıksularının artırılmasında yaygın olarak kullanılan metotlardan biri yapay sulak alanlardır (YSA). Türkiye’de inşa edilen YSA’lar; proje, inşaat ve işletme aşamalarında yapılan bazı hatalar nedeni ile verimli bir şekilde işletilememektedir. Bu tez, Kâzımkarabekir (Karaman/Türkiye) ilçesinin atıksularını arıtan yüzeyaltı akışlı YSA’nın işletmeye alındığı ilk yılda ki performansının belirlenmesine odaklanmaktadır. Temmuz 2017 ve Mayıs 2018 arası 11 aylık sürede Kâzımkarabekir YSA tesisinde ham atıksudan ve YSA çıkışından alınan numunelerinde; KOİ, BOİ<sub>5</sub>, TN, TP ile ağır metaller, poli aromatik hidrokarbonlar ve farmasötikler gibi mikrokirleticilerin seviyeleri izlenmiştir. Organik madde, nütrient ve mikrokirletici gruplarında her parametrede farklı giderim verimleri belirlenmiştir. Organik madde giderim verimleri için; 136 mg/L giriş atıksu konsantrasyonuna sahip BOİ<sub>5</sub> parametresinin YSA’da iyi giderildiği ve giderim veriminin %82,4 olduğu, 435 mg/L olan giriş KOİ konsantrasyonunun %42,4 verimle giderildiği belirlenmiştir. Nütrientler için giderim verimleri; ham atıksuda 4 mg/L olan TP parametresinde %37,9, 46,6 mg/L olan TN parametresinde %26,4 olarak belirlenmiştir. Bu çalışmada mikrokirletici grubundaki ağır metaller için Ni, Cd, Pb ve Hg parametreleri izlenmiştir. 7527,5 ng/L giriş atıksu konsantrasyonuna sahip Ni parametresinde giderim verimi düşük ve %18,5 olarak tespit edilmiştir. 3215,8 ng/L atıksu konsantrasyonuna sahip Pb parametresinde giderim verimi %78 olarak tespit edilmiştir. Cd ve Hg parametrelerinde ise giderim verimlerinin sırasıyla %60 ve %54 olduğu tespit edilmiştir. Bu çalışmada belirlenen PAH grupları için giderim verimleri; 114,7 ng/L giriş atıksu konsantrasyonuna sahip Naftalin için %34,8, 22 ng/L giriş atıksu konsantrasyonuna sahip Fluoranthene için %45,7 ve 9,8 ng/L giriş atıksu konsantrasyonuna sahip Benzo[k]fluoranthene için %33,6 olarak belirlenmiştir. Ayrıca Benzo[b]fluoranthene ve Benzo(a)pyrene için düşük giderim verimleri tespit edilmiştir. Farmasötik grubunda yer alan 17 $\alpha$ -ethynyoestradiol ve 17 $\beta$ -estradiol parametrelerinin değerleri LOQ değerinin altında olduğundan atıksuda tespit edilememiştir. Giriş atıksu konsantrasyonu 1034,6 ng/L Diklofenak parametresi için giderim verimi %32,7 ve giriş atıksu konsantrasyonu 659,1 ng/L olan Karbamazepin parametresi için ise %46,9 olarak tespit edilmiştir. Kâzımkarabekir YSA’nın işletmeye alındığı ilk yılda konvansiyonel parametreleri giderme yanında mikrokirletici gideriminde de etkin olduğu belirlenmiştir.

**Anahtar Kelimeler:** Yapay Sulak Alan; Atıksu; Arıtma, Mikrokirleticiler, PhACs, PAHs, Ağır metaller

**ABSTRACT****Ph.D. THESIS****REMOVING OF ORGANIC MATTER, NUTRIENTS AND MICRO  
POLLUTANTS FROM WASTEWATER BY A SUBSURFACE-FLOW  
CONSTRUCTED WETLANDS****Godfrey Fremeau TAHINDRAZANA****Konya Technical University  
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Constructed wetlands (CWs) are widely used in the treatment of wastewater of small settlements in Turkey. CWs that were built in Turkey could not be operated efficiently due to some failing during project, construction and operation stage. This thesis focuses on determination of the performance of subsurface flow CWs, to treatment of domestic wastewaters from Kazımkarabekir (Karaman/Turkey) on the first year of operation. Between July 2017 and May 2018, wastewater samples were analysed for COD, BOD<sub>5</sub>, total nitrogen (TN), total phosphorus (TP), and micropollutants as heavy metals, poly aromatic hydrocarbons (PAHs) and pharmaceutical active compounds (PhACs) for a period of 11 months. The samples were taken from the raw wastewater and CWs effluent. The different removal efficiency was determined for nutrients, organic matters and micropollutants groups in each parameter. Removal efficiency was determined for organic matters; 82.4% in BOD<sub>5</sub> parameter with 136 mg/L influent concentrations and 42.4% in COD parameter with 435 mg/L influent concentrations. Removal efficiency was determined for nutrients; 37.9% in TP parameter with 4 mg/L influent concentrations and 26.4% in TN parameter with 46.6 mg/L influent concentrations. In this study, heavy metals in micropollutants groups were selected, as Ni, Cd, Pb and Hg. Ni parameter which had 7527.5 ng/L influent concentration removal efficiency was determined to be very low with 18.5 % only, and Pb parameter which had 3215.8 ng/L influent concentration removal efficiency was determined to be better with 78 %. In the Cd and Hg parameters, removal efficiencies were found to be 60% and 54%, respectively. Removal efficiency for determined PAH groups in this study has been identified; 34.8% in Naphthalene with 114.7 ng/L influent concentrations, 45.7% in Fluoranthene with 22 ng/L influent concentrations and 33.6% in Benzo[k]fluoranthene with 9,8 ng/L influent concentrations. In addition, for Benzo[b]fluoranthene and Benzo(a)pyrene removal efficiency was determined to be low. PhACs compounds were analysed in this study, with 17 $\alpha$ -ethynylroestradiol and 17 $\beta$ -estradiol didn't get the value because their concentration was below the LOQ. For Diclofenac which had 1034.6 ng/L influent concentrations removal efficiency was determined as 32.7% and for Carbamazepine which had 659.1 ng/L influent concentrations removal efficiency was determined as 46.9%. Kazımkarabekir CW was found to be effective in removing both conventional parameters and micropollutants in the first year of operating.

**Keywords:** Constructed Wetland; Wastewater; Treatment, Micropollutants, PhACs, PAHs, Heavy Metals

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**Abbreviations:**

**APHA:** American Public Health Association

**BCS:** Biopharmaceutics Classification System

**BOD:** Biological Oxygen Demand

**COD:** chemical oxygen demand

**CWs:** Constructed Wetlands

**DCM:** dichloromethane

**DNA:** DeoxyriboNucleic Acid

**EEC:** *European Economic Community*

**EPA:** Environmental Protection Agency

**FAS:** Ferrous Ammonium Sulphate

**FWS:** Free Water surface Flow

**GC:** Gas Chromatography

**HSF:** Horizontal Subsurface Flow

**IARC:** **International Agency for Research on Cancer**

**IED:** Industrial Emissions Directive

**IPPCD:** Integrated Pollution Prevention and Control Directive

**JMP:** Joint Monitoring Programme

**MCM:** *Million Cubic Meters*

**mg/l:** milligram per litre

**mL:** millilitre

**ND:** Nitrates Directive

**NH<sub>3</sub>:** Hydrogen nitride (ammonia)

**NIP:** National Implementation Plan

**NSAID:** Non-Steroidal Anti-Inflammatory Drug

**PAHs :** Polycyclic aromatic hydrocarbons

**PhACs:** Pharmaceutically active compounds

**ppb:** part per billion

**PPCPs:** Pharmaceuticals and Personal Care Products

**PPPD:** Plant Protection Products Directive

**QDNR:** Queensland Department of Natural Resources

**RSD:** Relative Standard Deviation,

**STP:** Sewage Treatment Plant

***TKN***: Total Kjeldahl nitrogen

**TN**: Total nitrogen

**TP**: Total phosphorus

**TSS**: Total Suspended Solids

**USP** : United Stat Pharmacopeial Convention

**UV**: Ultra Violet

**UWWTD**: Urban Waste Water Treatment Directive

**VSF**: Vertical Subsurface Flow

**WFD**: Water Framework Directive



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## 1. INTRODUCTION

### 1.1.General

Everyone understands that water is essential for life. But many people are just beginning now to realise how essential it is to everything in life and virtually all the products used on a daily basis, so Water is essential to feed the world. Water will become one of the scarcest resources in the near future due to massive worldwide increase in the human population (D. Day,1996). Without improved water resources management, the progress towards poverty reduction targets, the Millennium Development Goals, and sustainable development in all its economic, social and environmental dimensions, will be jeopardized. 91% of the global population uses an improved drinking water source of 96% from Urban otherwise 84% from rural (Organization et al., 2015).

Most of the human activities which use water produce wastewater. Inadequate management of urban, industrial and agricultural wastewater means drinking-water of hundreds of millions of people is dangerously contaminated or chemically polluted.

In general, the demand for water, quantity of wastewater produced and its overall pollution load are continuously increasing worldwide.

While wastewater is a serious problem of the management water cycles, after use, water is still seen as a burden to be disposed off or a nuisance to be ignored. The results of this neglect are now obvious. The wastewater has an impact and immediate effect as the degradation of aquatic ecosystems and waterborne illness come to the freshwater used, having far-reaching implications on the well-being of communities and peoples' livelihoods (World Water Development Report, 2017).

Water safety and quality are fundamental to human development and well-being. Increasing scarcity of good quality water resources is accelerating and the use of wastewater is trending upwards. Wastewater re-use, recovers and improves water, nutrients, or energy, and is gradually becoming an essential strategy. Providing safe water is one of the best instruments for better health and reducing poverty.

With the growing demand, wastewater treatment is considered to be a reliable alternative of water resources, wastewater management shifting paradigms from treatment and disposal, reuse cycle and recovery.

In that way, wastewater treatment is not a reliable problem, but a solution and challenge in the societies.

Looking on the aspects of water, ecosystem resources management and wastewater. The Council Directive 91/271/EEC relating to urban wastewater treatment was adopted on 21 May 1991, which had a target to protect the environment from discharges of urban wastewaters, industrial and collection, treatment and discharge of domestic wastewater, mixture of wastewater from certain industrial sectors (WFD, 1991).

Therefore, Turkey by the National Implementation Plan (NIP) established a policy of Water Framework Directive (WFD) to ensure efficient management of water, groundwater and wastewater, treating harmful priority substances and protection of nature. Turkey will face the challenge of transposing and implementation of all elements set out in the WFD. As the WFD has become part of the *acquis*, Turkey is obliged to comply with it by date of accession (Turkey's water policy: National Frameworks and International Cooperation: Vakur Sumer and Cagri Miluk).

In Turkey, municipales water discharged volume was increasing from 3,2 MCM in 2008 againts 1 million MCM in 1994, thus the water management and environment protection policy was established in the last three decades, (Aysegul K. and al, 2011).

The overall objective of IPA (Environment Operational Programme in Turkey) is to remote the environment programme and improve the environment protection for the living population and animals by supporting the environmental infrastructures.

In Turkey the basic principles for water quality classes and standards governing the discharges in industrial wastewaters to inland water underlie the Water Pollution Control Regulation passed in 1988 and published on 4 September 1988 in the Official Gazette. Target 6.3 by 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe re-use globally ([www.sdg6monitoring.org/](http://www.sdg6monitoring.org/)).

The challenges in the conceptual design of wastewater treatment plants are to remove the maximum high residuals and micro pollutants; and to supply the low cost and maintenance, easier to provide like a constructed wetland. The Constructed Wetlands has the same processes of removing, degrading and nutrient uptaking, by biological and physical processes. In Turkey, it is encouraged that the practical way of development of constructed wetands treatment (Korkusuz et al., 2002), Korkusuz

(2005) mentioning that there were no full-scale constructed wetlands until 2003. Turkey has 1720 WCs which serves 620.275 people, equivalent to 0,95% of the population, and 48 of those CWs are in Konya as inventorying in 2016 (Nas, 2017) among CWs found in Turkey, Konya, is Karabekir's CWs.

## **1.2.Objective of the Study**

CWs are widely used for the treatment of domestic wastewaters of small communities in Turkey. About 1720 CWs was built in the last 15 years in Turkey. CWs have several advantages included land intensive, low energy, easy operation and maintenance, low investment/operational costs, landscape aesthetics, reuse of waters, and increased wildlife habitat compared to conventional systems. CWs that build in Turkey could not be operated efficiently due to making some faults about its project, construction and operation stage.

The objective was to study the performance of subsurface flow constructed wetlands as a low-cost technology for treating domestic wastewater. This paper presents the design, construction and performance of a subsurface-flow constructed wetland system as used in Kazımkarabekir (Karaman) during the first years of operation under a variety of loading and operating conditions. The population of Kazımkarabekir is 3094 people.

Kazımkarabekir CW is the first CW project designed and constructed by Iller Bank. Therefore, it is very important to evaluate the treatment efficiency of this CW project. The performance of this plant in Turkey is important in terms of deciding whether the CW project will be made thereafter.

While the treatment performance of CW systems has been widely documented within the literature, documentation on performance during start-up stages has been limited. Seasonal changes were observed for carbonaceous biochemical oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP) removal effectiveness.

In addition, micropollutant removal was investigated in the Kazımkarabekir CW plant. The removal efficiencies of 16 micropollutants with heavy metals, Poly-Aromatic Hydrocarbons and Pharmaceutical Active Compounds were investigated from micropollutant groups.

## 2. LITERATURE

Wastewater is water from different used and has a compound including dissolved contaminants, suspended solids (substitution of material faeces, food and vegetable preparation materials, fat...), and micro-organisms (bacteria,...) (Organization, 2006). The sources of wastewater in the world are from, domestic sewage, industrials and factories, agriculture and farms. So, the wastewater considered to be polluted by the environment and needed to be treated. To manage the wastewater, it requires knowledge of the wastewater characteristics (Otis et al., 1980). The principal target of wastewater treatment is to get out the danger dispothe the wastewater to the human health and allowing the industrial used and avoid the damage in the nature (Pescod, 1992).

In the wastewater, there are many compounds; like a nutrients, as valuable nutrients contained in wastewater are nitrogen, phosphorus, potassium,..., The nutrients origine sources in water are commonly the specific discharge locations, municipal waste systems and industries, agricultural and storm water runoffs; and organic matters release by human or organisms and into of degradation and reacting of the non leaving , they secreting the organic materials into their environment; and the hazardous pollutants like Heavy Metals, pharmaceuticals compounds, pesticides, and micro organisms; so those solids compounds presented 0,1% only of the wastewater if still 99,9 % remained is the water (Sperling, 2007).

### 2.1. Sources of Micropollutants in Wastewater

A micro pollutant is a residue from substances used non-biodegradable and run in our waters like pesticides, heavy metals, hormones, industrial chemicals and pharmaceuticals. It is a growing problem in our water environment because it remains a long-term hazardous in our ecosystems.

In environment, there are many different sources of micropollutants in wastewater. The main sources of micro pollutants are household uses and industrial discharge, stormwater runoff from cities, and surface run-off from agricultural areas.

### **2.1.1. Source of poly aromatic hydrocarbon**

PAHs are aromatic hydrocarbons with two or more fused benzene rings, formed during the thermal decomposition of organic molecules and their subsequent recombination (Haritash and Kaushik, 2009), coming as a result of pyrolytic processes, incomplete combustion of organic materials of human activities and industrials, like a coal, crude oil; and combustion of natural gas, heating and vehicle; in natural processes as carbonization (Organization, 2000).

PAHs are one of the interesting micro pollutants. The three types of PAHs resources are: pyrogenic, petrogenic and biological which is the main source of PAHs in environment (Abdel-Shafy and Mansour, 2016).

The atmosphere is one of the sources of PAHs in wastewater. The air has gases, aerosols, and particulates, which from the sea salt, volcanic aerosols, extra terrestrial matter, mineral dusts; and sources from the factories like transportation emissions, coal combustion; and fugitive particulate (Bradl, 2005), with the run fall. Those particles are trapped by precipitation and mixed with run off. By sewage treatments plants, the PAHs come into the waters and water surfaces to directly deposit, erosion and run-off (Umweltbundesamt, 2016). Others natural sources of PAHs are volcanic eruption, forest fires, exudates from trees and oil seeps. And the anthropogenic sources are coal tar, refuse, burning of fossil fuel, wood, garbage, used lubricating oil and oil filteres (Haritash and Kaushik, 2009).

### **2.1.2. Sources of heavy metals**

Heavy metals are among these polluting substances in the water. They are accumulated and transported easily in the environment. Heavy metals are occurring elements which have a high atomic weight. The density of toxicity depends on several factors such as dose, route exposure and chemical species. Heavy metals known as naturally occurring elements that have a high atomic weight, a density and toxic which depends on several factors including the dose, route of exposure, and chemical species. In addition, the nutritional status of individuals exposed in age gender, genetics (Tchounwou et al., 2012).

The anthropogenic sources of heavy metals in wastewater is human activities; among the agriculture activities like fertilizers, animal manures and pesticides used. The metallurgical activities are the mining, smelting, metal finishing; and others like energy

of transportation and production, waste disposal and microelectronic (Bradl, 2005). The Geologic is one of the heavy metals in environment which include trace elements from the crystal lattice, which is the primary minerals source forming during the cooling of the magma (Bradl, 2005). Among the geological sources are all types of rocks like rock igneous, sedimentary and metamorphic, which give up during the interaction with the environment transported and redistributed in surrounding with the phenome of rock cycle in general, weathering, soil formation and erosion, (Kobielska et al., 2018), and mixing with the water and wastewater.

### **2.1.3. Sources of pharmaceutical active compounds**

Human increase the usage of pharmaceutical compounds for medicinal, industries and agriculture like personal care and synthetic hormones; and now it is becoming a new problem of environment concerning the resources institutions and drinking water companies. The PhACs is among the micro pollutants found in the aquatic environment. They are from different sources like human and animals excretions, landfill leaching, improper disposal and manure or biosolids applications (Jayasiri et al., 2013). Also PhACs are introduced in wastewater mainly through ingested medicines excreted as un-metabolized parent compounds (or reactive metabolites) via urine, production facilities, hospitals and disposal of toilet medications (Wang et al., 2017). They are also used in farming as well as in asuaculture, as a veterinary drugs, feed additives, those activities become the most source of PhACs (Li and Randak, 2009). So, the PhACs have detected in the effluents of the wastewater treatment plants in many countries into the surface waters, seawaters, groundwaters and drinking waters (Fent et al., 2006) because some pollutants are not removed during the wastewater treatment. In wastewater, most variety of PhACs comes from the domestical sewage, hospital and others human activities which use drugs. The pollutants are metabolized after human intake and then left at the compounds not completely metabolized, hence excreted and finished in the sewage (Hijosa-Valsero et al., 2016).

## **2.2. Impacts of Organic Matter and Nutrients in Environment**

The effects of wastewater in the environment are largely negative. In the environment, 1,2 trillion gallons of raw sewage are estimated to be coming into the water bodies per year, which come from the untreated industrial wastewater, storm

water and runoff (EPA,1994a) and every ecosystem is contaminated by toxic chemicals sewage, other man-made forms of waste, and finally putting ecosystems at a serious risk.

The nutrients in wastewater have an impact in environment, the existence of nutrient causes harmful algal blooms and damage the environment and can create dead zones known as hypoxia. Human activities increased the rate of nitrogen and phosphorus in the water environment for the past several decades, they are impacting the rivers, lakes, bays, streams and coastal waters; which affected human health and environment and have an impact in economy (<https://www.epa.gov>). The high rate of the nitrogen and phosphorus in the water provoke the bloom algal in marine ecosystem, the bloom algal means harmful for the aquatic life, by decreasing the oxygen, prevent the photosynthesis, create the anoxic area; leading to unfavorable condition of fish and other aquatic animals, and impacting the human also by contaminated the water (<https://www.epa.gov>)

Other impact, nitrogen is limitation of plant productivity by nitrogen, Nitrogen is a primary limitation to plant productivity, primary environment source of pollution via gaseous and leaching (Udvardi et al., 2015), increasing the rate of nitrogen gaseous in environment as N<sub>2</sub>O causes the greenhouse gas, and as the NH<sub>3</sub> rising the ecological balances of ecosystem, so the soluble nitrogen into runoff of leachages come into the rivers, groundwater and streams (Follett and Hatfield, 2001), as Follett (Follett and Hatfield, 2001) described, even there have a benefits of nitrogen, but it is harmful effects for human and animals as well as ecological and environment.

Phosphorus can be found in most of the environment also by human activities, and natural cycles, phosphorus have a resulted in the environment (Liu et al., 2008).

Phosphates have many effects upon organisms alive. In aquatic ecosystems, when the phosphorus introduced into an aquatic ecosystem, the aquatic plant biomass increased and caused the algal blooms, which can have a negative effect on the aquatic ecosystem as decreasing the amount of light infiltration; in the bottom, the attached Phosphorus contributes to long term of Phosphorus which additions in bottom the sediments.

In Agricultural, phosphorus leachate from agriculture increase the fertility of waters in nutrients and caused the eutrophication, the surface involves a combination of high potential of phosphorus and favour condition (Mullins, 2009).

## **2.2.Impacts of Micropollutants in Environment**

### **2.2.1. Impacts of poly-aromatic hydrocarbons**

The presence of micro pollutants in wastewater has effects in the environment especially in the water, soil and human life.

PAHs are released into the air, to soil or water. The PAHs are introducing by water, air and soil by toxic substance, wastewater contaminated the microorganisms in environment (Igwe and Ikaogo, 2015). The PAHs movements depends of their properties such as easily dissolve in water and evaporate in air (Van Jaarsveld et al., 1997). As the PAHs insoluble in water, they are adsorbed on particulate and precipitated in the bottom, or solubilized in the lakes and rivers and contaminate the water (Igwe and Ikaogo, 2015), PAHs have an impact to aquatic life and birds with their high toxicity. Many PAHs toxic are mutagenic and classified as have carcinogenic properties, but not totally direct, over wise it is their reactive metabolic intermediates initiate the carcinogenesis. Humans are exposed to PAHs through dermal contact with air, soil and dust, and consumption of food and drinking water (Choi et al., 2010).

### **2.2.2. Impacts of pharmaceutical active compounds**

Pharmaceutical substances have been detected more than 600 in different environmental matrices worldwide as in surface water, ground water, drinking water and soil (Küster and Adler, 2014), most of them come from of human excretion result by metabolisms, intact from disposal of unwated and expired medicinal from domestical sewage and into the environment (Fick et al., 2009), as the pharmaceuticals become a positives treatment of human and animals, their improper use become a serious problem od environment (Shaaban, 2017). Depends on the sorption behaviour of the compound in soils, sediment water and treatment wastewater have been on which degree to transported in the environment (Boxall, 2004).

Once in the environment, the pharmaceuticals compounds will be distributed and transported by water, air and sol (Boxall, 2004); the distribution depends and effects the physic-chemical and characteristics of the compounds (Boxall, 2004); and the residues of compounds are designed to positively affect the physiological of the human health (Jayasiri et al., 2013) and affect also the animals having identical similar organs, tissus, cells or biomolecules (Hijosa-Valsero et al., 2016); the effect of animals of compounds

have been measured at concentration which may cause adverse effects of the residence aquatics (Jayasiri et al., 2013), the residual in aquatic environment on vertebrates is as a realistic concentration, and in invertebrates, as algae are sensitive also in the pharmaceutical compounds residual like *P. Subcapitata* (Li and Randak, 2009), *Daphnia magna* (Webb, 2001). Continual discharge of pharmaceuticals into the environmental compartments at these levels poses a chronic threat to human and wildlife (Küster and Adler, 2014).

### **2.2.3. Impacts of heavy metals**

Contamination of heavy metals has devastating the ecologic effects in environment (Sadiya Binte Swaleh, 2016). The heavy metals come from consumer waste and leachage from industry pollute the water sources as groundwater, lakes, streams, rivers; and acid rain exacerbate this process to realising the heavy metals in soils (Rajeswari and Sailaja, 2014). The heavy metals emissions in environment is provided by a wide range of the process and pathways, as well as in the air like combustion and extraction; to surface waters via runoff, transport and releases from storage; and soil via groundwaters and crops (Järup, 2003). So they are in environmental under pollutant category reason of their effects of toxicity in human, animals and plants, the contaminant may due by cycle of feeding, the plants are exposed to heavy metals by plants uptake, and human and animals eat the plants.

The contamination of heavy metals in water environment are becoming a serious problems of the toxicity of nature (Atieh et al., 2017), because the metal harm an aquatic organisms, the organisms though lethal and sub-lethal increased the susceptibility to fish disease and provoke a mortality and decreased the fecundity; uncontrolled discharges have disturbed the organism may cause death and finally extinction as an effect of some important species of fish (Sadiya Binte Swaleh, 2016). The aquatic life like algae, invertebrates and fish accumulate the trace of heavy metals to orders of magnitude of thousands to millions times (Kibria, 2014). Bioaccumulation and biomagnification has caused detrimental effect on the organism's body and also on several organs including digestive and reproductive health (Sadiya Binte Swaleh, 2016). As their hard to metabolize, the heavy metals can gathering in organisms (Rajeswari and Sailaja, 2014).

### **2.3. Constructed Wetlands for Wastewater Treatment**

Wetlands are among the most productive ecosystems in the world. It plays an integral role in the ecology of the watershed, the presence of water in wetlands creates the conditions favourable for growth of adapted plants like hydrophytes; and ameliorate a characteristic of wetland soil hydricity (EPA, 2006). Different types of life are found in wetland ecosystem, the microorganism's microbes, algae, bacteria; to macroorganisms as insects, amphibians, fish, birds, .... The topology of the wetlands and physical chemical features as climate, geological, the movement and abundance of water establish the life of plants and animals in wetland ecosystems ([www.epa.gov/wetlands](http://www.epa.gov/wetlands)).

Constructed wetlands are among the wastewater treatment plants, consisting the shallow ponds artificial; not only including natural marsh and swamp but artificial basin storage also, and create an habitat of aquatic life, wetland have more limited objectives of flood and pollution removed (Ellis et al., 2003), constructed wetlands basin filled the substrate as the filter like a sand or gravel, and vegetation which tolerate the condition (UN-HABITAT, 2008); and clay or synthetic liners and engineered structures flow control, water level and liquid detention time. The porosity containing inert like a rock and sand depends on the system (EPA, 2000).

Constructed Wetlands are investigating to be able removed the various pollutants and microbiological pollution from sewage wastewater; and have been designed to removed the nitrogen organic matter, suspended solids (Alexandros and Akratos, 2016); which have a biological, physical and chemical processes by the aquatic plants planted with (EPA, 2000), Kadlec reported also that they can used for different types of wastewater as secondary treatment, and viable for removing nutrients and other contaminants (Kadlec and Wallace, 2008).

The removal processes in constructed wetlands are in different way showing in Table 2.1. below, biological process by metabolic process, physical process and chemical process.

Table 2.1. Overview of Pollutant Removal Process (Kinsley et al., 2007).

<b>Pollutants</b>	<b>Removal Process</b>
Organic Material	biological degradation, sedimentation, microbial uptake
Organic Contaminants	adsorption, volatilization, photolysis, biotic/abiotic degradation
Suspended solids	sedimentation, filtration
Nitrogen	sedimentation, nitrification/denitrification, microbial uptake, plant uptake, volatilization
Phosphorus	sedimentation, filtration, adsorption, plant & microbial uptake
Pathogens	natural die-off, sedimentation, filtration, adsorption
Heavy metals	sedimentation, adsorption, plant uptake

The warmer regions have advantage for their climate in constructed wetlands, their have the best successful in the treatment, but the studies in the cool regions demonstrated the feasibility of removal of the cooler regions (Wittgren and Maehlum, 1997). The climate is important because the growth tissuus macrophytes for constructed wetlands used is follow a common seasonal in temperate climates (Kadlec and Wallace, 2008).

### **2.3.1. Ecology of constructed wetlands**

The constructed wetlands vegetations are essentials in component systems, and they play an important role in removal proses in the wastewater treatment (Brix, 2003). Almost the macrophyte plantes are the aquatic plants used for constructed wetlands, it used of the reason of the ability grow in or near of water; and also in constructed wetlands, their are mosses and some large algae be able to do the photosythese assimilate the inorganic carbon to produce organic matter, which provides source of energy for the heterotrophs , (Brix, 2003). Macrophytic plants provide much of the visible structure of wetland treatment systems (Kadlec and Wallace, 2008) and provide

a substrate for microorganisms, which are the most important processors of wastewater contaminants (Kadlec and Wallace, 2008) and also stabilise the surface of the beds, provide good conditions for physical filtration, prevent vertical flow systems from clogging, insulate the surface against frost during winter, and provide a huge surface area for attached microbial growth (Brix, 1997). They are many types of macrophyte in wetlands and constructed wetlands, the emergent aquatic macrophyte, floating-leaves aquatic macrophytes and submerged aquatic microphytes (Vymazal, 2008).

As a physical effect of presence of the macrophytes in constructed wetlands the presence of vegetation in wetlands distributes and reduces the current velocities of the water (Petticrew and Kalff, 1992), (Somes et al., 1996), creating better conditions for sedimentation of suspended solids, reduces the risk of erosion and re-suspension, and increases the contact time between the water and the plant surface areas and also important for stabilising the soil surface in treatment wetlands, as their dense root systems impede the formation of erosion channels (Brix, 1997). In vertical flow systems (VFS) they are an intermittent loading regime, helps to prevent clogging of the medium (Bahlo and Wach, 1990).

Macrophytes facilitate the soil hydraulic conductivity. In constructed wetlands with subsurface horizontal water flow, the living and dead roots and rhizomes create soil pores, as the roots and rhizomes grow they disturb and loosen the soil (Brix, 1997), when the roots and rhizomes die and decay, they may leave behind tubular pores and channels (macropores), which are thought by some to increase and stabilise the hydraulic conductivity of the soil (Kickuth, 1981). In vertical flow constructed wetlands and sludge mineralization beds, the development and growth of plants are important to counteract clogging, the root growth and the physical presence of the stems that moves by the action of wind keeps the bed substrate permeable to water (Brix, 1997).

The pollutant removal performance of vegetated submerged bed systems depends on many factors including influent wastewater quality, hydraulic and pollutant loading, climate, and the physical characteristics of the system (EPA, 2000). There are many general functions of vegetation in wetlands, like give a surface area for microbial growth, the stems and leaves of macrophytes that are submerged in the water column provide a huge surface area for biofilms (Gumbrecht, 1993b) and plant uptake is the principal removal mechanism only for some pollutants (Kadlec and Wallace, 2008). Physical functions include transpiration, show resistance, and particulate trapping, all of which are related to vegetation type and density (Kadlec and Wallace, 2008); the

metabolism of the macrophytes affects the treatment processes to different extents depending on the type of the constructed wetland (Brix, 1997).

The submerged stems and leaves of macrophytes in column of water surface provide a biofilms area (Gumbrecht, 1993a), (Gumbrecht, 1993b), (Chappell and Goulder, 1994). The algae, bacteria and protozoa photosynthetic colonized the dense communities of plant tissues. Likewise, the roots and rhizomes of the plants which are buried in soil of wetlands offer a substrate for attached growth of microorganisms (Hofmann, 1986). Thus, the substrat present biofilms which are above and below ground tissues of the macrophytes. And these biofilms formed a solid surface which include dead macrophyte tissues, that are responsible for the most of the microbial processing that occurs in constructed wetlands (Brix, 1997).

The roots of macrophytes assimilated nutrient by plant uptake. Macrophytes take up nutrients through their root systems and this uptake is also provided through immersed stems and leaves from the surrounding water (Brix, 1997).

The important of macrophytes is that their root release oxygen into the rhizosphere which then release biogeochemical cycles in the sediments, and give an effect on the redox status of the rediments (Barko et al., 1991); (Sorrell and Boon, 1992). Those oxygene releasings depend on the internal concentration of oxygen and the oxygen demand of the surrounding medium as well as permeability of the root-walls (Sorrell and Armstrong, 1994).

In the biological process, vegetations played a key role in the removal process at the constructed wetlands for the treatment of wastewaters.

The wetlands supply favourable environment conditions for the growth of microscopic organisms (Kadlec and Wallace, 2008) such as bacteria, micro-algae and fungi. They play an important key role in the removal of organic matters and pollutants in wetlands. The organisms also have a role of assimilation, transformation and recycling of the chemical constituents from wastewater coming into the constructed(Kadlec and Wallace, 2008).

In the constructed wetlands, plants and organisms have mechanisms. The root zones of plant have ability of assimilation and removal of contaminants, and supply the oxygen which is crucial for the activity and metabolism performed by microorganisms around of root zone (Stottmeister et al., 2003)

The microbial communities are responsible for the majority of the constituents degradations in wastewater. They facilitate water treatment through metabolic actions (Weber, 2016).

Equation based of CWs is as shown below:

$$Ah = \frac{Qd (\ln C_i - \ln C_e)}{KBOD} \quad (2.2)$$

KBOD

Ah = Surface area of bed (m<sup>2</sup>)

- Qd = average daily flow rate of sewage (m<sup>3</sup>/d)
- C<sub>i</sub> = influent BOD5 concentration (mg/l)
- C<sub>e</sub> = effluent BOD5 concentration (mg/l)
- KBOD = rate constant (m/d)

KBOD is determined from the expression  $KTdn$ , where,

- $K_T = K_{20} (1.06)^{(T-20)}$
- $K_{20}$  = rate constant at 20 oC (d<sup>-1</sup>)
- T = operational temperature of system (°C)
- d = depth of water column (m)
- n = porosity of the substrate medium (percentage expressed as fraction)

(UN-Habitat, 2008)

### 2.3.1. Type of constructed wetlands

The type of constructed wetlands depends on water flow regime, classified as Free Water Surface (FWS) and Sub Surface Flow too. It is also classified according to the type of macrophyte plant as well as flow direction. Different types of CWs can be combined to each other on hybrid systems in order to exploit the specific advantages of different systems (Hoffmann et al., 2011).

There are 2 design types of constructed wetlands according to the primary purpose in treatment: subsurface-flow and free water surface or surface-flow. These types are different in their main design characteristics as the processes responsible for removal of pollution (Vymazal, 2010). So there are three types of wetlands in widely used (Kadlec and Wallace, 2008):

- Free water surface (FWS)
- Horizontal subsurface (HSSF)
- Vertical (VF)

#### 2.3.1.1. Free water surface

The free water surface (FWS) (Figure 2.1.) is a open area constructed wetland with a floating vegetation and emergent plants (Kadlec and Wallace, 2008). The first FWS was established in North America, from 1960s to 1970s to treat wastewater with an ecological engineering of natural wetlands (Vymazal, 2008).

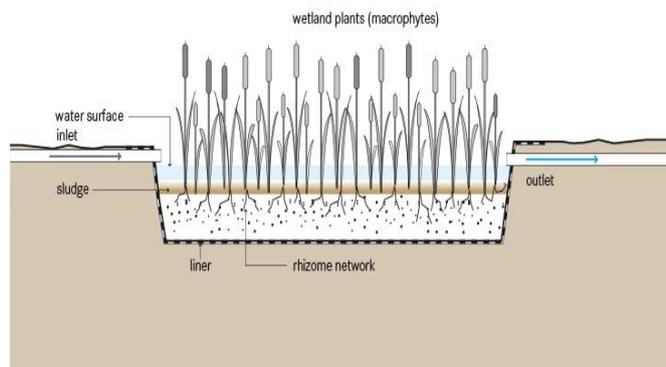


Figure 2.1 Free Water Surface constructed wetlands system (Tilley, 2014)

Free water surface (FWS) look in appearance and function resemble to the natural wetlands, with emergent vegetation, open waters combinations and water depths, and other similar features (EPA, 2000).

The FWS can treat municipal and industrial wastewater, with a suitable variety of dilute flows. It's not expensive to build. However, it needs a wide range area of land for establishment. Besides municipal wastewater; FWS CWs with emergent vegetation has also been used to treat various types of wastewaters (Vymazal, 2010), and with floating plants submerged and emergent vegetation inside (Sa'at and Kamariah, 2006); (Tilley, 2014).

The Free Water Surface is with emergent macrophytes with shallow depth basin containing 20-30 cm of soil root with 20-40 cm of depth (Vymazal, 2010). With a dense cover emergent vegetations of the surface, more than 50% of area is surrounded (Vymazal, 2010). The emergent vegetative macrophytes species in FWS are: *Phragmites australis* (Common reed), *Scirpus* (Schoenoplectus) *lacustris*; *Typha* spp. (Cattail), *Scirpus* spp. (Bulrush), *Sagittaria latifolia* (Arrowhead) , *Bolboschoenus* (Scirpus) *fluviatilis* (Marsh clubrush), *Eleocharis spicelata* (Tall spikerush), *Scirpus tubernaemontani* (= *Scirpus validus*) (Vymazal, 2010), mixed with diverse microorganisms bacteria which grow and submerge aquatic stems and root. These have a particular importance role for removal of the BOD5 in wastewater (EPA, 1988a).

#### **2.3.1.2. Sub surface flow constructed wetlands**

The subsurface flow (SSF) wetland also has a barrier of seepage prevention. It consists of basin or channel, but the bed depth contain porous media (EPA, 1988b). The bed media contained in SSF wetlands are such as crushed rock, gravel, small stones, sand or soil; and have aquatic plants planted with. When properly designed and operated, the wastewater flows under the surface media to contact the roots and rhizomes of the macrophytes vegetations. Unlike FWS, the SSF is not suitable for the living wildlife (EPA, 2000).

There are two types of flow in SSF; either the water flows horizontally or parallel to the surface; or flows vertically through the matrix of the systems. This is majority of planted layers. As it is an artificial wetland, the filled basin is impermeable on the bottom, and have a depth of 60 cm with a gravel layer or rocks of 10-20 mm of grain (Vymazal, 2010).

The main direction flow of the horizontal and vertical flow makes them to be different. The SSF can be further categorized into two types based on the pattern of flow; one with horizontal subsurface (HSSF) and one with vertical subsurface flow (VSSF) (Crites and Technobanoglous, 1998). The kind of emergent vegetations most frequent in SSF are reeds, bulrushes, cattails, sedges and rushes (EPA, 1988a). As indicated in the Table 2.3 below, the SSF has its particular advantages and disadvantages depending on the parameters and target of the building.

Table 2.3. Advantage and disadvantages of sub surface flow constructed wetlands (EPA, 2000).

<b>Advantages</b>	<b>Disadvantages</b>
Supply an effective passive treatment manner, and require minimum mechanisms equipment, energy and operation skilled	Require a wide area for establishment as compared to the treatment processes conventional.
Cost less expensive to build, operate and to maintain as compared to conventional treatment processes	Be able to remove BOD, COD, and nitrogen in renewable process. And can removed phosphorus, heavy metals, organic persistent.
Secondary operation treatment possible in year round only not in cold climates.	Reduction of rate removal in low temperature i.e cold winters, low rate removal of BOD, NH <sub>3</sub> , and NO <sub>3</sub> . Otherwise the retention time increased
Tertiary treatment possible and year round operation advanced in warm or moderate climate which is favourable. The wetland SF supply more thermal protection than FSW	With anoxic water contain provoke the limitation of potential nitrifications of the treatment to ammonia. Increasing the detention time and size of wetland, but this may not be cost effective.
The systems not produce the residual biosolids or sludge which requires the subsequent disposal and treatment.	Can remove the fecal coliform atleast by one log, but not sufficient to meet the discharged UV disinfection which has been successfully used in a number of applications.
Effective wetland and reliable for removal of BOD, COD, TSS, metals, and some persistent organics in municipal wastewaters. The removal of nitrogen and phosphorus to low levels is also possible but requires a much longer detention time.	SF can be smaller in size than FSW for the constituents removal
Mosquitoes and similar insect vectors are not a problem with SF wetlands as long as the system is properly operated and a subsurface water level maintained.	

### 2.3.1.3. Horizontal sub surface flow constructed wetlands

Horizontal sub surface flow constructed wetlands (HSSF CWs) (Figure 2.2) are compounds of sand filled basin and large gravel, with plant vegetation and substrate with filter material. The substrate filters out particles and microorganisms, and

degrades organic matters as well as removing suspended solids. The wastewater flow in inlet is fed slowly to the porous substrate under surface bed horizontally until it reaches the outlet zone (UN-HABITAT, 2008). HSSF is classified as a secondary treatment and can treat the industrial and municipal sewage wastewater and also can be used as a tertiary treatment for plants.

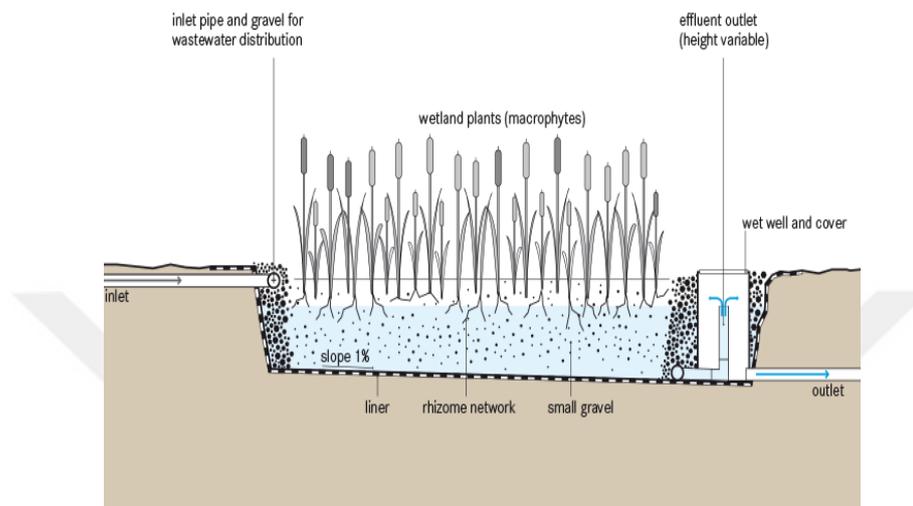


Figure 2.2. Horizontal Flow Constructed Wetland system (Tilley, 2014)

In Europe, normally most HSSF have had depth of 60 cm (Cooper et al., 1997). Unlike in the United States, HSSF wetland designed have beds of 30 cm-45cm in depth (Steiner and Watson, 1993), making them shallower than the HSSF in Europe.

The outlet and inlet media of HSSF is between 40-80 mm in diameter, so as to minimize the clogging and should extend to the top from the bottom; and the substrate size should be in the norm, and inlet and outlet zones should be 5-20 mm (UN-HABITAT, 2008). But EPA reports that the treatment zone size will be better with a size of 10-60 mm. It doesn't appear to be a clear advantage for removal of the pollutants with that size (EPA, 2000).

HSSF CWs Bed cross section area equation for (UN-HABITAT, 2008) is:

$$A_c = Q_s / K_f (dH/ds) \quad (2.6)$$

- $A_c$  = Cross sectional area of the bed (m<sup>2</sup>)
- $Q_s$  = average flow (m<sup>3</sup>/s)
- $K_f$  = hydraulic conductivity of the fully developed bed (m/s)
- $dH/ds$  = slope of bottom of the bed (m/m)

For graded gravels a value of  $K_f$  of  $1 \times 10^{-3}$  to  $3 \times 10^{-3}$  m/s is normally chosen.

### 2.3.1.4. Vertical sub surface flow constructed wetlands

Vertical Sub Surface Flow (VSSF) constructed wetland an artificial wetlands with a sand or gravel bottom and flot bed of sand or gavel, with vegetation macrophytes , the wastewater feeding is from in top and percolates through the bed to down finish by collecting in the drainage at the base (UN-HABITAT, 2008). Figure 2.3 shows VSSF CW System (Tilley, 2014).

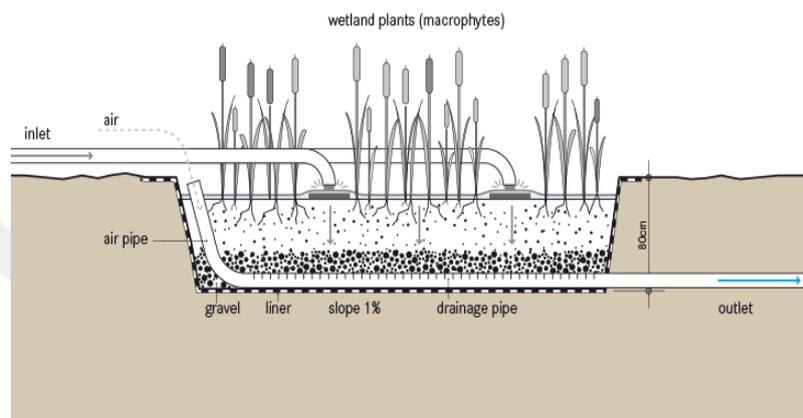


Figure 2.3. Vertical Flow (VF) Constructed Wetland System (Tilley, 2014).

Compared to HSSF, the VSSF systems have a large built with a large depths. In UK, the VSSF systems have a depth of 50-80 cm (Cooper et al., 1997), in Denmark recommended the minimum depth of 100 cm (Brix, 2003). The VSSF systems in Nepal have a same recommendation as in Danemark with 100 cm deep, but nowadays its shallow depther is being applied. The sand granular used between 0-4 mm as a substrate with  $d_{10} > 0.3$  mm,  $d_{60}/d_{10} < 4$  and having permeability of  $10^{-3}$  to  $10^{-4}$  m/s, but there is not one uniform standard substrate design for the construction of VSSF wetland. Various literatures reports effective grain size should be  $0.2 < d_{10} < 1.2$  mm, uniformity coefficient  $3 < d_{60}/d_{10} < 6$  and hydraulic conductivity  $K_f$   $10^{-3}$  to  $10^{-4}$  m/s (UN-HABITAT, 2008). For the VSSF slope, the slope bottom along the direction of flow from inlet to outlet to allow for easy draining when maintenance in required, a slope of 0.5 to 1% is recommended for ease of construction and proper draining, but no research has been done to determine an optimum slope (UN-HABITAT, 2008).

In a subtropical climate, it is possible to increase the applied loading rates above guidelines issued in Central Europe and achieve nitrification in VSSF system. The

average results by vertical beds of 75 cm depth showed better performance in comparison with vertical beds of 45 cm depth (Philippi *et al.*, 2004).

The application and reliability of these systems during domestic sewage treatment has previously been reviewed (Cooper *et al.*, 1997), (Sundaravadivel and Vigneswaran, 2001).

### **2.3.2. Operation and maintenance of CWs**

Operation and maintenance can be the terms of routine and start up with a long term, it should be apply a twice a year for effectiveness of the wetland operation treatment, as the constructed wetlands are artificial, the routine operation systems should be passive and requiring the little intervention every time (UN-HABITAT, 2008).

The routine operation and maintenance of FWS require the similarity of routine operation of the lagoons. Including the hydraulic and water depth control in influent and effluents cleaning, moving grass on berms and inspection routine; management of the vegetation is necessary also in the operation and routine (EPA, 2000).

In general the operation and maintenance requirements for CWs are relatively simple, allowing community organisations or a private, small-scale entrepreneur to manage the system after adequate technical support (Gauss, 2008). FWS wetlands offer effective treatment in a passive manner, minimizing mechanical equipment, energy, and skilled operator requirements (EPA, 2000).

The routine operation and maintenance requirements for SSF wetlands are hydraulic and water depth control, inlet/outlet structure cleaning, grass mowing on berms, inspection of berm integrity and routine monitoring (EPA, 2000) berms (walls) should be properly maintained (UN-HABITAT, 2008). Remove monthly the sediment particles from the influent distribution channel, and, harvest the plants according to their growth cycle, clean the filter bed surface, using adequate cutting devices and a rake (Gauss, 2008).

Water level and flow control are usually the only operational variables that have a significant impact on performance; maintaining uniform flow across the wetland through inlet and outlet adjustments, vegetation management to maintain the desired plant communities within the wetland, odor control, (UN-HABITAT, 2008).

## 2.4. Pollutant Removal Processes in CWs

These wetland systems are living ecosystems and the life and death cycles of the biota produce residuals which can be measured as BOD, TSS, nitrogen, phosphorus and fecal coliforms (EPA, 2000). The water quality of the effluent is strongly dependent on how effectively the constructed wetland cells can remove contaminants.

The FWS wetland is still effective for removal of BOD, TSS, trace metals, and some complex organics because the treatment of these occurs under both aerobic and anoxic conditions (EPA, 2000). Settleable organics are rapidly removed in FWS, systems under quiescent conditions by deposition and filtration (Vymazal, 2008).

### 2.4.1. Carbon removal in CWs

Wetland systems reduce many contaminants, including organics (Vymazal, 2008); whereas, amount of organic matters is the higher the sample is the high value and the water most polluted. So removal of the organic matters is one of the targets of the wastewater treatment with the necessary resources of oxidation, Wetlands are efficient users of external carbon sources, manifested by excellent reductions in BOD<sub>5</sub> and COD (Kadlec and Wallace, 2008).

The carbon influent in CWs is from the wastewater sources and biomass, so the carbon is used Biomass decay provides a carbon source for denitrification, but the same decay competes with nitrification for oxygen supply (Kadlec, 1996). Attached and suspended microbial growth is responsible for the removal of soluble organic compounds which are degraded aerobically as well as anaerobically (Vymazal, 2008). Oxygen is supplied to the wetland water column by diffusion through the air-water interface and via the photosynthetic activity of plants in the water column, namely periphyton and benthic algae (Kadlec, 2000);(QDNR, 2000)

So, the major oxygen source for the subsurface components (soil, gravel, rock, and other media, in trenches or beds) is the oxygen transmitted by the vegetation to the root zone. In most cases the subsurface flow system is designed to maintain flow below the surface of the bed, so there can be very little direct atmospheric re-aeration (Seidel, 1966); (EPA, 1988a). The selection of plant species is therefore an important factor (EPA, 1988a).

The BOD removal processes in CWs are; physical removal, the sedimentation of suspended solids, that means accumulation of organic matters and sledges in bottom as

sediment (Brix, 1993); and soluble BOD<sub>5</sub> is removed by microbial growth on the media and attached to the plant roots and rhizomes penetrating the bed (EPA, 1993); and Biofiltration (Ellis et al., 2003).

The sedimentation, biofiltration, microbial decomposition and oxidation are the process to removed COD in CWs (Ellis et al., 2003).

#### **2.4.1. Nitrogen removal in CWs**

Nitrogen is an essential nutrient for plants and animals in the environment, it is like a sources of their food. However, an excess amount of nitrogen in a waterway may lead to low levels of dissolved oxygen and negatively alter various plant life and organisms. Sources of nitrogen include: wastewater treatment plants, runoff from fertilized lawns and croplands, failing septic systems, runoff from animal manure and storage areas, and industrial discharges (EPA, 2013)

Nitrification/denitrification is the major path of nitrogen removal (Seidel, 1966); (EPA, 1988a). Removals of 60-86 percent were reported at Santee (Neel et al., 1961); (EPA, 1988a). Nitrogen removals have been reported that indicate detention times of 5-7 days will generally produce an effluent with TKN <10 mg/L. Typical pilot-scale results are shown in Figure 3-5 along with a regression curve superimposed on the scatter of data (EPA, 1988a); (EPA, 1988b).

Nitrogen is most effectively removed in FWS constructed wetlands by nitrification and denitrification. FWS treatment wetlands typically have aerated zones, especially near the water surface because of atmospheric diffusion, and anoxic and anaerobic zones in and near the sediments (Vymazal, 2008).

#### **2.4.2. Phosphorus removal in CWs**

Phosphorus is an essential nutrient for plants and animals. It is naturally limited in most fresh water systems because it is not as abundant as carbon and nitrogen; introducing a small amount of additional phosphorus into a waterway can have adverse effects. Sources of phosphorus include soil and rocks, wastewater treatment plants, runoff from fertilized lawns and cropland, runoff from animal manure storage areas, disturbed land areas, and commercial cleaning preparations (EPA, 2013).

Phosphorus removal in many wetland systems is not very effective because of the limited contact opportunities between the wastewater and the soil. A significant clay

content and the presence of iron and aluminum will enhance the potential for phosphorus removal (Seidel, 1966) (EPA, 1988a).

### **2.4.3. Suspended solids removal in CWs**

Suspended solids removal is very effective in both types of CWs. Most of the removal occurs within the first few meters beyond the inlet, owing to the quiescent conditions and the shallow depth of liquid in the system. Controlled dispersion of the influent flow with proper diffuser pipe design can help to ensure low velocities for solids removal and even loading of the wetland so that anoxic conditions are prevented at the upstream end of the channels.

If the water in the wetlands is not shielded from sunlight by the vegetation, algae could become a problem (EPA, 1988b).

## **2.5. Micropollutant Removal in CWs**

The CWs are one of the wastewater treatment used to remove the micropollutants, as it accumulated a variety of microbiological communities, plant growth and have an available of physical process that may be able to offer different pathways leading to degradation of micropollutants.

### **2.5.1. Heavy metals removal**

The predominant removal mechanisms in the CWs were attributed mostly to physico-chemical and biological. There are limited data available on the metal removal capability of FWS wetlands; because the removal mechanisms are similar to those described above for phosphorus, the response is not very effective.

Major physico-chemical removal processes of heavy metals occurring in CWs include sedimentation and filtration, sorption and precipitation and co-precipitation (Lesage, 2006). There is greater opportunity for contact and sorption in SFS systems and metals removal can be very effective (Seidel, 1966), (EPA, 1988a). Metals are taken up by plants, and in many cases stored preferentially in the roots and rhizomes (Kadlec, 1996). The chemical precipitation by high alkalinity and pH is removed the heavy metals (Ellis et al., 2003); precipitation was enhanced by wetland metabolism which increased the pH of inflowing acidic waters to near neutrality. Sedimentation and filtration are allowing the removal of heavy metals associated with particulate matter

(Lesage, 2006) Removal of Cu, Zn, and Cd at the rates of 99, 97, and 99 percent respectively, (Crites, 1988). Phosphorus removal and metals removal will likely be finite due to exhaustion of exchange sites (EPA, 1988a). The sorption is the adsorption of Metals in the surface of the substrate; it can be exchanged by other cations by the process of cation exchange (Lesage, 2006).

The biological removal processes are providing by plant up take and microbial removal. Micro-organisms removal processes are provided by their role in the biogeochemical cycles which affect metal speciation, biosorption, reduction and methylation of heavy metals (Lesage, 2006), (Kosolapov et al., 2004); Biosorption is the passive metabolism-independent sequestration of metals by interactions with live or dead microbial biomass and is an important approach for the bioremediation of metal-contaminated environments (Kosolapov et al., 2004).

### **2.5.3. Poly-aromatic hydrocarbons removal**

PAHs may undergo adsorption, volatilization, photolysis, and chemical degradation, microbial degradation is the major degradation process (Haritash and Kaushik, 2009).

PAHs may also be lost by biodegradation and chemical transformations in water and sediments (Wild and Jones, 1995). The rate of biodegradation depends on pH, temperature, oxygen, microbial population, degree of acclimation, accessibility of nutrients, chemical structure of the compound, cellular transport properties, and chemical partitioning in growth medium (Haritash and Kaushik, 2009). PAHs removal depends on the environmental conditions, number and type of the microorganisms, nature and chemical structure of the chemical compound being degraded; they are biodegraded/biotransformed into less complex metabolites, and through mineralization into inorganic minerals, H<sub>2</sub>O, CO<sub>2</sub> (aerobic) or CH<sub>4</sub> (anaerobic) (Haritash and Kaushik, 2009). For Hwang (Hwang et al., 2007), the temperature, acidity/alkalinity (pH), oxygen, nutrients, light irradiation, and bioavailability are considered the most common relevant factors affecting PAHs bioremediation of degradation of PAHs. In microbial metabolism in constructed wetlands, PAHs can be degraded by some of microorganisms were found to be capable of transforming and degrading PAHs and these abilities may be useful in removing them from the environment, ubiquitously

distributed in the natural environment, such as in soils (bacteria and non-ligninolytic fungi) and woody materials (ligninolytic fungi) (Maigari, 2015).

Phytoremediation also one of the biological removed processes of wetlands, Phytoremediation in wetlands can be used to remove a wide variety of pollutants and toxicants (Horne, 2000), phytoremediation of bioremediation in which biological organisms, processes, or products are used for environmental detoxification with the help of microbes such as bacteria and fungi (Indika and Mahaulpatha, 2015), by processes of Phytoextraction, Phytodegradation, Phytostabilization, Rhizofiltration, Phytovolatilization, Phytodesalination (Ali et al., 2013)

Adsorption is one of the main processes to remove PAHs, adsorption, mass transfer process involves the accumulation of substances at the interface of two phases (such as liquid-liquid, gas-liquid, gas-solid, and liquid-solid) (Sarukkalige, 2017).

#### **2.5.4. Pharmaceutical active compounds removal**

Constructed wetlands has an ability to remove the PhACs in wastewaters by different types of processes like biodegradation/photodegradation, adsorption/sorption, plant up take (Dordio and Carvalho, 2018), sedimentation (Wang et al., 2017).

The potential of Sub Surface Flows for the removal of contaminants occurring in urban wastewater has attracted increasing interest over the past decade with a view of treating wastewaters from small populations (Matamoros and Bayona, 2006).

In constructed wetlands treatment, the important and more advanced processes like.

Photodegradation, adsorption/sorption, biodegradation and plant up take (Dordio and Carvalho, 2018).

Adsorption is dependent on both hydrophobic and electrostatic interactions of the pharmaceutical with particulates and microorganisms (Hijosa-Valsero et al., 2016). Sorption of dissolved organic contaminants on soil, organic carbon, mineral surfaces and biofilms coating the gravel bed can be a significant mechanism for their removal (Kadlec, 1996), (Zhang et al., 2012).

Biodegradation of the PhACs is limited, not all of the compounds are degraded by biodegradation, some substances may be removed more efficiently by enhance biology; other substances are only marginally affected and some not at all (Baresel et al., 2015). The microbial biodegradation of PhACs compounds may undergo:

mineralization, transformation to more hydrophobic compounds, which partition onto the solid phase; and transformation to more hydrophilic compounds, which remain in the liquid phase (Halling-Sørensen et al., 1998), (Kümmerer, 2003), (Zhang et al., 2012), the coexistence of several micro-environments in CWs allows for a variety of microbiological communities, which might be able to offer different metabolic pathways leading to PhACs degradation (Hijosa-Valsero et al., 2010) the presence of vegetation and types of vegetation also have an effect of PhACs removals (Zhang et al., 2008).

The efficiency of photodegradation of PhACs depends on several factors such as the seasonal variation for photolysis, light intensity and light attenuation by water depth (Buser et al., 1998).



### 3. MATERIALS AND METHODS

#### 3.1. Study Area

Kazımkarabekir is one of the Karaman province cities in the Central Anatolia Region, has a status city in 1989. The name was taken from Kazımkarabekir Pasha. The city is located in Konya-Karaman on the state road, 85 km from Konya and 23 km from Karaman; Hadım to the south of İlçen, Çumra to the north, Karaman to the east.

Population of Kazımkarabekir is 3094 people. Kazımkarabekir has an area of 296.4 km<sup>2</sup>, 37 ° 14 ' north parallel and 32 ° 57 ' east meridian. Height of the district above sealevel is 1030 Meter, and has a total of 6 villages created.

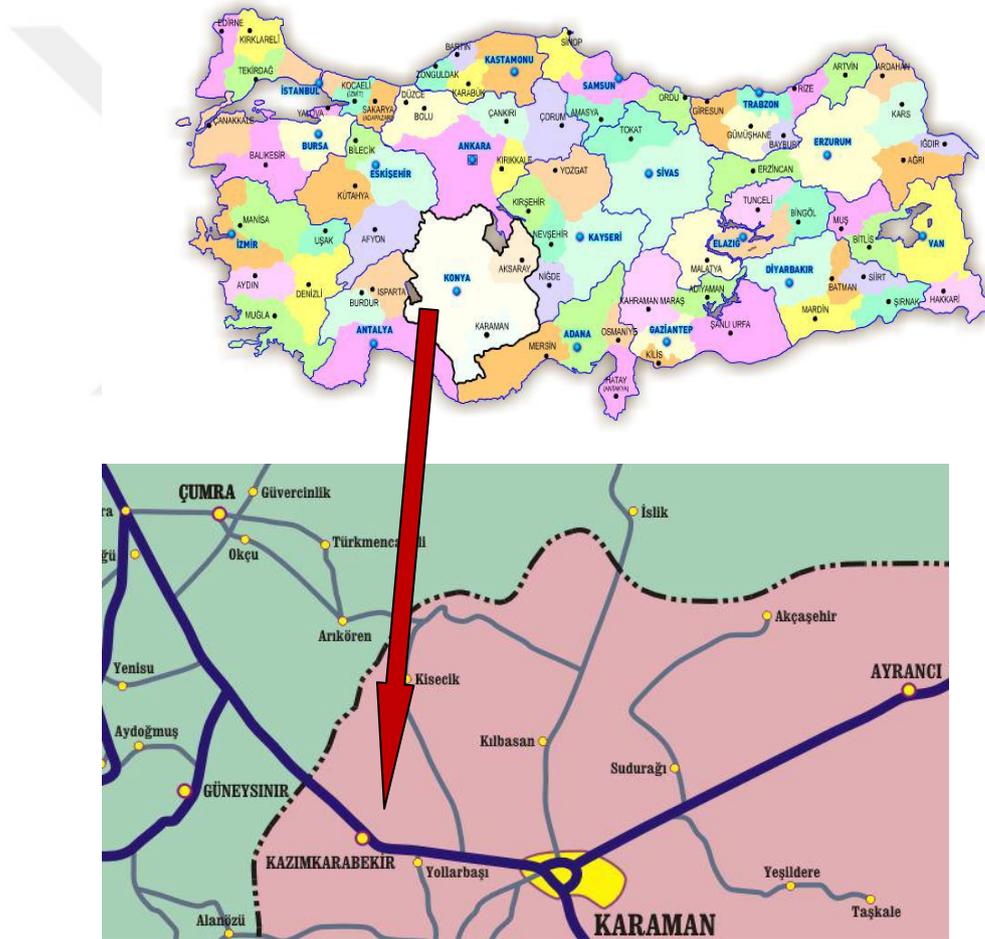


Figure 3.1. Study area (Kazımkarabekir, Konya/Turkey)

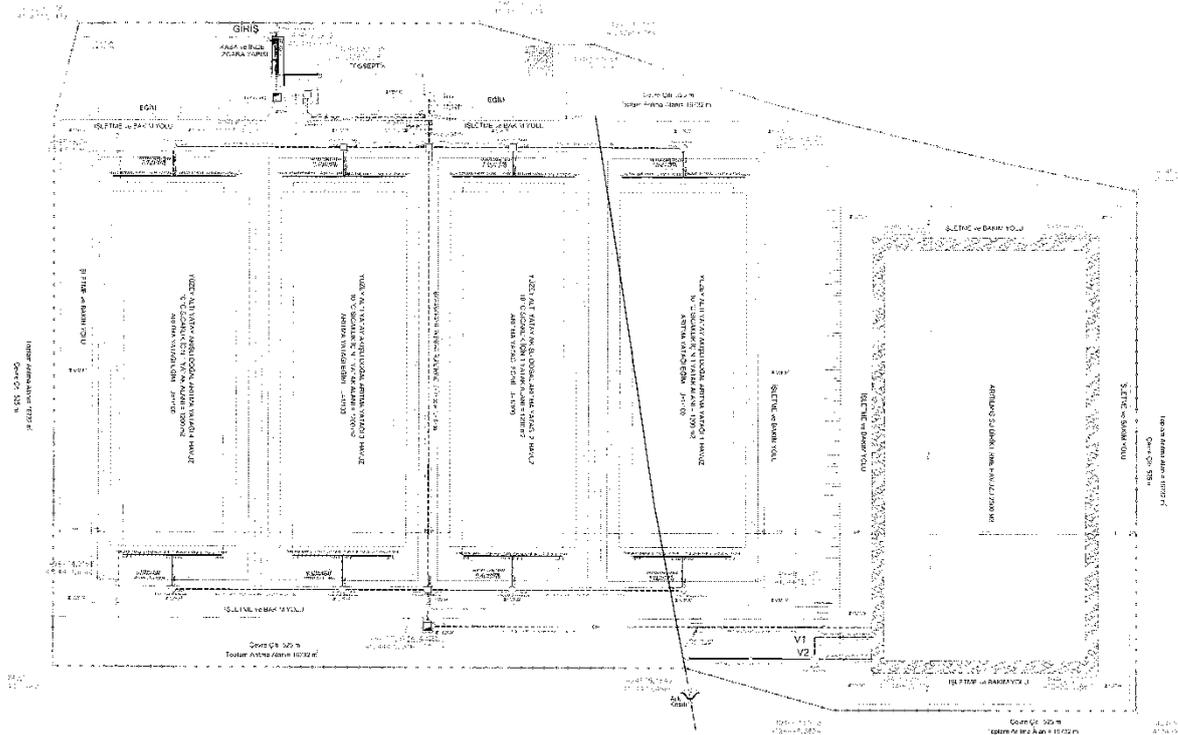


Figure 3.2. Kazımkarabekir's HSSF CWs plans (Kazımkarabekir WWTP Project Report, 2015)

Karabekir WC's is a type of Horizontal Flow SSF Wetland, which has 4 basins in parallel fulfil of gravel layer, rock and emergent plants. The inlet is feeds by control well and distributes into those 4 basins, and outlet is ensured by regulator well.

Karabekir WC's has Coarse grill with 40 mm spacing, fine grating with 20 mm spacing, 4 cubic seams with 272 m<sup>3</sup> volume has been designed and constructed.

And ; 1200 m<sup>2</sup> surface area (LxB: 60m x 20m) to be composed of 4 wetlands. CW's can keep 10 °C winter conditions according to the water temperature and the surface area per person is calculated as 2.4 m<sup>2</sup> / person. The slope of the bed was accepted as 1% and the depth of the bed area was initially 0.7 m and the end was designed as 1.3 m. (Kazımkarabekir WWTP Project Report, 2015)



Figure 3.6. Gravel substrats of CWs



Figure 3.7. Course and Fine Screen



Figure 3.8. View of HSSF Karabekir's CWs

### 3.2. Sampling Points and Frequency

The sampling frequency is per 1 or 2 months depending on the parameters during one year, starting from June 2017 to May 2018. So 12 to 6 sampling must be taken during the study.

The samples are from Karabekir's WC's treatment, taking to the inlet and outlet and bringing to the laboratories for analysis. The samples are taking every mounts to analysis the common analyse compounds of the study.



Figure 3.10. Effluent and Influent samples

### 3.3. Analytical Procedures and Laboratory Analysis

#### 3.3.1. Conventional water quality parameters

The pH in wastewater refers to the measurement of hydrogen ion activity of acidic/basic of wastewater. Determination of pH is important in the wastewater treatment process because extreme levels are common problems in wastewater; the pH of the environment has an effect on the rate of microbial growth. To analyze the pH, we used pH metre, and the analysis has done in the laboratory with the sample take.

The weather temperature is the most important parameters for the wastewater. Several biogeochemical processes that regulate the removal of nutrient in wetlands are affected by temperature, thus influencing the overall treatment efficiency, (Kadlec H.R. and Al, 2001).

Nitrogen exists in several forms; the total nitrogen is among the principal nitrogen types of concern to wastewater treatment nitrogen's.

Total nitrogen analysis have done by using the the kit LCK 338 of Hach Lange Total Nitrogen cuvette test 20-100 mg/L TN<sub>b</sub> and instruction with, and the photometric detection to reading the final result with the spectrophotometer Hach Lange DR 5000™ UV-Vis Spectrophotometer Beam Height: 10 mm

Phosphorus may be found in several forms in Municipal wastewater, organic and the rest in inorganic. Total Phosphorus is the sum of reactive, condensed and organic phosphorous, and which the important in wastewater. Phosphorus compounds can be determined by various methods, as colorimetric and photometric. The Hach Lange's Kit LCK350 Phosphate cuvette tube cell vial test 2 - 20mg/L PO<sub>4</sub>-P is used to analysis the total phosphorus and the photometric detection to read the result with the spectrophotometer Hach Lange DR 5000™ UV-Vis Spectrophotometer Beam Height: 10 mm.

COD is the process to measuring the amount of oxygen consumed for the oxidation of total organic matters (biodegradable and non biodegradable in sample).The COD analyse method is follow the procedure described in the Standard Methods of APHA standard method 5220 C Titrimetric Method.

The BOD is one of important parameters, which is an indication of the content of oxygen needed by consumed by Heterotrophic bacteria for oxidation of organic matters and to decompose organic compounds in waste water.

The BOD<sub>5</sub> used is following the method according to procedure described in the Standard Methods of APHA, standard method 5210 C 5-Days BOD Test.

Table 3.1. Wastewater parameters and Analytical Procedures

Parameters	Methods
pH	pH meter
TN	LCK 338 Hach Lange Nitrogen cuvette test (20-100 mg/L TN <sub>b</sub> )
TP	LCK 350 Hach Lange Phosphate cuvette test (2 - 20mg/L PO <sub>4</sub> -P)
COD	SM 5220 C Titrimetric Method.
BOD	SM 5210 C 5-Days BOD Test



Figure 3.11. BOD's incubator temperatures



Figure: 3.12. BOD's Incubator



Figure 3.13. Nanometric cap of BOD's bottle



Figure 3.14. Thermoreactor for COD analyses

### 3.3.2. Analytical procedures of micropollutants analyses

Samples were putting into glass containers and conserving at + 4 °C. Extractions of water samples had done within two weeks. Analyzes of PAHs and heavy metals from micro circulators were achieved at Selçuk University Advanced Technology Research and Application Center. PhACs analyzes were performed by an accredited laboratory.

Table 3.2 below are summarized the measurement used for micropollutants analysis in this study.

Table 3.2. The methods of analysis of Micro pollutants proposed and used for the study.

Micro pollutants	Methods				
	LOQ	LOD	Method	Device	Extraction
	ng/L				
Naphtahalene	71	21,3	EPA 8270D	GC-MS	EPA 3510C
Fluoranthene	7,61	2,28			
Benzo[b] fluoranthene	5,10	1,53			
Benzo[k] fluoranthene	6,45	1,94			
Benzo(a) pyrene	7,06	2,12			
Indeno[1,2,3-cd] pyrene	59,03	17,71			
Benzo[g,h,i] perylene	1,44	0,43			
17 $\alpha$ -ethinyloestradiol	500	165	EPA 1694	LC-MS/MS	Direct injection
17 $\beta$ -estradiol					
Diclofenac	100	33			
Carbamazapine					
Nickel		0,4	EPA 3051 EPA 200.8	ICP-MS	Direct injection / EPA 3051 A
Lead		0,04			
Cadum		0,09			
Mercury		16			

Table 3.3. Chemical structure and some physico-chemical properties of PAHs in the study.

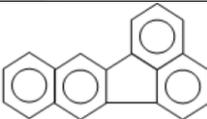
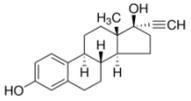
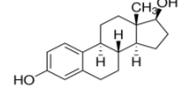
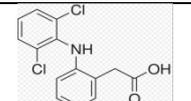
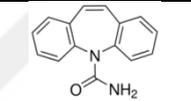
Compounds	CAS NO	Molecular formula	Molecular weight (g/mol)	structure	Log $K_{ow}$
<b>PAHs</b>					
Benzo(a) pyrene	<u>50-32-8</u>	$C_{20}H_{12}$	252.3		6.06
Benzo[b] fluoranthene	<u>205-99-2</u>	$C_{20}H_{12}$	552.3		6.04
Benzo[g,h,i] perylene	191-24-2	$C_{22}H_{12}$	276.34		6.50
Benzo[k] fluoranthene	<u>207-08-9</u>	$C_{20}H_{12}$	252.3		6.06
Indeno[1,2,3-cd] pyrene	193-39-5	$C_{22}H_{12}$	276.3		6.58
Fluoranthene	206-44-0	$C_{16}H_{10}$	202.26		4.90
Naphtahalene	91-20-3	$C_{10}H_8$	128.17		3.29

Table 3.4. Chemical structure and physico-chemical properties of PhACs and heavy metals.

Compounds	CAS NO	Molecular formula	Molecular weight (g/mol)	structure	Log K <sub>ow</sub>
<b>Pharmaceuticals Active Compounds</b>					
17 alfa- etinilestradiol (EE2)	57-63-6	<u>C<sub>20</sub>H<sub>24</sub>O<sub>2</sub></u>	296.41		3.67
17 beta-estradiol (E2)	50-28-2	<u>C<sub>18</sub>H<sub>24</sub>O<sub>2</sub></u>	272.39		4.01
Diclofenac	15307-86-5	<u>C<sub>14</sub>H<sub>11</sub>Cl<sub>2</sub>NO<sub>2</sub></u>	296.147		4.51
Carbamazepine	298-46-4	<u>C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O</u>	236.274		2.45
<b>Heavy Metals</b>					
Cadium	7440-43-9	Cd	112.41	-	-
Lead	7439-92-1	Pb	207.20	-	-
Mercury	7439-97-6	Hg	200.59	-	-
Nickel	7440-02-0	Ni	58.69	-	-

### 3.3.2.1. Poly-aromatic hydrocarbons (PAHs)

Gas Chromatography Agilent Technologies GC-MS 7890B is used for PAHs analysis. The 7890B GC has enhanced firmware to extend Capillary Flow capabilities and enhanced data system soft-ware to simplify set-up and operation of backflush. (Agilent 7890B Gas Chromatograph Data Sheet). For this GC-System 7890B, the Agilent GC- injector Sampler 80 is used with for sample injection.

Those PAHs are among the 16 PAHs of the EPA, which are known among the harmful and have the strong effects in the environment that present the water.

The compounds are:

- Benzo(a)pyrene;
- Benzo(b)fluoranthene;
- Benzo(k)fluoranthene;
- Benzo(g, h, i)perylene;
- Indeno(1,2,3-cd)pyrene;

- Fluoranthene;
- Naphthalene.

### 3.3.2.2. Heavy metals

The ICP standard method was used. The measurement of Heavy metal samples was based in the TS EN ISO 17294-1 / 2 method. Eight calibration points were adopted, between 1, 10, 50, 100, 250, 500, 1000 and 2000 ppb for the samples and these calibration points were according device.

The preparation of Calibration standards was by diluting the standard samples with ultra-pure water, diluting with a 10 mg / l of 2000 ppb a maximum and polyethylene storage in the refrigerator under suitable conditions. Took 10 ml into the Samples and shaken well with 100 µl nitric acid. If the sample were visible and there were acid-insoluble particles, took 10 ml of filtered sample with a 10 ml syringe filter of 0.45 diameter pores; and added with 100 µl of the nitric acid then after closed and shaken.

The Samples were prepared and put at temperature chamber of Perkin Elmer Elan DRC-e ICP-MS (Inductively coupled plasma mass spectrometry) where the heavy metal contents were determining.

The properties of specific curve Calibrations for heavy metal and results of recovery and repetition are given in Table 3.5.

Table 3. 5. Properties of specific curve Calibrations for heavy metal and results of recovery and repetition.

Heavy Metals	R <sup>2</sup> value (Linearity)	Extended Measurement uncertainty	Recovery Range	Repetition (%RSD)
Cadum	≥ 0,999	%9,1	%86-104	%4,41
Lead	≥ 0,999	%8,6	%88-102	%4,07
Mercury	≥ 0,999	-	-	-
Nickel	≥ 0,999	%8,4	%86-100	%3,97

### 3.3.2.3. Pharmaceutically active compounds (PhACs)

The study is necessary for the determining the PhACs in wastewater and evaluating their amount that are being discharged, so the compounds analysis on this study is:

- 17 alpha- ethinylestradiol (EE2)
- 17  $\beta$  - estradiol (E2)
- Diclofenac
- Carbamazepine

The analysis of the PhACs was sent into the accredited laboratory services.

The analysis method of direct-injection Liquid Chromatography-Mass Spectrometry-Mass Spectrometry (LC-MS/MS) was used to detection the PhACs, following the EPA 1694 procedures. The water samples containing particulate matter were pressed through syringe filters with a pore of 0.45  $\mu\text{m}$  diameters then addition in the internal standard (Chloropiriphos D10) without pretreatment before injecting in LC/MS-MS. At least 6 points calibration curve was formed by method water spike and  $R^2$  calibration values less than 0.95 were renewed.

Before starting the analysis, the calibration used must confirmed by a solution with a medium concentration of solutions. Validation acceptance criteria are  $\pm 10\%$  for the specified concentration. Table 3.6. Below show the details of the PhACs determined and the values obtained by the accredited laboratory.

Table 3.6. Descriptive conditions and calibration data of PhACs

Compounds	Extraction methods	Device	Calibration range	$R^2$	LOQ (ng/L)	Recovery	%RSD
17 alfa- etinilestradiol (EE2)	Direct injection	LC/MS MS	100-2000 ppt	Min 0,995	500	%90	<%10
500							
100							
100							
17 beta- estradiol (E2)							
Diclofenac							
Carbamazepine							

The Agilent Quad LC/MS-MS (Agilent, 6460, HPLC series 1200) was used for PhACs analysis. For acidic analysis Poroshell 120 SB-C18 (4,6mm I.D. x 150mm x 2,7 micron particle size), for Basic analysis Zorbax extend C18 (3,0mm I.D. x 100 mm x 3,7 micron particle size) columns are used.

#### 4. RESULTS AND DISCUSSION

The characterization of municipal wastewater varies significantly in terms of place and time, depending on variations in the discharged amounts of substances. The target of the treatment depends on the type of wastewater compounds treated as wastewater characteristics in BOD, nitrogen, phosphorus, and heavy metals and toxic compounds.

The removal of pollutants in water can be obtained through chemical, physical and biological processes. The aim of wastewater treatment is to have a low impact on the receiving water. In HSSF CWs, organic compounds are degraded aerobically as well as anaerobically by bacteria attached to plant underground organs and media surface (Vymazal, 2008).

The Physico-chemical characteristics play a key role in many parameters of CWs; for example, the rate of absorption is controlled by the soil pH and temperature (Kadlec and Reddy, 2001). The nutrient uptake by plants and microbiological transformations of wastewater components and litter wetlands are affected directly and indirectly by the climatic conditions (Wittgren and Maehlum, 1997).

The pH is important in the living water as healthy aquatic systems can function only within a limited pH range, (Kadlec Wallace, 2009). The pH strongly affects the efficiency of metal removal in wetlands. Ammonium conversion into nitrites during nitrification leads to proton production (Marchand et al., 2010).

Table 4.1. Average, maximum and minimum concentration of pH.

Average		Max		Min	
Influent	Effluent	Influent	Effluent	Influent	Effluent
7,5	7,62	8,81	9,03	6,24	6,66

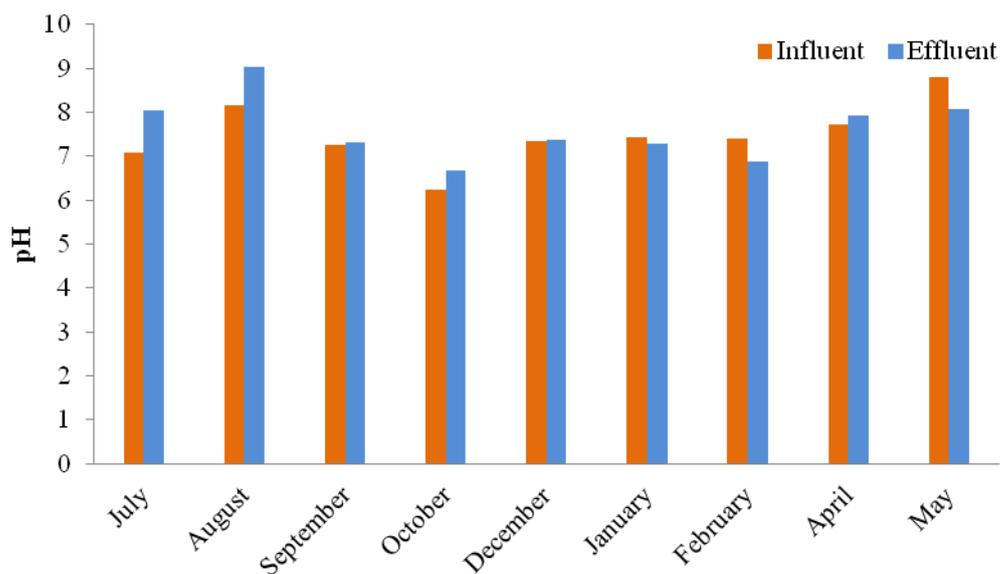


Figure 4.1. pH of the influent and effluent samples from Karabekir HSSF CWs.

The study revealed that the pH varied among the influent and effluent during study period. The pH in influent ranged from 6,25 to 8.81 and effluent from 6,66 to 9,03. Looking at the Figure 4.19, the tendency of the graph shows result of pH with an effect of the season, whereby in winter season, the pH seemed to be low.

Surface water discharge permits frequently and requires  $6,5 < \text{pH} < 9,0$ . Wetland water chemistry and biology are likewise affected by pH (Kadlec Wallace, 2009). So looking at the Figure above, pH of Karabekir's CWs is within the optimal range of the pH required by CWs. The pH beyond optimal range caused untreatment of bacteria; the bacteria are not able to exist outside range of  $4,0 < \text{pH} < 9,5$ ; the denitrifiers operate best in the range of  $6,5 < \text{pH} < 7,5$ , and nitrifiers prefer  $\text{pH} = 7,2$  and higher (Kadlec Wallace, 2009).

#### 4.1. Organic Matters Removal

CWs with horizontal sub-surface flow (HSF CWs) usually provide high  $\text{BOD}_5$  and COD removal. Organic compounds are degraded by both aerobic and anaerobic bacteria in the rhizosphere of vegetated beds (Vymazal, 1999). The Kazımkarabekir's CWs have ability to remove  $\text{BOD}_5$  and COD. The processing system can be achieved by the  $\text{BOD}_5$  removal efficiency more than 90% with an average of 82%. The removal efficiency is conformed with Spreling (Sperling, 2007). Proposal from European Community requirements for discharges from urban wastewater treatment plants to 70–

90 %. Otherwise, the removal of the COD until 82% is higher but average removal efficiency of COD in general was low with 42% if (Sperling, 2007) mentioned 75% of removal.

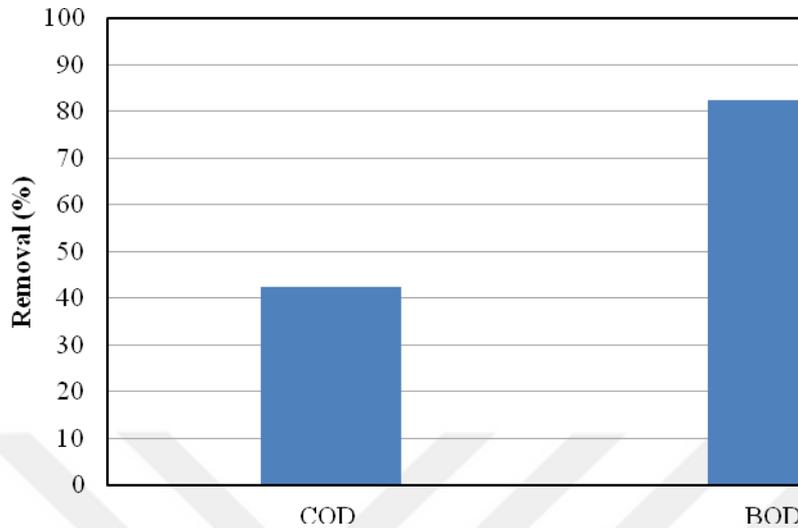


Figure 4.2. Removal efficiency of organic matters in the Karabekir's CW

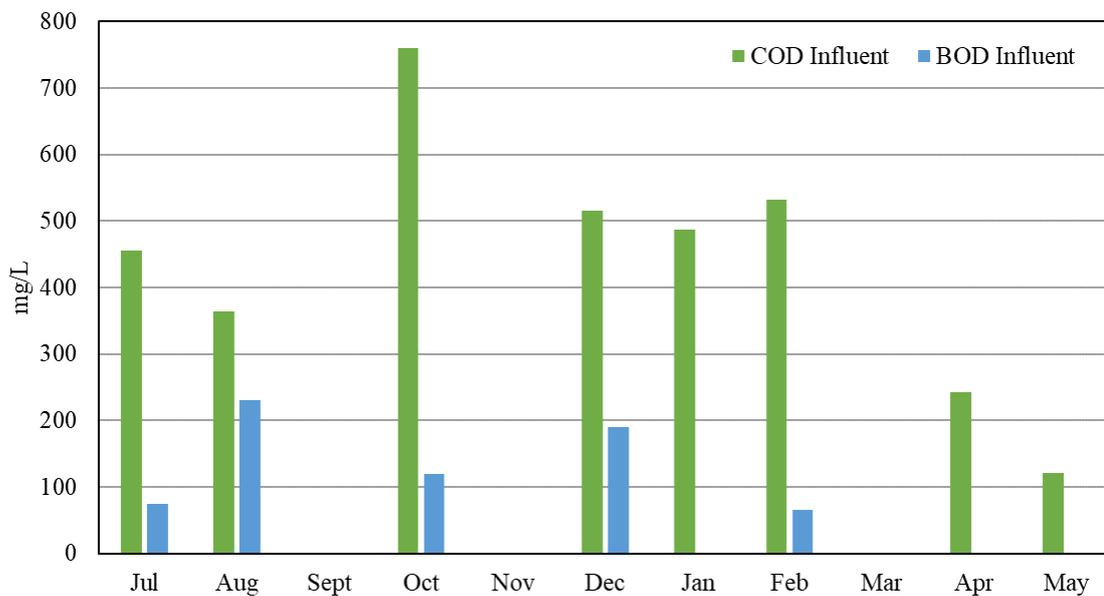


Figure 4.3. Influent concentration of BOD<sub>5</sub> and COD in Karabekir's HSSF CWs.

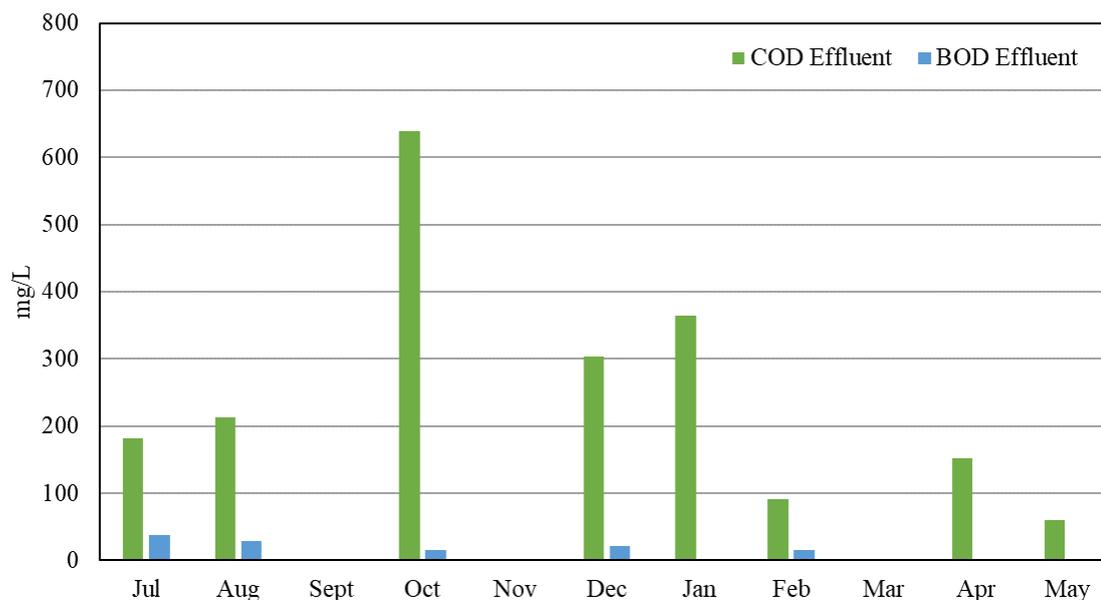


Figure 4.4. Effluents concentration of BOD<sub>5</sub> and COD in Karabekir's HSSF CWs.

Figure 4.3 and 4.4, show the BOD<sub>5</sub> and COD results. These results show variations between different months, the BOD<sub>5</sub> concentration in the influent of HSSF CWs ranging from 65 mg/L to 230 mg/L. The lowest concentration was in February and the highest concentration was in August while BOD<sub>5</sub> of the effluent concentration was ranged from 16 mg/L as lowest (February) to 38 mg/L as highest (July).

The concentration of COD shown in Figure 4.3 and 4.4 is show variations between influent and effluent. For influent in the Figure 4.2, from July (2017) to May (2018), in September (760 mg/L) and October (729,2 mg/L) the concentration of COD were found to be at the highest rate during the year. However, in April (243,3 mg/L) and May (121,6 mg/L) were lowest during the periods. Looking at the effluent, the result shows the same observation as the highest were 638 mg/L in September and 608 mg/L in October against the lowest rate which is 60 mg/L in May.

Table 4.2. Concentration of BOD<sub>5</sub> in different CWs plants

Influent	Min (mg/L)	Average (mg/L)	Max (mg/L)
Metcalf and Eddy (Tchobanoglus et al., 2003)	110	220	400
(Kantawanichkul and Wannasri, 2013)	108,8	120,9	134,9
(Józwiakowski et al., 2018)	62,0	163,2	309,0
(Temel et al., 2017)	131,6		172,66
(Korkusuz et al., 2005)	40	65	90
Karabekir's HSSF CWs	65,0	136,0	230,0

Looking in Table 4.9, the concentration reported by Metcal and Eddy (Tchobanoglus et al., 2003) in minimum (110 mg/L), average (220 mg/L) and maximum (400 mg/L) concentration. Also one study was conducted at Chiang Mai University from Thailand, Kantawanichkul (Kantawanichkul and Wannasri, 2013) reported that the domestic wastewaters concentration with average 120.9 mg/L, minimum of 108.8 mg/L and maximum of 134.9 mg/L. Infact, in front of those influent concentration in table 4.2 below, the influent of wastewater from Karabekir's CWs seems to be having similar concentration of BOD<sub>5</sub> to the study reported by Kantawanichkul (2013) lower than the concentration reported by Metcalf and Eddy (Tchobanoglus et al., 2003). Reported by Kadlec (Kadlec, 1996) BOD<sub>5</sub> concentrations in composition of municipal wastewaters was BOD<sub>5</sub> 220 mg/L and reported by EPA (EPA, 1988b) and 100-300 mg/L was the average of the BOD<sub>5</sub>. The Composition of BOD<sub>5</sub> concentration in municipal wastewaters reported by Kadlec and Knight (Kadlec, 1996) was 220 mg/L. In Turkey as the BOD<sub>5</sub> identified and reported by TÜRAAT (Bilgehan, 2017), the average concentration of BOD<sub>5</sub> influent in municipal wastewaters was 191 mg/L. That means the average concentration of BOD<sub>5</sub> in influent wastewater composition in Karabekir's HSSF CWs was low because the city provided less BOD<sub>5</sub> of organic matters in their wastewaters. However, the concentrations must not be same. It varies widely as a consequence of water consumption which varies substantially in cities and villages and also among countries (Vymazal, 2008).

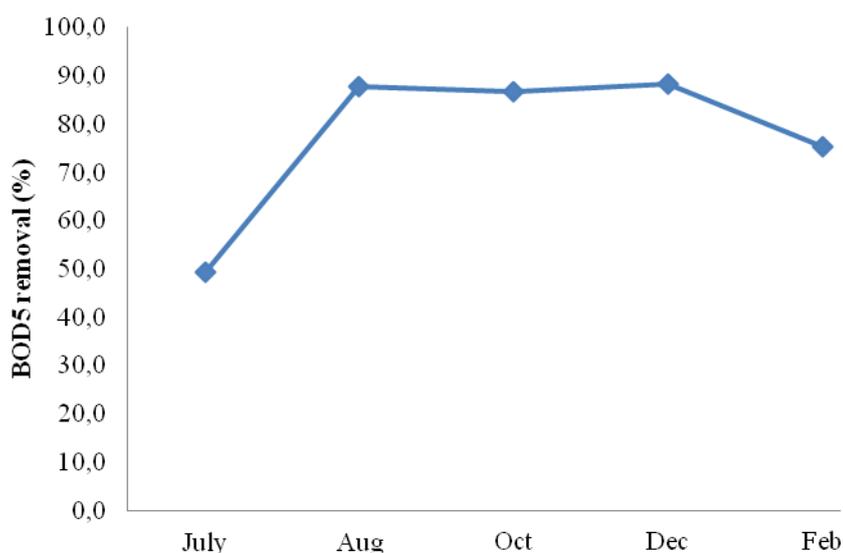


Figure 4.5. BOD<sub>5</sub> removal efficiency of the Karabekir's HSSF CWs

Figure 4.5 demonstrates the BOD<sub>5</sub>'s concentrations removal efficiencies. Only the removal efficiency of July was lower than 50%. Better removal efficiency was illustrated in August (88,4%).

As a result of Garfi (Garfi et al., 2012) researched in Spain (Barcelona and León), a seasonal trend removal efficiency of BOD<sub>5</sub> was observed between summer and winter, whereby contaminant mass removal rate efficiency was significantly high. So the effect of temperature is one of the important aspects influencing wetland performance for wastewater treatment to remove the BOD<sub>5</sub>.

Table 4.3. Average, maximum and minimum concentration of BOD<sub>5</sub> in Kazımkarabekir CWs.

	Influent (mg/L)	Effluent (mg/L)
Max	230,0	38,0
Average	136,0	24,0
Min	65,0	16,0

Table 4.3 shows the average BOD<sub>5</sub> concentration levels of wastewater recorded in Karabekir's CWs between July to February. The influent detected was 136 mg/L when the effluent was 24 mg/L. In this period, the maximum concentration of wastewater influent from city was 230 mg/L when the minimum was 65 mg/L. Reported by EPA (EPA, 2000), the effluent in primary constructed wetlands ranged between 40-200 mg/L and effluents in ponds ranged between 11-35 mg/L. Otherwise, the concentration of the BOD<sub>5</sub> of wastewater after the treatment with an effluent of 38 mg/L as the maximum concentration identified with 16 mg/L of minimum. Table 4.3 also shows the removal efficiency of the BOD<sub>5</sub> concentration at the same periods, which had a value of respectively 82 %, compared to Europe BOD<sub>5</sub> removal reported by Haberl (Haberl et al., 1995) 79%, the efficiency of Kazımkarabekir's above of this rate.

Table 4.4. BOD<sub>5</sub> removal efficiencies in HSSF CWs.

HSSF	Influent (mg/L)	Effluent (mg/L)	%
(Vymazal, 2009)	50,4-157	5,7-18,3	
(Vymazal, 2010)	170	42	75
(Kantawanichkul and Wannasri, 2013)	108,8		91,2- 94,1
(Li et al., 2018)	67,3	12,2	71,6
(Józwiakowski et al., 2018)	163,2	21,7	
Kazımkarabekir's HSSF CWs	136	24	82

Vymazal (2009) Removal of BOD<sub>5</sub> in constructed wetland during the period of 1991–2004. Removal of BOD<sub>5</sub> in constructed wetland Spalene´ Poric´ during the period 1992–2006 and Kazımkarabekir’s BOD<sub>5</sub> influent, effluent and removal efficiency.

Table 4.5. BOD<sub>5</sub> removal efficiencies in different types of CWs.

CWs types	Influent	Effluent	%	Sources
FSW	161	42	74	(Vymazal, 2010)
FSW	97,5	7,3	71,2	(Li et al., 2017)
VF	274	28	90	(Vymazal, 2010)
VF	90,6	8.4	81,8	(Li et al., 2017)
HSSF	136,0	24,0	82	Kazımkarabekir’s HSSF CWs

Table 4.5 above shows the same system of treatment of Karabekir’s HSSF CWs. In Table 4.4, Vymazal reported the influent and effluent concentration of BOD<sub>5</sub> of Ondrejov and wetland Spalene´ Poric HSSF CWs, compared to Karabekir’s HSSF CWs the influent and effluent results. The average concentration of BOD<sub>5</sub> of Karabekir’s HSSF CWs was low, but the results of influent and effluent reported by Li (Li et al., 2017) from China was lower than Karabekir’s HSSF CWs. That means, the Karabekir’s city provide more BOD<sub>5</sub> in wastewater than reported by Vymazal and less than reported by Li (Li et al., 2017). However, with the removal of 75% reported by Vymazal (Vymazal, 2010); and in front of BOD<sub>5</sub> rate value reported by Li (2017) with removal efficiency of 71%, the Karabekir’s HSSF CWs had better result with 82% average rate, but in front of the removal efficiency of BOD<sub>5</sub> reported by Kantawanichkul (Kantawanichkul and Wannasri, 2013) studied in Thailand (in Table:4.4). In the range of 91.2- 94.1 %, the removal of Karabeki’s was low, reported by Frazer-Williams (Frazer-Williams, 2010) as BOD<sub>5</sub> removal. In Europe in general was 79% , so, the result of the Karabekir’s HSSF CWs means, it removed more BOD<sub>5</sub> than the other and treatment plant was satisfying because it gave good results compared to the general result from Europe and the Karabekir’s HSSF CWs worked well with 82% which is similar to the study of Tunçsiper (Tunçsiper et al., 2009) which is about 81% of BOD<sub>5</sub> removal in Marmara.

Table 4.5 shows the BOD<sub>5</sub> results of influent, effluent and removal efficiencies of the different systems of constructed wetlands. Looking in the table 4.5 compared to the FV and FWS systems, the Karabekir’s HSSF CWs BOD<sub>5</sub> removal was in the same level rate value removal of FV with 82% when 90% reported by Vymazal (2010) and 81,8% by Li (2017) when the FV removal efficiency was better with 90% removal. On

the other hand, the FWS BOD<sub>5</sub> removals are lowest compared to HSSF and VSSF. In general, the removal efficiency of Karabekir's HSSF CWs was more under 50%, meaning that Karabekir's HSSF CWs is illegible as the treatment of BOD<sub>5</sub> for wastewater treatment plant.

In general the performance of Kazımkarabekir's HFFS CWs was better. This performance may be due to the well degradation of organic matters in the wetland processes as the good aeration of the wetland, organic compounds are degraded aerobically as well as anaerobically (Vymazal, 2008), and could purify the organic matter with a huge surface area where soil particles can form a layer of biofilm (Qin and Chen, 2016). The attached and suspended microbial growth is responsible for removal of soluble organics (Vymazal, 2008).

Table 4.6. Concentration of COD in different CWs plants

Influent	Min (mg/L)	Average (mg/L)	Max (mg/L)
Metcalf and Eddy (Tchobanoglous et al., 1991)	250	500	850
Metcalf and Eddy (Tchobanoglous et al., 2003)	250	500	1000
(Kantawanichkul and Wannasri, 2013)	241,2	267,4	297,6
(Jóźwiakowski et al., 2018)	101,0	329,8	580,0
(Temel et al., 2017)	254		400
(Korkusuz et al., 2005)	221	279,4	348
Kazımkarabekir's HSSF CWs	121,6	467,7	760

Table 4.6 shows Metcalf and Eddy explanations of 500 mg/l the average of the COD's influent with the minimum of 250 mg/L and maximum of 850-1000 mg/L. The study of Kantawanichkul (Kantawanichkul and Wannasri, 2013) indicated the COD average concentrations of influent to be 267.4 mg/L with minimum of 241.2 mg/L and maximum of 297.6 mg/L, but for Karabekir's indicated that the average concentration of COD was 467,7 mg/L, minimum concentration of 121,6 mg/L and maximum of 760 mg/L. Comparing those results, the concentration of Karabekir's wastewater influents looked had a wide range between maximum, average and minimum as compared to the concentration reported by Kantawanichkul (Kantawanichkul and Wannasri, 2013) and the average concentration of CODs in influent indicated by EPA (EPA, 1988b) of 250 – 800 mg/L. On the other hand, the concentration reported by TÜRAAT (Bilgehan, 2017) of influent concentration of Turkey was 444 mg/L. Those results are similar of the Karabekir's concentrations wastewater influents. But in front of the concentration of influent mentioned by Metcalf and Eddy, the COD influent of Karabekir's CWs was

lower than the Composition of COD concentrations in municipal wastewaters reported by study of Kadlec and Knight (Kadlec, 1996) which was 500 mg L, meaning that the concentration value of the COD in the organic matters in wastewater for Kazımkarabekir's city was less.

Table 4.7. Average, maximum and minimum concentration of COD in Kazımkarabekir CWs.

	Influent (mg/L)	Effluent (mg/L)
Max	760,0	638,4
Average	435	250,7
Min	121,6	60,0

The results described the concentration value of influent and effluent of the COD in the CWs treatment, where the average was 435 mg/L for influent when 250, 7 mg/L for effluent, when 121, 6 mg/L minimum of influent and 60 mg/L for effluent. Results also show as maximum concentration was 760 mg/L in the influent conversely 638, 4 mg/L for effluent. The HSSF CWs also showed a significant CODs removal efficiency as 42 %, compared to Europe BOD<sub>5</sub> removal efficiency reported by Haberl (Haberl et al., 1995)70%, the removal efficiency of Karabker's was looked low in front of this rate.

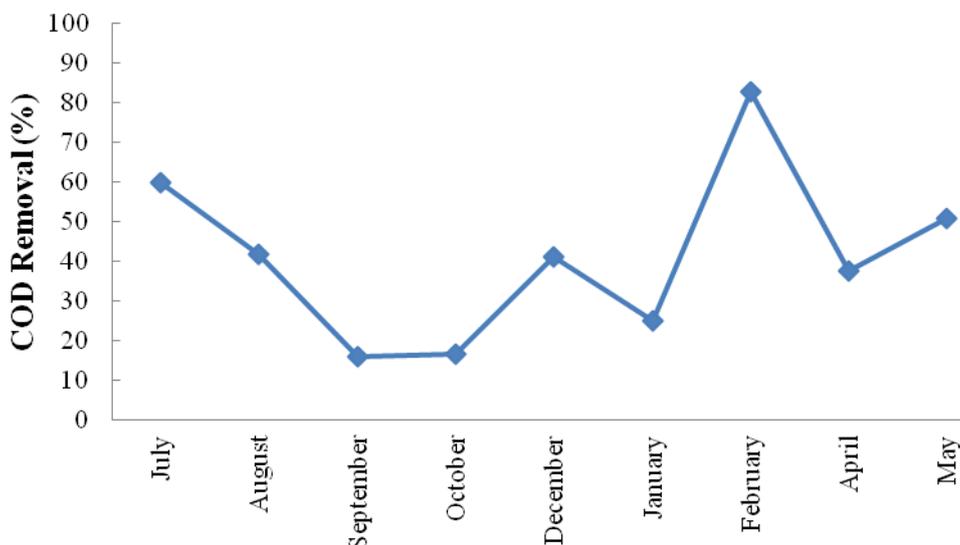


Figure 4.6. COD removal efficiency of the Karabekir's HSSF CWs.

The removal efficiency of the COD in CWs treatment from August (2017) to January (2018) was seen to be low under 50%. Only in July (60%) and especially February (82%) was seen to be highest of the removal efficiency during the periods.

As observed in the performance removal of Karabekir's HSSF WCs treatment, the removal of COD does not depend more on the season. Temperature had surprisingly little effect on COD removal (Marianna Garfi and al, 2012).

As Vymazal (2008) surveyed in the world-wide BOD<sub>5</sub> and COD removal, their efficiencies removal varied between 75 and 93% and between 64 and 82%, but as shown in the Table 4.6 below the removal efficiency of COD and BOD Karabekir's HSSF WCs treatment were lower.

Table 4.8. COD removal efficiencies in HSSF CWs.

HSSF	Influent	Effluent	% Removal
(Vymazal, 2005)	284	72	75
(Vymazal, 2009)	344-133	53-29	
(Kantawanichkul and Wannasri, 2013)	297,6	241,2	54,8-64,8
(Li et al., 2018)	166,4	37,3	70,7
(Józwiakowski et al., 2018)	329,8	57,8	
Kazımkarabekir's HSSF CWs	435	250,7	42

In the Table 4.8, the removal efficiencies reported by Vymazal was 75% and Xiaoyan Li was 70%, compared to the removal efficiency of COD reported by Kantawanichkul (Kantawanichkul and Wannasri, 2013) (54.8-64.8%) in HF, those both in the first are high; also as indicated by Frazer-Williams (Frazer-Williams, 2010) the removal efficiency of COD In Europe 70%; but compared to all, the removal efficiency of Karabekir's HSSF CWs is looked low with 40% of removal efficiency rate, which is lower than the study of Tunçsiper (Tunçsiper et al., 2009) to Marmara about the COD removal ( 59%).

Table 4.9. COD removal efficiencies in different types of CWs.

CWs types	Influent	Effluent	% Removal	Sources
FSW	134,9	34,6	58,1	Xiaoyan Li (2018)
VF	181,6	27,0	72,6	Xiaoyan Li (2018)
HSSF	435	250,7	42	Karabekir's HSSF CWs

Even in the different systems of constructed wetlands, the removal efficiency of COD of Karabekir's CWs was low. Table 4.9 shows the removal efficiency of COD in FSW of 58,1% for FSW and for VF is seen to be highest with the rate of 72,6 %.

Similarly comparing the VF reported by Korkusuz (Korkusuz et al., 2004) in Ankara, which ranged between 47% to 44% of COD removal.

Compared to all those removal efficiencies, the Karabekir's HSSF CWs system removed low rate of COD as organic matter in wastewater from the Karabekir's city.

#### 4.2. Nutrients Removal

Nitrogen and phosphorous are the nutrients in high quantities found in wastewater. In the wetlands, nitrogen and phosphorus present in forms particulate as organic and inorganic, dissolved. They are present in different compartments on various processes in the wetland. The wetlands reduce nutrients by sedimentation through sorbing nutrients to sediments, taking up nutrients by plant biomass and denitrification (Fisher and Acreman, 2004). In fact, the rate removal efficiency of Karabekir's HSSF CWs seems to be low, with 38% for the total Phosphorus and 26% for the total nitrogen when the removal estimated by Sperling (Sperling, 2007) in European Community requirements for discharges from urban wastewater treatment plants was 80% for the total phosphorus and 70–80% for the total nitrogen with a removal in relation to the load of the influent.

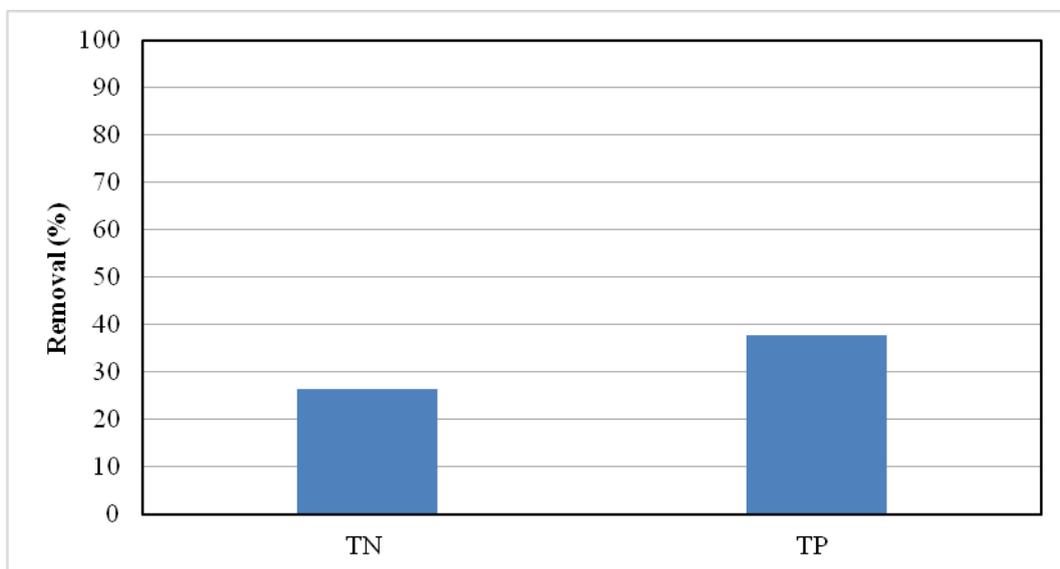


Figure 4.7. Removal efficiency of nutrients during the study from Karabekir's CWs.

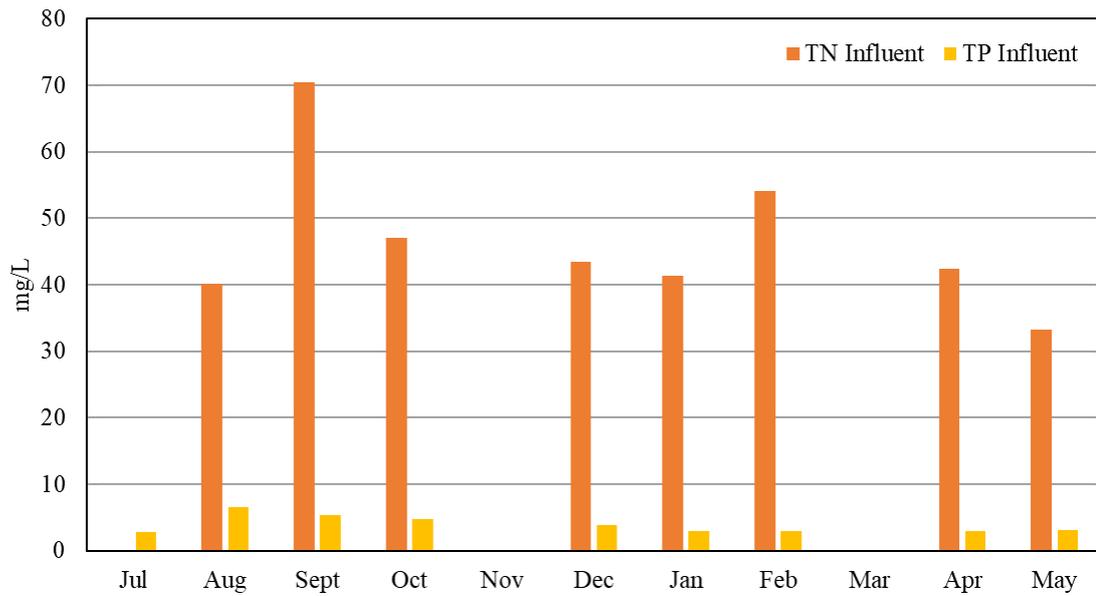


Figure 4.8. Influent concentration of TN and TP from Karabekir's CWs between July 2017-May 2018.

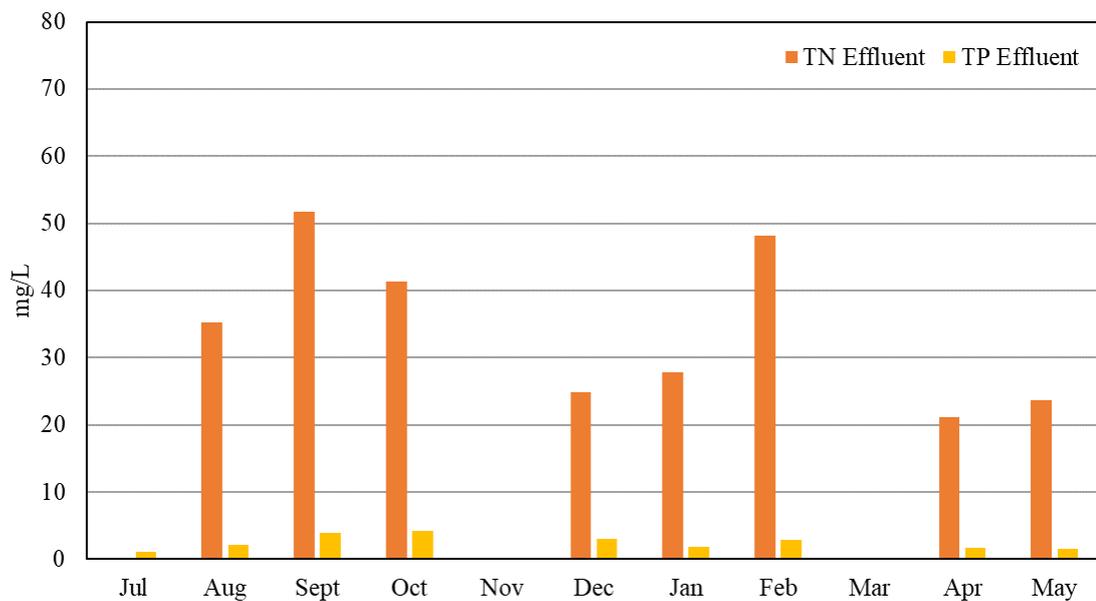


Figure 4.9. Effluent concentration of TN and TP from Karabekir's CWs between July 2017-May 2018.

Figure 4.8 shows the influent concentration of the TP results during the period of study. From August to October, the raw concentration of domestically influent ranged between 6,61 mg/L highest (August) to 2,8 mg/L lowest (July). In the Figure 4.7, for

effluent between September to December, the concentration was ranged between 4,22 mg/L (October) to 1,1 mg/L (July). In general, for some months the difference between influent and effluent concentrations of TP was small like in October (4,79 mg/L-4,22 mg/L) and December (3,93 mg/L-3,02 mg/L). On the other hand, the difference in others months was wide like in August (6,61 mg/L-2,15 mg/L) and May (3,15 mg/L-1,52 mg/L).

Overall, the values of influents and effluents of TN concentrations in constructed wetland over the entire period of August to May are shown in Figure 4.8 and Figure 4.9, whereby the concentration of TN in the influents was generally ranged between 70 mg/L to 33 mg/L. The highest was identified in the period of September. The lowest influent concentrations for that period were found in May. For the effluent (Figure 4.9), the concentration is ranged between 21, 2 mg/L (highest in April) to 51, 7 mg/L (lowest in September).

Looking those results, in summer the concentration of TP in wastewater influent was higher than in winter season.

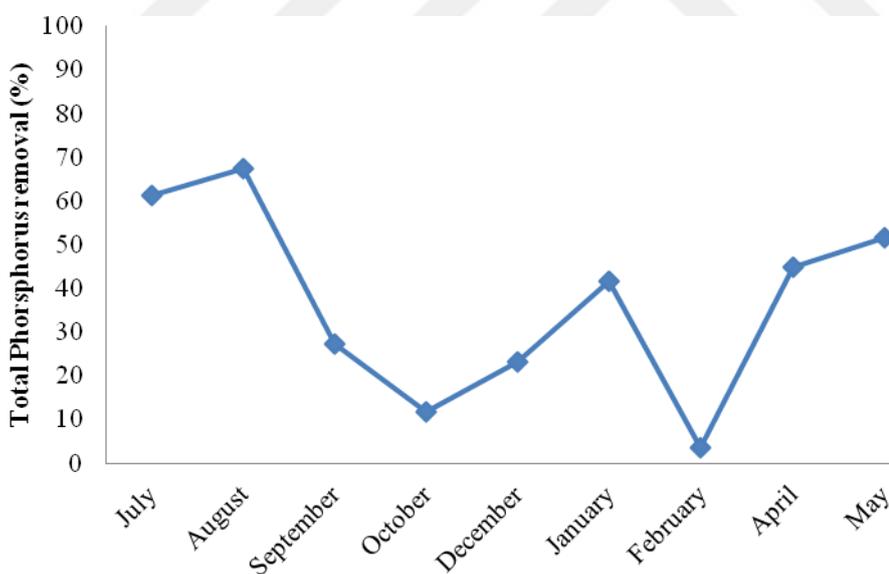


Figure 4.10. Removal efficiency of TP in Kazımkarabekir's CWs.

Looking at each period, the removal efficiency of the Total Phosphorus between July to August was very important with the rate removal ranging between 61% to 67%. In contrary, in February, the rate removal was very low (3,4%). In general, the rate removal efficiency of Karabekir's CWs was established between 30% to 50%. The TP's

removal efficiency showed that there were not clearly seasonal changes in removal efficiency observed during period.

Table 4.10. Average, maximum and minimum concentration of TP in Karabekir's CWs.

	Influent (mg/L)	Effluent (mg/L)
Average	3,96	2,46
Min	2,85	1,10
Max	6,61	4,22

Typically, Karabekir's CWs treatment was removed less than 70% of the total phosphorus whereby the total phosphorus removal varies between 67,5 % to 3,4% (average 37%). The concentration of total phosphorus determined in the CWs was the average raw, influent and effluent concentrations which were 3,96 mg/L, 2,46 mg/L, meaning that the maximum were 6,61 mg/L, 4,22 mg/L, and the minimum were 2,85 mg/L, 1,10 mg/L.

P removal in HSSF-CWs is primarily removed by chemical processes involving adsorption and precipitation reactions with calcium (Ca) magnesium (Mg), iron (Fe) and aluminum (Al) ions which may be part of the chemical composition of substrate media and these reactions seem to be less directly sensitive to temperature (Mesquita et al., 2017).

Table 4.11. Concentration of TP in different CWs plants

Influent	Min (mg/L)	Average (mg/L)	Max (mg/L)
Metcalf and Eddy (Tchobanoglus et al., 2003)	4	8	15
(Józwiakowski et al., 2018)	5,2	24,8	42,8
(Temel et al., 2017)	0,99		7,23
(Korkusuz et al., 2005)	5,98	6,14	6,19
Karabekir's HSSF CWs	2,85	3,96	6,61

Table 4.11. shows the concentration of Total Phosphorus in wastewater, as shown in the study of Metcalf and Eddy that reported the concentration of 8 mg/L of average and the 15 mg/L of concentration maximum. But for Study of HSSF by (Józwiakowski et al., 2018) in south-eastern Poland showed very highest concentration of TP in wastewater, with 24,8 mg/L of average concentration until 42,8 mg/l the maximum. Otherwise, the study done in Turkey by Temel (Temel et al., 2017) from Samsun, the TP concentration in domestic wastewater was ranged between 0,99-7,23 mg/L. Also Korkusuz (Korkusuz et al., 2005) from Ankara indicated the average

concentration of 6,14 mg/L when 6,19 mg/L was the maximum concentration. This concentration confirmed by TÜRAAT (Bilgehan, 2017) studied with 6 mg/L influent average concentration of TP in turkey when the composition TP concentration in municipal wastewaters reported by study of (Kadlec and Wallace, 2008) was 8 mg/L. So in front of all those studies, the TP concentration of wastewater from Karabekir's city into HSSF CWs was seen to be low with average of 3,96 mg/L as compared to the Turkey TPs wastewater concentration reported by those studies. This means that the city did not provide much nutrient Phosphorus in the wastewater.

Table 4.12. TP removal efficiencies in HSSF CWs.

HSSF	Influent	Effluent	Removal (%)
(Vymazal, 2007)	8,75	5,15	41,1
(Vymazal, 2010)	9,6	4,8	50
(Li et al., 2018)	1,9	0,5	70,9
(Jóźwiakowski et al., 2018)	26,4	6,1	72,7
Karabekir's HSSF CWs	3,96	2,46	39

Table 4.13. TP removal efficiencies in different types of CWs.

CWs types	Influent	Effluent	Removal (%)	Sources
FSW	14,7	9,7	34	(Vymazal, 2010)
FSW	1,1	0,3	50,4	(Li et al., 2018)
VF	10,3	4,5	56	(Vymazal, 2010)
VF	3,0	0,4	75,6	(Li et al., 2018)
HSSF	3,96	2,46	39	Karabekir's HSSF CWs

Compared to other study of HSSF CWs system efficiency removal of TP, the removal efficiency of Karabekir's HSSF CWs was lower with only 39% of rate removal. With 6, 14 mg/L influent concentrations of total phosphorus in wastewater studied by Korkusuz (Korkusuz et al., 2004) in Ankara, the removal efficiency was ranged between 45% to 4%. The result of removal efficiency reported by Jóźwiakowski (Jóźwiakowski et al., 2018) and (Li et al., 2018) indicated the removal efficiency above of 70%. Total phosphorus was removed with efficiency from 18,3% to 99.6% Jóźwiakowski (Jóźwiakowski et al., 2018). In the constructed wetland systems, Vymazal (Vymazal, 2010) indicated the average of removal efficiency of total phosphorus ranged between 32% to 50%. With the other systems of CWs, the removal efficiency of FSW was ranged between 34% (Vymazal, 2010) to 50,4% (Li et al., 2018), if the removal efficiency of VF was ranged between 56% (Vymazal, 2010) to

75,6% (Li et al., 2018); over wise, the removal efficiency of Karabekir's HSSF CWs was similar of the FWS removal efficiency in the Table 4.12; the other HSSF were ranged between 41.1% (Vymazal, 2007) to 72,7% (Józwiakowski et al. 2018). In fact, that means, the Karabekir's HSSF CWs had a low rate removal efficiency of TP, the system removed less of the TP in the wastewater, may be the cause of the remove P in constructed wetlands include only sorption on antecedent substrates, storage in biomass, and the formation and accretion of new sediments and soils (Kadlec, 1996), as the Karabekir's HSSF CWs a new Constructed wetland on treatment, the amount of microbial storage depends also on trophic status of the wetland (Vymazal, 2007).

About the effluent, the concentration of effluent TP of Karabekir's CWs was low with 2,6 mg/L, comparing to others studies, Vymazal ((Vymazal, 2007), (Vymazal, 2010)) reported the concentration ranged between 5,15 to 4,8 mg/L, event reported by Józwiakowski (Józwiakowski et al., 2018) looked very highest with 6,1 mg/L, only the study of (Li et al., 2018) indicated the concentration of effluent lowest with 0,5 mg/L. It is important to analyse the effluent, because, after the CWs treatment the effluent waters may reuse or especially release into the environment, which can cause damage if the concentration of TP is still high, like for Karabekir's HSSF CWs the water after treatment realise in the environment so with the concentration of effluent TP after treatment, the water can't have a risk of environment pollutions , even a small amount of phosphorus to a water body can have negative consequences for water quality, adverse effects include: algae blooms, accelerated plant growth, and low dissolved oxygen from the decomposition of additional vegetation (EPA, 2010).

With transformations biotic/abiotic of Nitrogen, it has a complex cycle biogeochemical (Vymazal, 2007). The processes that affect removal and retention of nitrogen during wastewater treatment in constructed wetlands (CWs) are the NH<sub>3</sub> volatilization, nitrification, denitrification, nitrogen fixation, plant and microbial uptake, mineralization (ammonification), nitrate reduction to ammonium (nitrate-ammonification), anaerobic ammonia oxidation (ANAMMOX), fragmentation, sorption, desorption, burial, and leaching (Vymazal, 2007).

Table 4.14. Concentration of TN in different CWs plants

Influent	Min (mg/L)	Average (mg/L)	Max (mg/L)
Metcalf and Eddy(Tchobanoglus et al., 2003)	20	40	85
(Józwiakowski et al., 2018)	37,1	70,4	13,7
(Temel et al., 2017)	18,3		65
(Korkusuz et al., 2005)	28,1	34,6	50,8
Karabekir HSSF CWs	33,30	46,55	70,50

In Table 4.14, shows the quality of wastewater in the TN concentration, ranged between 20-85 mg/L reported by Metcalf and Eddy (Tchobanoglus et al., 2003) and EPA (EPA, 1988a); 20 – 85 mg/L, those studies considered as a reference of the ranged of concentration of the TN in influent wastewater; so for Karabekir's City, the concentration of TN was ranged between 33,3 mg/L to 70,5 mg/L, the minimum concentration was looking high; except the maximum was low; comparing to others studies in Turkey, TÜRAAT (Bilgehan, 2017) realised the studies around of turkey and considering as one of the mainly reference of wastewater treatment, TÜRAAT reported 46 mg/L of average concentration of TN in the wastewater in Turkey; Korkusuz. (Korkusuz et al., 2005) reported the TN influent that used for studied to Ankara with the concentration of TN ranged between 28,3 mg/L to 65 mg/L; also, The study of Temel (Temel et al., 2017) from Samsun reported the concentration of TN influent ranged 28,1 mg/L to 50,8 mg/L; those studied mentioned that those TN influent concentrations was lower than Karabeki's TN influents, and reported by Metcalf and Eddy and EPA; but reported by Józwiakowski (Józwiakowski et al., 2018), the concentration of TN looked highest ranged between 37,1 mg/L to 137 mg/L. To summarized, the TN concentration influents form Karabekir's city was normal, with average concentration of TN of 46,5 mg/L compared to 40 mg/L reported by Metcalf and Eddy, especially closely to 46 mg/L average concentration reported by TÜRAAT.

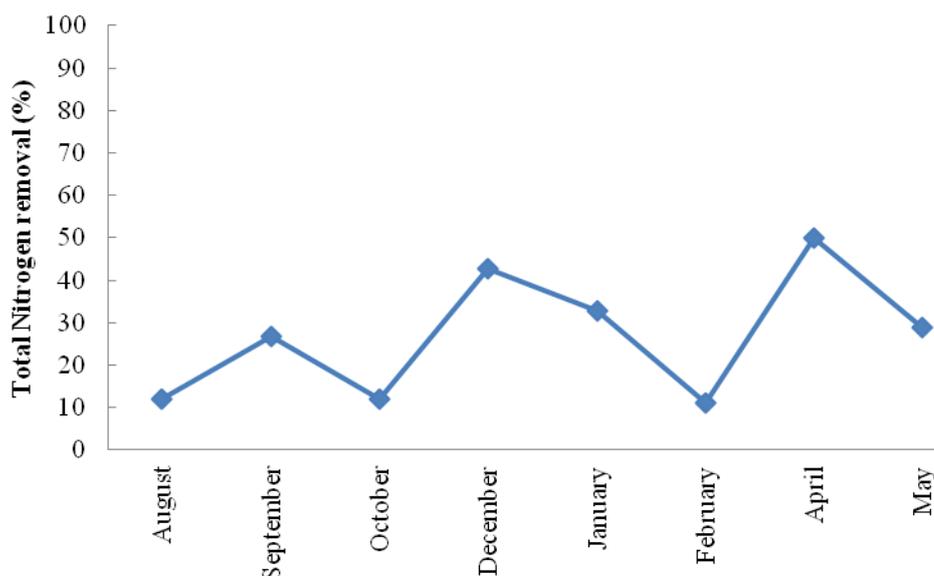


Figure 4.11. Removal efficiency of TN in Kazimkarabekir's CWs

The efficiency of TN removal for the investigated systems of Karabekir CWs is shown in the Figure 4.11; the CWs removed the TN ranged between 50% to 11 %. The results determined that during August (12%), October (12%) and February (11%) the rate removal efficiency of TN was very low around 10%. Furthermore, removal efficiency of CW was demonstrated better performance in December (42%) especially April (50%).

Table 4.15. Average, maximum and minimum concentration of TN in Karabekir CWs.

	TN Influent (mg/L)	TN Effluent (mg/L)
Average	46,55	34,25
Min	33,30	21,20
Max	70,50	51,70

The average influent concentration of Total Nitrogen over the period of studied was 46, 5 mg/L, with the maximum concentration of 70, 50 mg/L and the minimum of 33, 30 mg/L; over wise, the average Total nitrogen concentrations of effluent over the same period was 34, 25 mg/L, and 34, 25 mg/L of maximum and 21, 20 mg/L the minimum (table 4.14).

The Table 4.15 also shows the removal efficient of Total Nitrogen of the constructed wetland, it was identified as very low with average removal of 27, 1% , if 50% was the maximum and 11,1% was the minimum.

Table 4.16. TN removal efficiencies in HSSF CWs.

<b>HSSF</b>	<b>Influent</b>	<b>Effluent</b>	<b>Removal (%)</b>
(Vymazal, 2007)	46,6	26,9	42,3
(Kadlec and Wallace, 2008)	54	36	33
(Vymazal, 2010)	63	36	43
(Li et al., 2018)	19,4	6,2	61,9
(Józwiakowski et al., 2018)	70,4	32,9	51,3
Karabekir HSSF CWs	46,55	34,25	26,5

Table 4.17. TN removal efficiencies in different types of CWs.

<b>CWs types</b>	<b>Influent</b>	<b>Effluent</b>	<b>Removal (%)</b>	<b>Sources</b>
VF	73	41	43	(Vymazal, 2010)
FWS	42,6	23,5	45	(Vymazal 2010)
VF	12,8	3,7	56,0	(Li et al., 2018)
FWS	29,1	8,8	63,7	(Li et al., 2018)
HSSF	46,55	34,25	26,5	Karabekir HSSF CWs

Looking at the TN effluent in Table 4.16, Kadlec and Wallace studies (Kadlec and Wallace, 2008) indicated 36 mg/L effluent of TN and Vymazal (Vymazal, 2007), (Vymazal, 2010) revealing the concentration of 26,9 mg/L and 36 mg/L both considered as the reference of WCs study comparing their literature reported from both. The TN concentration effluents of Karabekir HSSF CWs was normal with 34,25 mg/L. As known, the high concentration of TN released into the environment can have damaging effects on the environment, Kadlec and Wallace (Kadlec and Wallace, 2008) confirmed their effect on the oxygen content of receiving waters, and their toxicity to aquatic invertebrate and vertebrate species.

The removal efficiency is most important for this study. Table 4.16 shows the removal efficiency, influent and effluent concentration of TN in the HSSF CWs system. This table shows the removal rate of HSSF from different studies. In these different studies, Vymazal (Vymazal, 2007), (Vymazal, 2010) indicated the efficiency removal of 42,3% and 43% of the TN, (Kadlec and Wallace, 2008) reported the removal efficiency of 33%. Other recent studies such as Józwiakowski (Józwiakowski et al., 2018) reported the removal efficiency of 51,3% and Li (Li et al., 2018) determined the removal efficiency of 61,9% which is much better than all. Some studies from Turkey by Korkusuz (Korkusuz et al., 2004) in Ankara reported the removal of TN range between 44% to 39%. Compared to all those studies, the removal efficiency of

Karabekir HSSF CWs was confirmed to be very low with 26,5 %, meaning that the Karabekir HSSF CWs cannot remove the TN above 50% removal efficiency.

Table 4.17 shows the removal efficiency of TN in different CWs systems. For VF, the removal efficiency reported by Vymazal (Vymazal, 2010) was 43% , then reported by Li (Li et al., 2018) was 56% which is more better. Otherwise for FWS, indicated by Vymazal (Vymazal, 2010) the removal efficient of TN was 45%, then by Li (Li et al., 2018) was 63,7% always better than all. Comparing all, for Karabekir HSSF CWs was 26,5% and this removal confirmed to be lower than the others. To summarize the results in the Table 4.17, the FSW had a highest removal rate efficiency of TN for all those different systems, after that the VF.

To conclude, the TN effluents from Karabekir HSSF CWs don't have risk to pollute the environment around, but the TN removal efficiency of Karabekir's CWs systems was low. But, in general, the TN removal in HF CWs is respectively weak, as reported by Vymazal (Vymazal, 2009). The reason of that weakness removal is that the nitrogen-removing mechanisms are limited because of lack of oxygen in filtration beds due to continuous water-logging of the bed and the absence of free water column.

### **4.3. Micropollutants Removal**

The presence of organic micropollutants in the aquatic environment is strongly related to their difficult elimination by conventional water and wastewater treatment processes (Gorito et al., 2018). Constructed wetlands are a viable technology that can remove organic micropollutants through synergic processes that involve interactions between vegetation biomass and microorganisms such as hydrolysis, volatilization, sorption, biodegradation, and photolysis (Salcedo et al., 2018). Contaminants are removed from wastewater through several mechanisms processes such as sedimentation, microbial degradation; precipitation and plant uptake remove most contaminants (Renee Lorion, 2010).

#### **4.3.1. Heavy metals**

Metals may be incorporated into the wetland biomass by way of primary production process (EPA, 2000). Heavy metals in a wetland system may be sorbed to wetland soil or sediment, or may be chelated or complexed with organic matter (Renee Lorion, 2010). Important removal mechanisms for metals include cation exchange and

chelation with wetland soils and sediments, binding with humic materials, precipitation as insoluble salts of sulfides, carbonates, and oxyhydroxides, and uptake by plants, algae, and bacteria (EPA, 2000).

Table 4.18. Average, maximum and minimum concentration of heavy metals in Kazımkarabekir CW.

	Average (ng/L)		Max (ng/L)		Min (ng/L)		Removal (%)
	Influent	Effluent	Influent	Effluent	Influent	Effluent	
<b>Ni</b>	7527,5	6131	13650	11800	3770	4380	18,5
<b>Cd</b>	69,7	27,8	222	95	0	0	60,0
<b>Pb</b>	3215,8	6131,7	10220	1440	160	70	78,0
<b>Hg</b>	101	46,7	180	100	20	0	54,0

The average, minimum and maximum concentration of heavy metals in influent and effluent of the CWs are observed in Table 4.18.

The removal rate of Lead (Pb) is quite good, around 78 %, opposite of removal rate of Nickel (Ni) which is quite low (18, 5%). But for Cadmium (60%) and Mercury (54 %) are one average rates

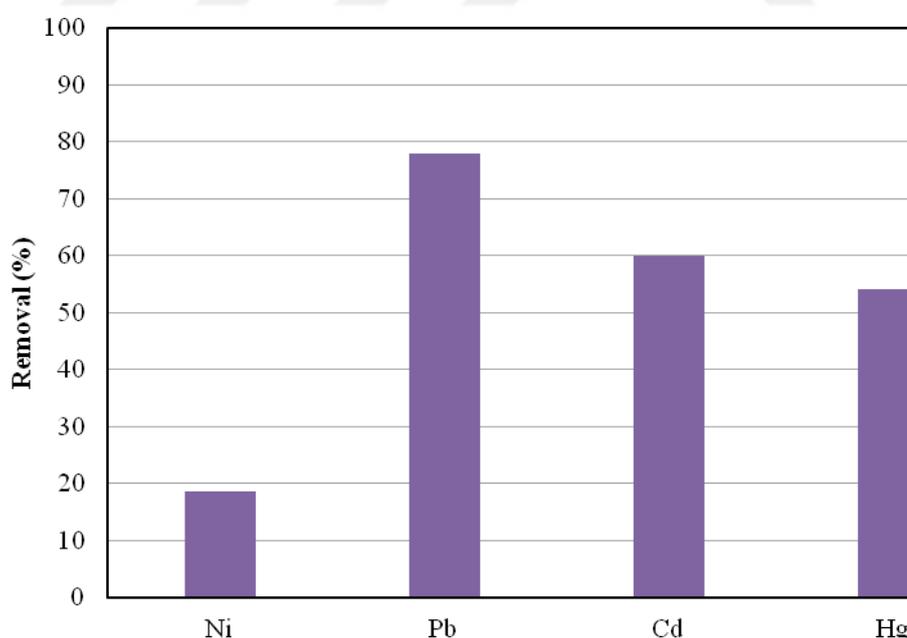


Figure 4.12. Removal efficiency of heavy metals in the Karabekir's CW.

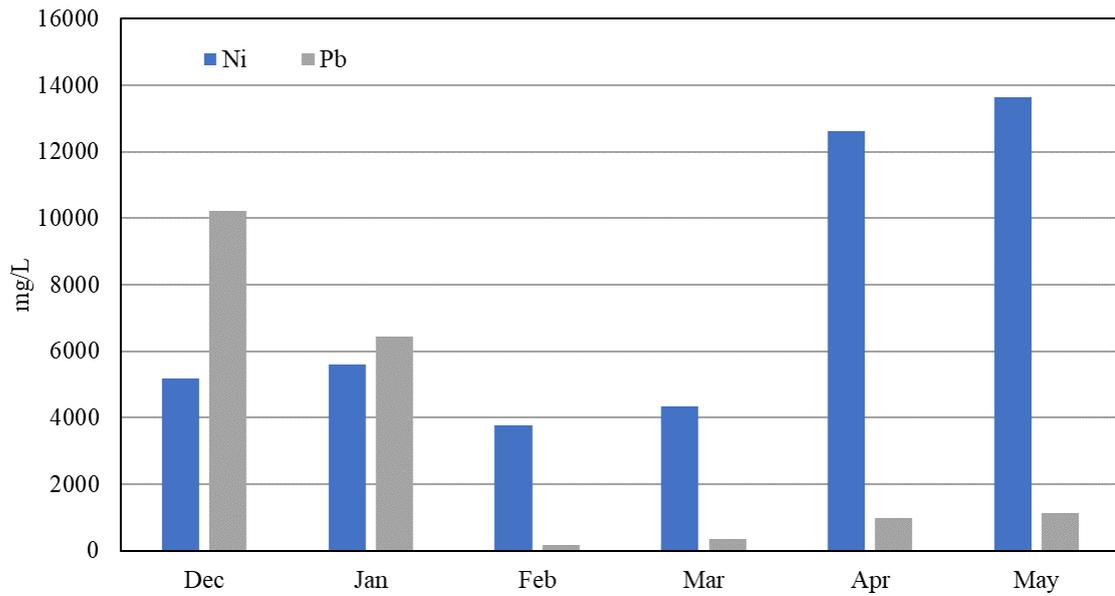


Figure 4.14. Influent concentration of Nickel and Lead from Karabekir's CWs between December 2017 to May 2018.

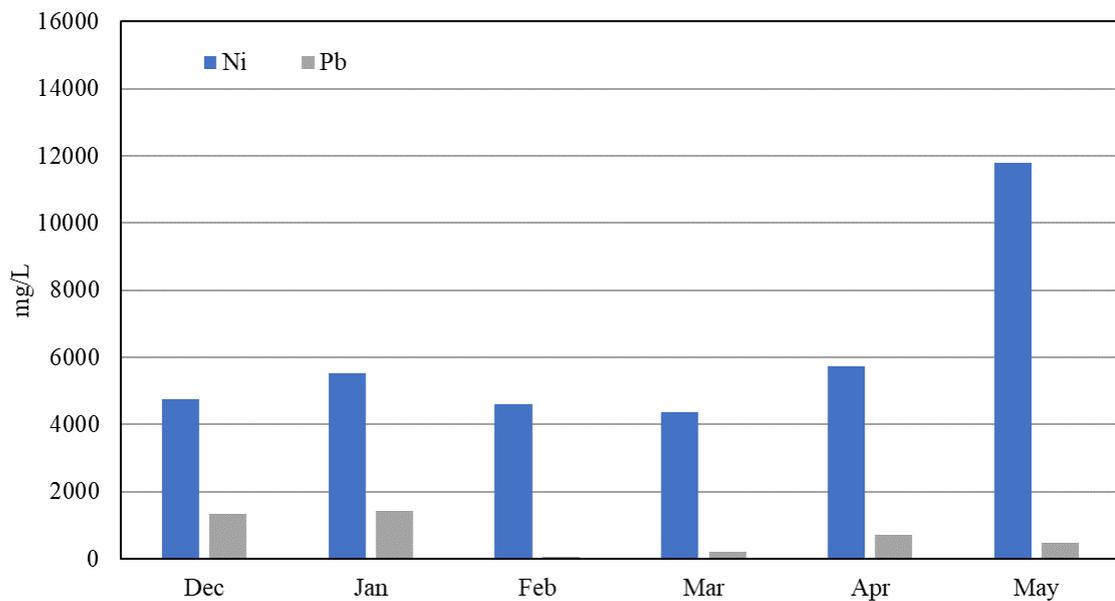


Figure 4.15. Effluent concentration of Nickel and Lead from Karabekir's CWs between December 2017 to May 2018.

Figure 4.14 shows the influent concentrations of nickel and Lead. The low concentration value of the influent of Nickel was seen in February and March (3700-4300 ng/L) and its highest initial value was determined in the period of April and May

(12617 – 13650 ng/L). For the effluent concentration (in Table 4.16), the lowest value concentration of Nickel was identified in March (4383 ng/L) when the highest value was in May (11802 ng/L). With remarks, the effluent concentrations of the Nickel in February and March were found to be higher than the influent. The same results have been seen in many literatures like result of Slavošovice CWs, 58400 ng/L of influent and 65400 ng/L of effluent identified by Kröpfelová (Kröpfelová et al., 2009), and by Lesage (Lesage, 2006) in Sint-Niklaas-Heimolen CWS with the influent concentrations of 200 ng/L and effluent of 330 ng/L.

The variation of Lead concentrations during the period of study was very wide (Figure 4.14). In December and January, the concentration of Lead in the wastewater influent was observed to have highest value as in the figure 4.10 (10220 ng/L - 6435 ng/L), while in other periods, the concentration of influent wasn't more than 1500 ng/L. As illustrated in Figure 4.15, the highest concentration of the effluent of Lead was observed in December (1331 ng/L) and January (1441 ng/L).

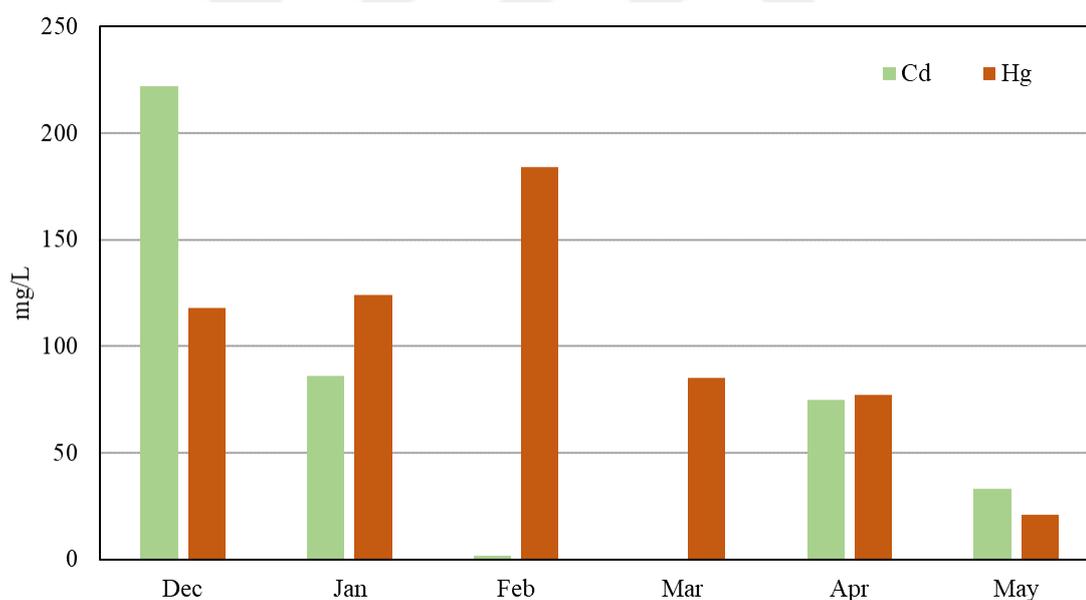


Figure 4.16. Influent concentration of Cadmium and Mercury from Karabekir's CWs between December 2017 to May 2018.

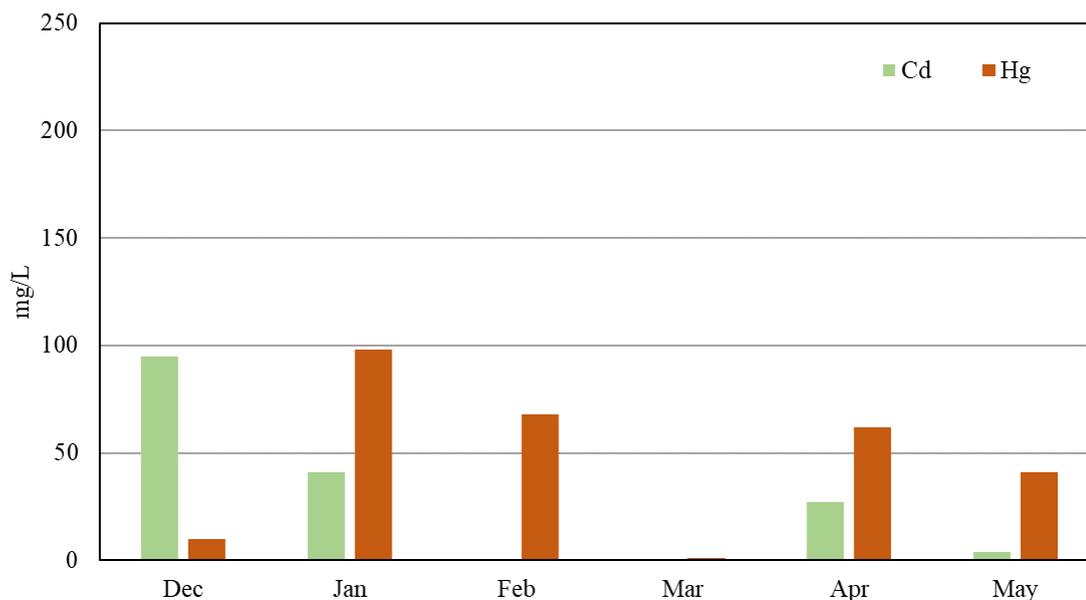


Figure 4.17. Effluent concentration of Cadmium and Mercury from Karabekir's CWs between December 2017 to May 2018.

Referring to others Heavy metals, the existence of the Cadmium in wastewater from Karabekir's city was also weak. Figure 4.16 shows the influent in the period of March whereby the concentration was under Limit Of Detection (LOD= 0,09 ng/L) of the Lead. It was 0 ng/L meaning that it's the lowest concentration of the influent. Moreover, the lowest concentration of effluent also was 0 ng/L in February and March, under LOD also; the highest value concentration of cadmium for influent was 95 ng/L, seen in December (Figure 4.17).

The Mercury identified in the small quantity of concentration in Karabekir wastewaters; presented in Figure 4.16, the concentration value was under 200 ng/L, the highest value concentration Mercury in the influents was observed in February (184 ng/L), if the effluent concentrations was identified in January (98 mg/L) in figure 4.13, mentioned that the lowest value concentration of effluent of Mercury was under of its LODs (16 ng/L), which observed in period of December (10 ng/l) and March (1ng/L). The concentration of Mercury in May was differs of the others, because, the concentration of effluent (41 ng/L) was higher than the influent (21ng/L), as in the literature, the same similar results was found in the studied of Lesage (Lesage, 2006) in Deurle CWs to Belguim with value concentration of 21 ng/L influent to 49 ng/L concentration of effluent.

To conclude, the concentration of heavy metals in wastewater influents from Karabekir's city and effluents after the treatment, don't pass over limits of the basic environmental quality standards for surface water, the limit of the standards quality is: 50000 ng/L for Nickel, Lead, and Mercury; and 1000 ng/L for Cadmium (Lesage et al., 2007).

The Figure 4.12, describes that the removal efficiency of heavy metals is observed to be different according to the period of time and Heavy Metals compounds. The Nickel removal efficiency was very low especially the period of sampling. Removal efficiency was under 15%, except in April where it attempts to be over 50%, for some months. Removal efficiency was also identified to be negative, like in February and March which was recorded to be -22%, -1,2%.

Rate of removal efficiency of Mercury had a larger variability during the period of study, between 98% (in April) and 95% (May). The amount of rate removal efficiency of December and March period was raised above 90 % while that of April was decreased fewer than 20% and in the May became negative.

The Cadmium removal efficiency among the better of the results of Heavy Metals removal, not only steady and more than 50%, in period of May more highest, raised until 87% Cadmium removal; although, the period of March, the removal was 0%, this was the cause of the no concentration of compound detected in the wastewater influents. For Lead, the removal efficiency was better in most of the period, the removal efficiency was excesses of 50%, in exception, the period of April which was 25%.

Table 4.19. Concentration of heavy metals in HSSF CWs.

Heavy Metals	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Sources
Ni (CW of Břehov)	2240	1210	46,0	(Kröpfelová et al., 2009)
Ni (CW Mořina)	17500	8900	49,1	
Ni (CW Slavošovice)	5840	6540	-12,0	
Ni (CW Hasselt-Kiewit)	3800	0	100	(Lesage et al., 2007)
Ni (CW Karabekir)	7527,5	6131,7	18,5	Karabekir's CWs
Cd (CW of Břehov)	330	100	69,7	(Kröpfelová et al., 2009)
Cd (CW Mořina)	320	70	78,1	
Cd (CW Slavošovice)	100	100	0	
Cd (CW Hasselt-Kiewit)	330	0	100	(Lesage et al., 2007)
Cd (CW Karabekir)	69,7	27,8	60,0	Karabekir's CWs

Pb(CW of Břehov)	13,2	2,9	78,0	(Kröpfelová et al., 2009)
Pb (CW Mořina)	15600	2460	84,2	
Pd (CW Slavošovice)	3660	2720	25,7	
Pd (CW Hasselt-Kiewit)	47000	3100	93	(Lesage et al., 2007)
Pd (CW Karabekir)	3215,8	707,3	78,0	Karabekir's CWs
Hg (CW of Břehov)	180	110	38,9	(Kröpfelová et al., 2009)
Hg (CW Mořina)	170	120	29,4	
Hg (CW Slavošovice)	190	100	47,4	
Hg (CW Hasselt-Kiewit)	260	35	86	(Lesage et al., 2007)
Hg (CW Karabekir)	101,5	46,7	54,0	Karabekir's CWs

The Table 4.19 demonstrates the results of the other HSSF CWs, as compared to the Karabekir's HFFS CWs. As the table suggests, the concentration of influent of Nickel in Karabekir's city is not really high (7527,5 ng/L) as compared to the CW of Břehov and CW of Mořina (17500 ng/L). But the removal efficiency was observed to be lower (18,5%) than the Nickel removal efficiency reported by Kröpfelová (Kröpfelová et al., 2009) 46-94% and Lesage (Lesage et al., 2007) 100%. By looking at the table 4.18, in general, the removal efficiency of Nickel CWs was around 40-50%, and it was confirmed by others studies like the study of Sardar Khan (Khan et al., 2009) 40.9% and Maine (Maine et al., 2009)(2009) 39%.

For Cadmium as presented in the Table 4.18, Karabekir's City produced lowest quantity of Cadmium (96,7 ng/L), as compared to others which is almost more than 300 ng/L. In general, the removal efficiency of Cadmium was better. From Table 4.19, Karabekir's CWs was 60%. 78% was reported by Kröpfelová (Kröpfelová et al., 2009) in Mořina CWs, the study of Lesage (Lesage et al., 2007) in Hasselt-Kiewit CWs indicated until 100% of removal rate; to confirmed the highest removal efficiency of Cadmium, a similar literature mentioned also removal efficiency of in CWs to 93,55% of Abrha studied (Abrha, 2013), 86,20% reported by Si (Si et al., 2014), 91,9% detected by Sardar Khan (Khan et al., 2009); comparing of those studies, the Cadmium removal efficiency of Karabekir's HSSF CWs was looked to be low with 60%, but close to other CWs removal as for Břehov CWs which removed 69,7% (Kröpfelová et al., 2009), event looked higher than the results reported by Sheoran (Sheoran and Sheoran, 2006) 20% and Arroyo Paula (Arroyo et al., 2010) 22,3%.

The concentration of Lead in wastewater Influent from Karabekir's City was found to be low, with the concentration of 3220 ng/L compared of the Lead concentrations of Mořina CWs (15600 ng/L) and Břehov CWs (13200 mg/L) reported

by Kröpfelová (Kröpfelová et al., 2009), but very high compared to the concentrations reported by Lesage (Lesage et al., 2007) from Hasselt-Kiewit CWs (4700 ng/L). Lead is among the heavy metals more operational to removed by CWs, in the study Lead had an excellent removal efficiency with 78% ; moreover, as illustrated by many literature also, 93% Lead removed at Hasselt-Kiewit CWs as reported by Lesage (Lesage et al., 2007) and 78.0% at Mořina CWs, 84, 2% at Slavošovice CWs indicated Kröpfelová (Kröpfelová et al., 2009) and also reported by Vymazal (2003) in Nucice CWs with 98% removal rate; with 78, 0% efficiency removal, the Karabekir's CWs treatment was more active with Lead removal like the others CWs.

The Mercury also the heavy metals found in domestic wastewaters, the concentration of Mercury was among in small quantity also, as shows in the Table 4.18, less than 300 ng/L was determined in influent, the highest concentration was reported by Lesage (Lesage et al., 2007) from Hasselt-Kiewit CWs with 260 ng/L, the other was around of 100-200 ng/L, as indicated by Kröpfelová (Kröpfelová et al., 2009) in his study, the concentration of Mercury ranged between to 170-190 ng/L in the influent of Mořina CWs and Slavošovice CWs, from Karabekir's CWs, the concentration of Mercury in the wastewater from City was identified very lower (100 mg/L) than the both CWs below. The CWs can remove the Mercury in varying rate, some CWs could remove more than 50%, like the study reported by Lesage (Lesage et al., 2007) at Hasselt-Kiewit CWs could removed the mercury until 86%, also reported by Nelson (Nelson et al., 2006) to 83 %, some studied indicated more higher removal rate of Mercury until 99% (Dorman et al., 2009); however, the others studies showed the low rate removal efficiency of Mercury, some under 50%, like observed at Mořina CWs (29,4%) and Břehov CWs (38,9%) (Kröpfelová et al., 2009), event very lowest with 18, 84% removal reported by Paula (Arroyo et al., 2010); furthermore, the removal efficiency of Mercury of Karabekir's CWs (54,0%) was better comparing to removal efficiency of Mercury in general.

Table 4.20. Heavy metals removal efficiencies in different types of CWs.

Heavy Metals	Type	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Sources
Ni	FWS CW Deurle	7400	860	88	(Lesage et al., 2007)
Cd					
Pd		5000	1800	64	(Lesage et al., 2007)
Hg		210	490	-138	(Lesage et al., 2007)
Ni	VSSF CW Zemst- Larebeek	12000	9100	26	(Lesage et al., 2007)
Cd		160	0	100	(Lesage et al., 2007)
Pd		7300	0	100	(Lesage et al., 2007)
Hg		13000	0	100	(Lesage et al., 2007)
Ni	CW Karabekir	7527,5	6131,7	18,5	
Cd		69,7	27,8	60,0	
Pd		3215,8	707,3	78,0	
Hg		101,5	46,7	54,0	

Looking in the different systems of CWs in the Table 4.20, it shows that the VSSF CWs was removed better the heavy metals in the systems after HSSF CWs and FWS CWs, but it doesn't means in general, it depends of the many factors, it would be necessary to monitor more HSSF constructed wetlands with different design parameters (Kröpfelová et al., 2009), they are strongly dependent on influent concentrations and hydraulic loading rates (Lesage, 2006), (Kadlec, 1996)), the removal efficiencies between different CWs should be carefully interpreted (Lesage et al., 2007).

#### 4.3.2. Poly aromatic hydrocarbons

Removal of PAHs is primordial to conserve the environment of the casual disease and other problems from these pollutants. Therefore a way to find an issue of degradation of PAHs is very important solution of the problem. The degradation depends on the environmental conditions, number and type of the microorganisms, nature and chemical structure of the chemical compound being degraded (Haritash and Kaushik, 2009). Many processes can be used to remove the PAHs, in this study. The CWs was tested to remove the PAHs in wastewater from Karabekir's city. The study started on July 2017 and was completed on May 2018 by taking sample during a period of 10 months (between July –May). The GC-System was used for the analysis with a LOQ. The same LOQ applied for all the PAHs micro pollutants in this study, and the

quantity used in detection was in ppb. In general, the PAHs results showed, the different removal efficiency of 79,5 % the highest (Naphthalene) and 11, 4% the lowest (Benzo[k]fluoranthene) (Table:4.20).

The table 4.21 reports the average, maximum and minimum concentration of the influent and effluent and then the percentage removal of annual loadings for PAHs in Karabekir's CWs

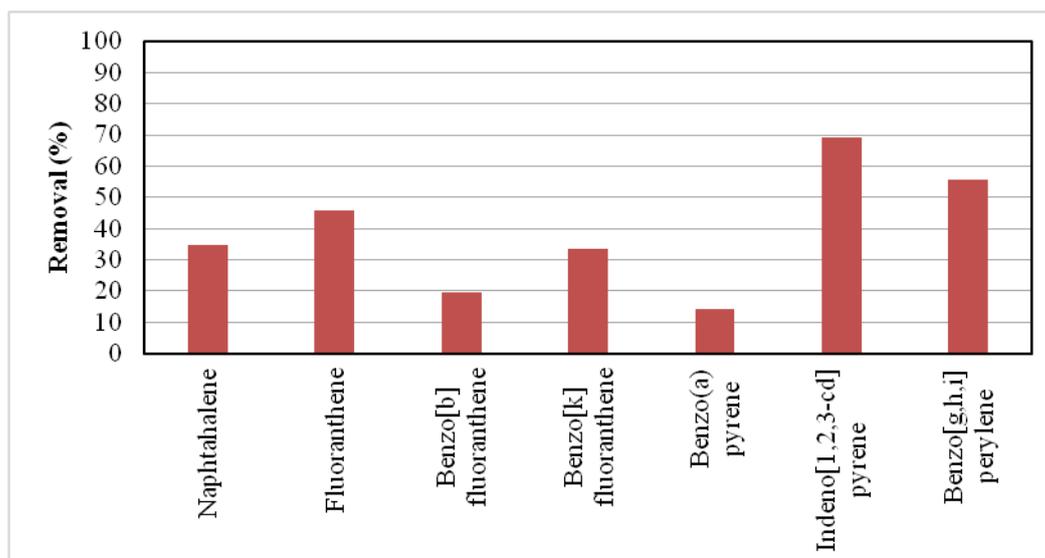


Figure 4.18. Removal efficiency of PAHs in the Karabekir's CW

Table 4.21. Average, maximum and minimum concentration of PAHs in Kazımkarabekir CW.

PAHs	Average (ng/L)		Max (ng/L)		Min (ng/L)		Removal (%)
	Influent	Effluent	Influent	Effluent	Influent	Effluent	
Naphthalene	114,4	74,7	374,8	227,4	23,5	0	34,8
Fluoranthene	22	12	34,8	29,8	0	0	45,7
Benzo[b]fluoranthene	23,9	19,2	66,1	39,8	0	0	19,6
Benzo[k]fluoranthene	9,8	6,5	49	23,9	0	0	33,6
Benzo(a)pyrene	96,2	59,3	216,3	206,7	19,7	11,8	14,4
Indeno[1,2,3-cd]pyrene	118,6	36,8	231,9	69	31,6	0	69
Benzo[g,h,i]perylene	42,4	18,8	110	60,5	0,0000	0	55,6

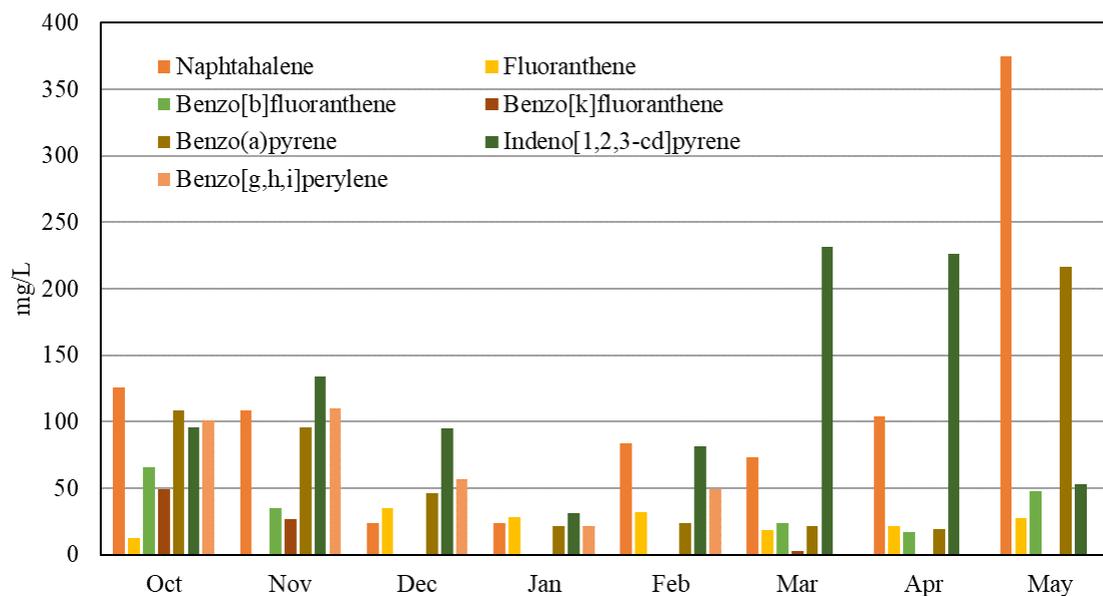


Figure 4.19. Influent concentrations of Naphthalene, Fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo(a)pyrene, Indeno[1,2,3-cd] pyrene, Benzo[g,h,i] perylene from Kazımkarabekir's CWs between October 2017 to May 2018.

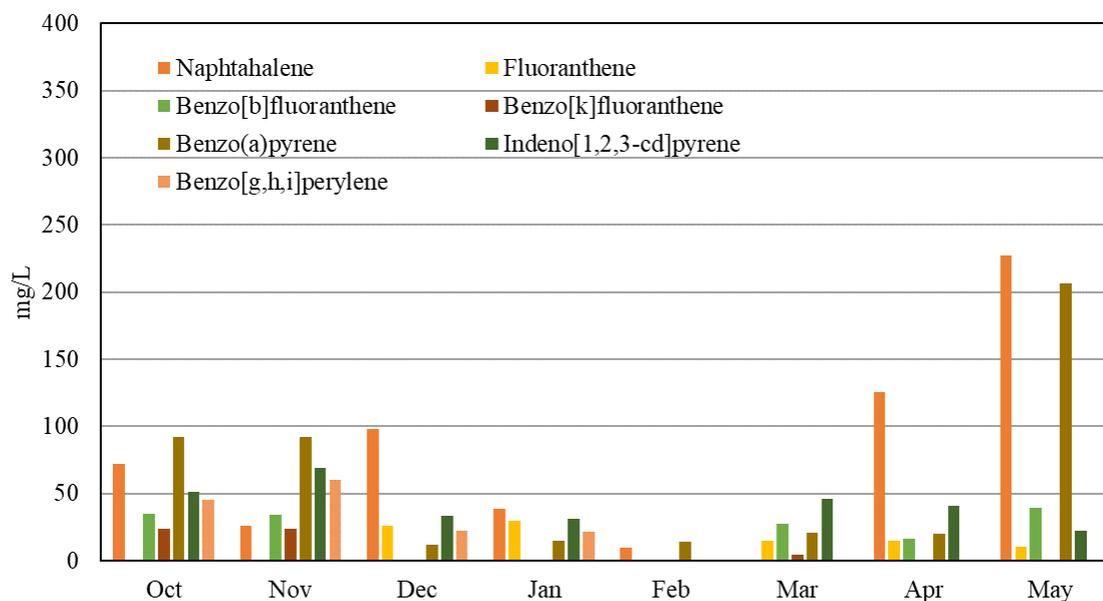


Figure 4.20. Effluent concentrations of Naphthalene, Fluoranthene, Benzo[b] fluoranthene, Benzo[k] fluoranthene, Benzo(a) pyrene, Indeno[1,2,3-cd] pyrene, Benzo[g,h,i] perylene from Kazımkarabekir's CWs between October 2017 to May 2018.

The Naphthalene is one of the PAHs of study in Karabekir's wastewater. In general, most of the concentration of influents observed in studied were around 100

ng/L with an exception in the period of May (Figure 4.19) where the concentration value was raised to 374,8 ng/L. This was the higher concentration value in the influent. On the other hand, the lower concentration value was observed in the period of December (23 ng/L) and January (23ng/L). Those lower values were identified under value of LOD (21,3 ng/L) and LOQ (71 ng/L) of Naphthalene; for the effluent (in Figure 4.20), the highest concentration obtained was 227,4 ng/L in May; the average concentration value of influent of Naphthalene was 74,7 ng/L and lower concentration value was 0 ng/L in March, apparently two concentration value of effluents were under of LOD of (10 ng/L in February and 0 ng/L in March), and three value under LOQ (November 26,04 ng/L, February and March).

The concentration of Fluoranthene in wastewater influents and effluents was supplied in small quantity compared to Naphthalene, the Fluoranthene value concentrations of Influent obtained were around of 20 ng/L in most of the periods, as in the Figure 4.19, the higher concentration value getting was 32,2 ng/L, in front of the lower concentration value of 0 ng/L, it was under the Fluoranthene LOD values (2,28 ng/L) and LOQ (7,61 ng/L); after the sewage treatment of CW, the effluent concentrations in the Figure 4.20, more of the results were Fluoranthene LOD (2,28 ng/L) and LOQ (7,61 ng/L) values (0 ng/L in October, November, February), the higher concentration value was observed in December (26,08 ng/L)

Among the PAHs missed during many period of the study is Benzo[b]fluoranthene, didn't detected in wastewater during period of December to February (0 ng/L); although, demonstrates in the Figure 4.19 above, the higher concentration was observed in the period of October (66,09 ng/L) and May (48,1 ng/L), the average concentration values of Benzo[b]fluoranthene was 23,9 ng/L; about the effluents (in Figure 4.20) after the treatment, the higher concentration was observed in period of May (39,8 ng/L), October (35,32 ng/L) and November (34,7 ng/L), with average concentration of Benzo[b]fluoranthene of 19,2 ng/L.

Before the process of CW treatments, the influent average concentration values of Benzo[k]fluoranthene was 9,8 ng/ presented in the Figure 4.19, the most of the concentration value identified were under the LOQ (6,45 ng/L) and LOD (1,94 ng/L) concentration values of Benzo[k]fluoranthene determined, like the results obtained in the period of the December, January, February and May, where the results identified were 0 ng/L respectively; however, some periods, the concentration was raised above of 0 ng/L, but still under LOQ as found in March (2,6 ng/L) and April (0,2 ng/L); whereas,

the high value concentration of Benzo[k]fluoranthene was observed in October (48,96 ng/L) and November (26,57 ng/L). After the treatment process, in the Figure 4.20 shows the effluent concentration values, the higher concentration value was 23 ng/L observed in October and November, if the average concentration of effluent calculated was 6, 5 ng/L.

For Benzo(a)pyrene concentration value in the Figure 4.19 show that the peak concentration value was 216 ng/L in the period of May, and lower observed was 19,7 ng/L (April), most of the Benzo(a)pyrene concentration observed in the figure 4.13 around of 20 ng/L. About the effluent (Figure 4.20), the maximum concentration was 206 ng/L (May) there was no more different between maximum concentration of Influent and effluent; and lower concentration value of effluent was in period of December (11 ng/L).

The Benzo[g,h,i]perylene among the pollutants didn't found during most of the period of study also, for three months (March, April and May) the Benzo[g,h,i]perylene hadn't be existed in the Karabekir's sewage; in the months of existence of Benzo[g,h,i]perylene, the peak concentration value observed in the Figure 4.19 was 109,7 ng/L, the average concentration value obtained was 6,1 ng/L; after the passage of sewage through the system, the influent presented in Figure 4.20, the higher concentration of effluent in the figure was 60 ng/L (November) and 45,7 ng/L (October), the minimum decreased into 0 ng/L.

The concentration value of Indeno[1,2,3-cd]pyrene presented in the Figure 4.19 (influent) and figure 3.15 (effluents), Indeno[1,2,3-cd]pyrene among had the higher concentration value of influent after the Naphthalene, and had be existed during all the period; about the influents (Figure 4.19), the peak of concentration identified was 231,9 ng/L in the period of March and 226,3 ng/L in the period of April, the minimum concentration value was found in the period January of 31,6 ng/L; other way, the most concentration of effluent after treatment (Figure 4.20) observed was around of 50 ng/L, the peak of concentration value obtained was 68,9 ng/L in November.

For PAHs, as observing in those Figures, the concentrations relate to the season, most of the PAHs compounds identified the non existence or low of the concentrations in the wastewater influents in winter but were elevated in summer.

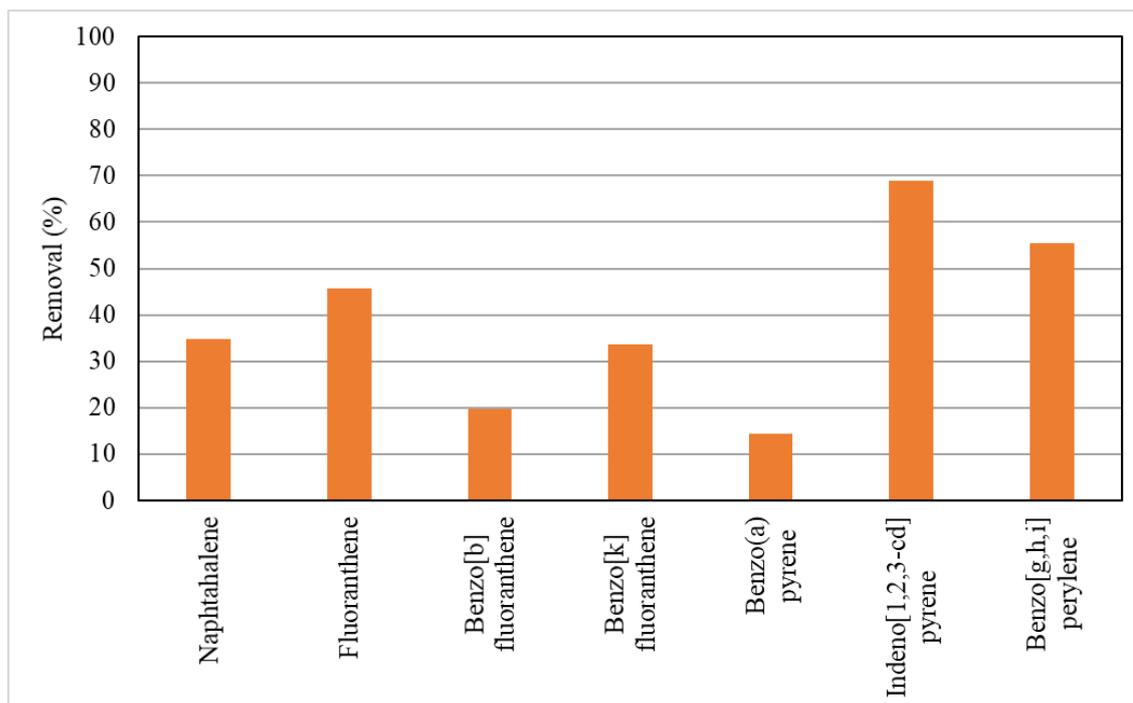


Figure 4.21. Removal efficiency of PAHs in Kazimkarabekir CW between October 2017 to May 2018.

The removal of PAHs in study were different (Figure 4.21), and the removal of PAHs compounds is different between the period also; for Naphthalene, mentioned that the removal was widely varying between negative and positive (100 % -315 %), in some period the removal were widely positive like removal in March (100%), October (93%), in contrast, some other were negative like removal identified in January (-65%) and April (-21%), for other period was largely negative like observed in December (-315%), those negative results were gave but large concentration of the effluent than the influent. About Fluoranthene, the removal during the period of study ranged between 60% the high removal to -3% the lowest, many period of months (October, November and February) the removal of Fluoranthene were 0%, cause of the non existence of micro-pollutant in the influent, like Benzo[b]fluoranthene also, four months non existence in the influent started to December till March, some case for Benzo[g,h,i]perylene, which not presented for four months also between January to May. Thinking the removal of PAHs during these periods, between Decembers to March, some PAHs micro-pollutants were quite existence in wastewaters, this may conclude that in winter, the activity of the population to used the PAHs was decreased or cancelled, because the study confirmed non existence of some pollutants in the influents discharged from the city, but not relate to removal efficiency of the PAHs

Table 4.22. Concentration of PAHs in HSSF CWs.

PAHs	Influent (ng/L)	Effluent (ng/L)	Removal (%)	System	Sources
Naphthalene	1168	76,5	93	FWS	(Li et al., 2017)
	114,7	74,7	34,8	HSSF	Karabekir's HSSF CWs
Fluoranthene	600	40	94	VSSF	(Tromp et al., 2012)
	125	33	79	FWS	(Li et al., 2017)
	22	12	45,7	HSSF	Karabekir's HSSF CWs
	220	30	89	FWS	(Li et al., 2017)
Benzo[b]fluoranthene(BbF)	23,9	19,2	19,6	HSSF	Karabekir's HSSF CWs
	200	17	91	VSSF	(Tromp et al., 2012)
Benzo[k]fluoranthene(BkF)	280	70	81	FWS	(Li et al., 2017)
	9,8	6,5	33,6	HSSF	Karabekir's HSSF CWs
	290	50	74	FWS	(Li et al., 2017)
Benzo(a)pyrene(BaP)	300	18	94	VSSF	(Tromp et al., 2012)
	69,2	59,3	14,4	HSSF	Karabekir's HSSF CWs
	600	80	87	VSSF	(Tromp et al., 2012)
Benzo[g,h,i]perylene(BgP)	42,4	18,8	55,6	HSSF	Karabekir's HSSF CWs
Indeno[1,2,3-cd]pyrene(IcP)	118,6	36,8	69	HSSF	Karabekir's HSSF CWs

In the Table 4.22 shows the different studied of PAHs in CWs, the same pattern for comparisons between the concentrations at different influent, effluent and removal efficiency; in general, the removal efficiency of PAHs in CWs were better as summarizing in Table 4.21 . The concentration of Naphthalene at Karabekir's CWs influents (114, 7 ng/L) was very lower than the influent of Shunyi's CWs of Bejiign (1168 ng/l), but the FWS of Shunyi's (93%) removed better the Naphthalene than HSSF CWs of Karabekir's (34, 8 %). About Fluoranthene, the Karabekir's discharged looked had highest concentration with 0.285mg/L, but the removal efficiency was lower with 45,7 % than of FWS of Shunyi's (Li et al., 2017) with 79% removal rate, and 94% of VSSF at Amersfoort city to Amsterdam (Tromp et al., 2012). Benzo[b]fluoranthene concentration of Karabekir's discharged was low (23,9 ng/L) compared of concentration value reported by Li (Li et al., 2017) of 220 ng/L; also, the FWS of Shunyi's removed higher rate of Benzo[b]fluoranthene (89%) than HSSF CWs Karabekir's which was 19,6 %. Looking the Benzo[k]fluoranthene, the discharge from Karabekir's city was very lowest with 9, 8 ng/L, moreover, the removal efficiency was low also (33, 6%) compared of both studied show in the table 4.21 with 91% (Tromp et al., 2012) and 81% (Li et al., 2017) removal rate. For Benzo(a)pyrene and Benzo[g,h,i]perylene , similar as the others PAHs above, the concentration of Benzo(a)pyrene and Benzo[g,h,i]perylene at Karabekir's CWs influent concentrations were lowest with 69,2 ng/L and 42,4 ng/L; then, the removal efficiency of Benzo(a)pyrene (14,4%) was lower

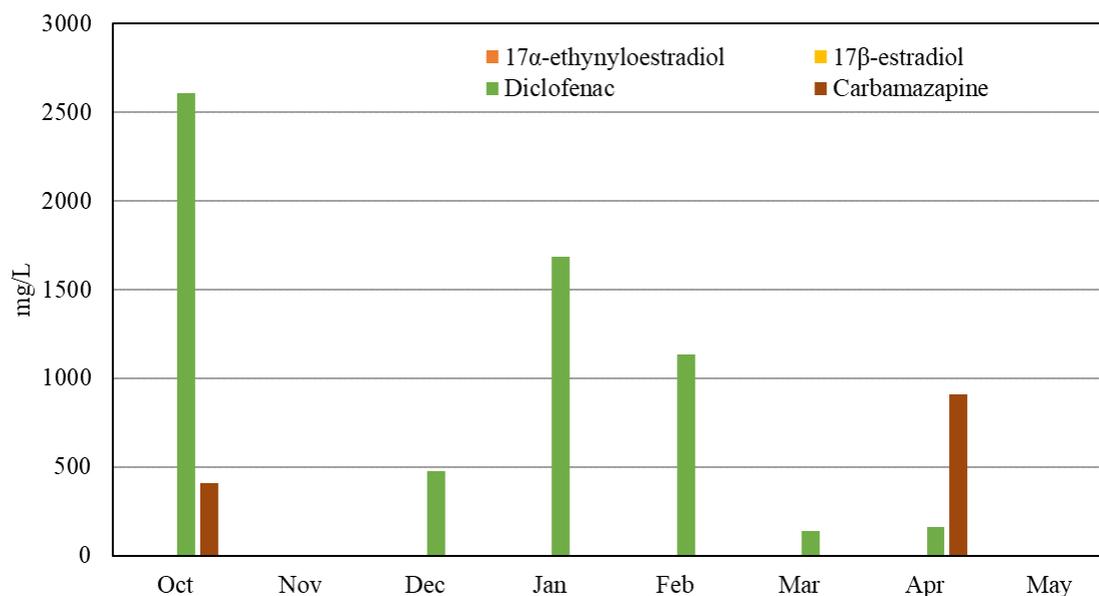
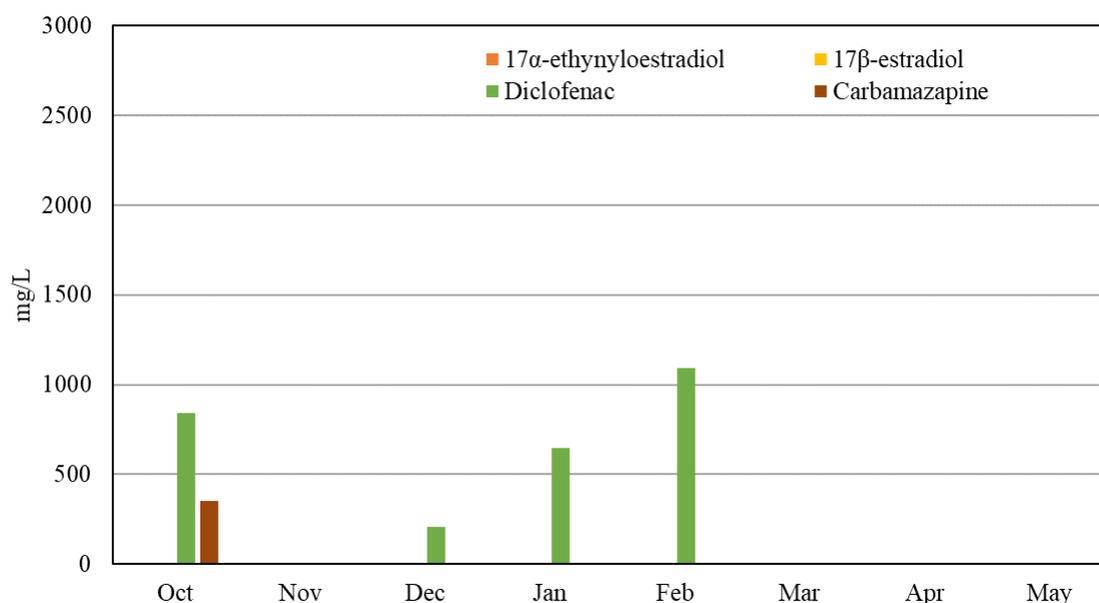
also than the removal result indicated by Tromp (Tromp et al., 2012) (94%) and Li (Li et al., 2017) (87%) as indicated by Haritash (Haritash and Kaushik, 2009); and for Benzo[g,h,i]perylene (55,6 %) was among better of the PAHs study, but still low comparing to the result gave up by Tromp (Tromp et al., 2012) came from VSSF at Amersfoort city (87%). In general, the Karabekir's City had low concentration discharged of PAHs, as confirmed in the studied, the removal efficiency of PAHs in HSSF of Karabekir's CWs looked very low compared to literatures and the others CWs systems used for others studied (FWS and VFFS), but according by Haritash (Haritash and Kaushik, 2009) the removal of PAHs in constructed wetlands in general ranged between 90–95%; so, the reason may be, the adsorption, desorption and solubilisation process of PAHs behaviors in Karabekir's CWs had an inefficacy to removed the PAHs cause of the new CW and the biomass of organisms and formation of substrat which are responsible of those processes are not yet enough, like the plant was recently growth at almost the end of the study.

#### **4.3.3. Pharmaceutically active compounds**

To reduce the pharmaceutical load discharged into the environment around of Karabekir's city, Karabekir's CWs setting up to removed the pollutants in wastewater from the city as the pharmaceutically active compounds. The removal of the pharmaceutically active compounds in CWs often involves a diverse and complex set of physical, chemical and biological processes, which can be affected by the design and operational parameters selected for (Zhang et al., 2012). The unity is used on this study is nano gramme per litre. In the result of the study the Limit Of Quantification (LOQ) detecting was 500 ng/L for  $17\alpha$ -ethinyloestradiol and  $17\beta$ -estradiol; and 100 ng/l for Diclofenac and Carbamazapine, those LOQ used during the LC-MS-MS analysis of the PhAcs. The periods of the analysis were started in October 2018 and finished in April 2018 (6 months). The results were below presented with a low efficiency removal of PhAcs, fewer than 50% and others didn't provide the results because of the detection under the LOQ ( $17\alpha$ -ethinyloestradiol and  $17\beta$ -estradiol)

Table 4.23. Average, maximum and minimum concentration of PhACs in Kazımkarabekir CW.

	Average (ng/L)		Max (ng/L)		Min (ng/L)		Removal (%)
	Influent	Effluent	Influent	Effluent	Influent	Effluent	
17 $\alpha$ -ethinyloestradiol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0
17 $\beta$ -estradiol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0
Diclofenac	1034,7	695,8	2610	1090,6	140	204,6	32,7
Carbamazapine	659,1	350	0,91	350	0,10	350	46,9

Figure 4.22. Influent concentrations of Diclofenac, carbamazepine, 17 $\alpha$ -ethinyloestradiol and 17 $\beta$ -estradiol in Karabekir CWs between October 2017 to May 2018.Figure 4.23. Effluent concentrations of Diclofenac, carbamazepine, 17 $\alpha$ -ethinyloestradiol and 17 $\beta$ -estradiol in Karabekir CWs between October 2017 to May 2018.

The Figure 4.22 and 4.23, summarizing the value concentrations of Diclofenac in the wastewater samples collected from influent and effluent of Karabekir's CWs, Diclofenac observed its presence in all period of the study; the concentrations of Diclofenac in the influent of wastewater ranged between 2610 ng/L of maximum value (October) to 140 ng/L (March) the minimum (Figure 4.22); moreover, after the CWs process, in Figure 4.23, the effluent value concentrations of Diclofenac were ranged between 1091 ng/L the maximum (February) to 140 ng/L (February and March) the minimum, those effluents of the months were close of the LOQ (100 mg/L).

In the Figure 4.22 shows that the Carbamazepine concentration values of influent Karabekir's CWs were 908 ng/L maximum in April and 410 ng/L in October, only those both result were above of LOQ (100 ng/L), most of the months, the results were below of LOQ like the result for December, January, February and March; and figure 4.18 shows the effluent concentration values, only in October had mentioned a result above of LOQ, it was 350 ng/L, the others months results were below of the LOQ; during the periods, only in the October and April there were illustrated the active removal process in CWs between influent and effluent, for those four months (December, January, February, march), the concentration values of influent and effluent were under the LOQ.

The  $17\alpha$ -ethnyloestradiol and  $17\beta$ -estradiol influents and effluents results were below of the LOQ of the LC-MS-MS analysis (500 ng/L), so why not compounds were detected. Comparing to concentration of Diclofenac and carbamazepine in wastewater influents and effluents, the both PhACs have be seen the rate removal during the CWs process and showed that, the different value concentrations between influent and effluent were existing.

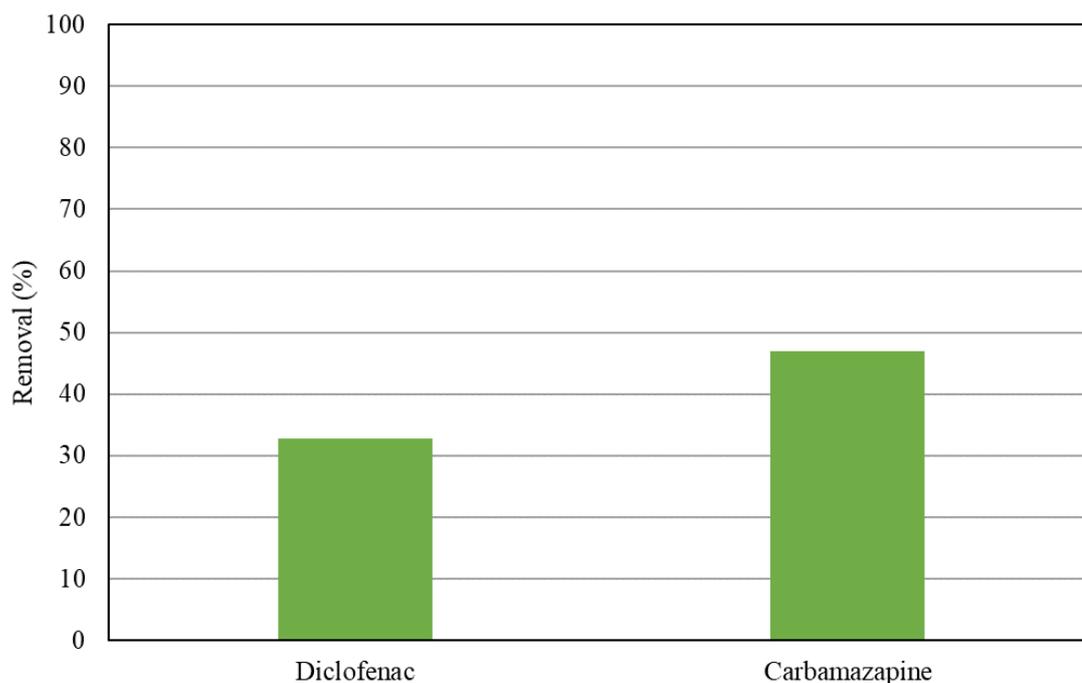


Figure 4.24. Removal efficiencies of Diclofenac and Carbamazepine in Kazımkarabekir CW

In the Figure 4.24 shows the removal efficiencies of the PhACs micro-pollutants. The Diclofenac removal efficiencies of Karabekir's CWs during the periods ranged between 67,8% (October) maximum to 4,1% (February) minimum, located that the removal efficiency are variable, in general the removal efficiency more over 30%. For Carbamazepine, the removal rate of pollutants was between 89% maximum (in April) to 0% in most of the periods where there had been a weak or no influents loading of Carbamazepine and no removal rate, as December, January, February and March, only 2 months had the removal (October and April). For  $17\alpha$ -ethynylloestradiol and  $17\beta$ -estradiol there was no removal of those contaminants in the CWs for all the periods, because those pollutants not found or in low quantity (under LOD and LOQ) in the discharge influents of Karabekir's wastewaters.

Table 4.24. Removal efficiencies of Carbamazepine and Diclofenac in HSSF CWs.

PhACs	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Sources
Carbamazepine	2060		26	(Matamoros et al., 2008a)
	990	820	24-48	(Hijosa-Valsero et al., 2016)
		450	38	(Matamoros et al., 2009)
			5	(Matamoros et al., 2008b)
	1830-1810		24–28	(Zhang et al., 2012)
Diclofenac	659,1	350	46,9	Karabekir CWs
	820		73	(Matamoros et al., 2008a)
		500	21	(Matamoros et al., 2009)
			0–11 ; 0–45	(Matamoros and Bayona, 2006)
	410	480	17-52	(Hijosa-Valsero et al., 2016)
	1470- 1400		24–44	(Zhang et al., 2012)
	1034,7	695,8	32,7	Karabekir CWs

In the Table 4.24 shows the influent, effluent and removal efficiency of concentration of Carbamazepine and Diclofenac in the different HSSF WC's, compare to HSSF Karabekir CWs.

For Carbamazepine, the concentration of influent and effluent are different between the studied, in the effluent, the highest concentration presented in the table is 2060 ng/L value reported by Matamoros (Matamoros et al., 2009), and from China reported by Zhang (Si et al., 2014) of 1800 ng/L, comparing of those both, the concentration of Carbamazepine in Karabekir CWs was the lowest with 659,1 ng/L, this influent concentration was similar of the effluent concentration reported by Matamoros (Matamoros et al., 2009), and Zhang (Zhang et al., 2012) in the table above; so it means the Karabekir's city didn't discharged many quantity of Carbamazepine.

About the efficiency removal of Carbamazepine in HSSF reported in the table below, the removal was ranged between 5% (Matamoros et al., 2008a) to 48% (Hijosa-Valsero M. and al, 2016), most of the efficiency removal around of 20%, study of Zhang (Zhang et al., 2012) from China indicated removal range between 24–28%, also Matamoros (Matamoros and Bayona, 2006) determined 26% removal efficiency on his studied, similarly Hijosa (Hijosa-Valsero et al., 2016) 24%; therefore, HSSF Karabekir CWs was removed to 46,9 % , this result is better compared to the majority of the studied reported by those literatures, and mentioned that the treatment of the Karabekir's CWs was operated well to removed the Carbamazepine.

About Diclofenac, the effluent of Karabekir CWs in the table 4.23 is look similar as in the literature, but the influent was little bit low (1030 ng/L) comparing of the study reported by Zhang (Zhang et al., 2012) with the concentration of 1470- 1400 ng/L, but

looked highest in front of the study reported by Hijosa (Hijosa-Valsero et al., 2016) with the concentration of 410 ng/L.

The removal efficiency of Diclofenac of Karabekir CWs was low with the efficiency removal of 32, 7 %, but comparing to the others studies on the same system, the result was better, the study of Matamoros (Matamoros and Bayona, 2006) found the removal of 0–11 %; to other hand of his study, most of the HFFS studies reported indicated the removal rate range between 40-50%, the result of removal of Diclofenac were variousnas shows in the table 4.23; in terms of removal efficiency indicate that the removal of HSSF is vary of the country and the parameters of constructed wetlands, Hijosa (Hijosa-Valsero et al., 2010), as Vymazal (Vymazal, 2008) reported, it may be due of the remaining pollutants had different removal efficiencies depending on the characteristics of the CW, known that PPCPs are not completely removed in wastewater treatment plants .Therefore, the results obtained confirmed that, the Diclofenac is difficult to removed in constructed wetlands.

Table 4.25. Carbamazepine and Diclofenac removal efficiencies in different types of CWs.

CWs types	PhACs	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Sources
FWS	carbamazepine	820	980	15-25	(Hijosa-Valsero et al., 2016)
	carbamazepine	370	230	39	(Llorens et al., 2009)
	carbamazepine			30	(Bernhard et al., 2006)
	Diclofenac	480	420	22	(Hijosa-Valsero et al., 2016)
	Diclofenac	1250	188	85	(Llorens et al., 2009)
	Diclofenac			96	(Matamoros et al., 2008b)
VFS	carbamazepine	2060		20–26	(Matamoros and Bayona, 2006)
	Diclofenac	820		53–73	(Matamoros and Bayona, 2006)
HSSF Karabekir's	carbamazepine	659,1	350	46,9	
	Diclofenac	1034,7	695,8	32,7	

In this Table 4.25 shows the influent, effluent and removal of Carbamazepine and Diclofenac in different system of the CWs. The FWS studied by Matamoros (Matamoros et al., 2008b) 96% and Llorens et al. (2009) 85% removal of Diclofenac seems higher than Karabekir's CWs results (32,7 %), whereas, the result of study of Hijosa (Hijosa-Valsero et al., 2016) had lower performance removal (22%) than Karabekir's CWs; about, Carbamazepine removal efficiency of the FWS studied by Llorens (Llorens et al., 2009) and Bernhard (Bernhard et al., 2006) reported that removal efficiency were 39% and 30%, and reported by Hijosa(Hijosa-Valsero et al.,

2016) also 15-25%, they were lower than removal efficiency of Karabekir's CWs (46,6%). In the VF system, the result of Diclofenac removal, as shows the table 4.24, Matamoros (Matamoros and Bayona, 2006) identified the highest removal efficiency of 53–73 %, if 32,7% to Karabekir's CWs; but with 20–26% of Carbamazepine removal reported by Matamoros (Matamoros and Bayona, 2006) lower than 46,9% of Karabekir's CWs. So, we could say that the removal of Diclofenac in Karabekir's HSSF CWs was better than the FWS and VF system, but the Diclofenac was less removed in those both CWs system as results shows by those studied and those of previous researches. To conclude, the VF and HSSF removal efficiency of Carbamazepine and Diclofenac are lower than the FWS; concerning Diclofenac, WWTP which observed removal efficiencies of 22-33% for Diclofenac (Bendz et al., 2005); (Ternes et al., 2007), for Carbamazepine, may be the CWs system could removed above of 30% Carbamazepine in CWs.

## 5. CONCLUSION AND RECOMMENDATIONS

The study focusses to monitoring of a real scale HSSF CWs which treated the domestic wastewater of Karabekir's city. These CWs have coarse and fine screen, fosseptic and CW ponds, responding on the criteria of Water Pollution and Control Regulation in Turkey.

The analysis on this study based in the influent and effluent taking samples and examined in the laboratory to determine the concentration value of the influents and effluents of wastewater; and the removal efficiency of the CWs of: nutrient as TN, TP; and organic matters like BOD<sub>5</sub> and COD; and micropollutans as heavy metals, PAHs and PhACs.

During on this study, in the strating of the sampling, the plant was not yet growing up, but some month before the end (March) of the study, the plant was growth; but as the length of with plant and without plant were short, the result didn't show the main different removal between the both time.

To study the nutrients, the concentration of TP identified in the CWs was varied between the months, the average of influent concentrations was 4 mg/L, if effluent concentrations was 2,5 mg/L, and the removal efficiencies was 37%; comparing with the literatures of CWs HSSF and others types of CWs, looking the VSSF and FWS, the removal efficiency of Karabekir's HSSF CWs was low. This lowest removal may be due to the process removal of the Phosphorus, the Phosphorus removal is through the physical and chemical processes in the wetlands, the soluble reactive phosphorus is taken up by plants and converted to tissue phosphorus or may become sorbed to wetland soils and sediments (Vymazal, 2007), if the processes is not work well the removal of phosphorus is quite low. For the TN, the concentrations of influent is in generally was 46,6 mg/L, in the effluent was 34,3 mg/L; however, the CWs removed 26,4% of TN.

The organic matters are among one of important parameters of study, removal process of organic matters in different constructed wetland is associated with biological, chemical, and physical mechanisms, such as settling, adsorption, microbial activity, and photo-degradation, in particulate the removal processes of organic matters is, by sedimentation and filtration, whereas the amount of dissolved organic matter can increase or decrease according to the design of the constructed wetland (Park et al., 2018). The result of BOD<sub>5</sub> was varied between the months, the BOD<sub>5</sub> concentration in the influent was 136 ng/L and in the effluent was 24 ng/L, if the removal efficiency was

better in general, in most of the months, the removal efficiency was illustrated above of 80%; over wise, the removal efficiency of COD was low with 42,2%; in front of BOD5, the concentration of COD in influent was 435 ng/L if the effluent was 250 ng/L; this low removal was, may be due to the relation with the others parameters which not available or inhibit the removal of COD, because the ability of constructed wetlands to removed the organic matters and treat the COD have been reported by many authors with varying different results, which depends on the season, system and different of constructed wetlands and quality of quantity of the organic matters loading in (Aboulroos et al., 2012)

The heavy metals among the micropollutants chosen, the compounds studied for the heavy metals are: the Nickel (Ni), Cadmium (Cd), Lead (Pb) and Mercury (Hg). The lowest concentration value of the influent of nickel was 7527,5 ng/L and effluent concentrations value was 6131,6 ng/L, for some months (February and March) the effluent concentrations were to be higher than the influent, however the average removal efficiency in general was under 18%, in February and March the removal efficiency was negative -22%, -1,2%, this negative result may be due to Hydraulic retention time (HRT), the effluent samples may take must respect the length time of the HRT between the influent and the effluent, but the real HRT time not yet studied. For the Cadmium, the influent concentration was 69,67 ng/L, the lowest influent concentrations was identified under LOD (in March) 95 ng/L; for the effluent, the average concentration value was 46,7 ng/L, for the periods of February and March the value were under LOD, the average removal efficiency of Cadmium was 60%, in May the removal was maximum with 87%, but for the February and March were 0%. The concentration of Lead in the influent was 3215,8 ng/L, the effluent concentration was 707,3ng/L, the removal efficiency was better in general, with the average removal efficiency of 78%. For the Mercury, 184 ng/L the highest concentration value of influent and 21 ng/L the lowest, and for the effluent, 98 ng/L the highest value concentration and 1ng/L the lowest, the effluent concentration value of the December and March was under the LOD of Mercury, the removal efficiency of Mercury was very variable, between 98% (in March) to -95% (May), however, the average was 54%. So concluded that the CWs Karabekir's process was affective with removal of the heavy metals, most of the heavy metals compounds were removed under 50% excepted the Nickel, and looking the tendency of the removal efficiency in the figure 4.22, the season

quite affected the heavy metals removal, because in winter, most removal efficiency of heavy metals were decreased.

The PAHs is among the micropollutants was study, the compounds as Naphtahalene, Fluoranthene, Benzo[b] fluoranthene, Benzo[k] fluoranthene, Benzo(a) pyrene, Indeno[1,2,3-cd] pyrene and Benzo[g,h,i] perylene. The influent concentration of Naphtahalene ranged between 114,7 ng/l and 74,7 ng/L of effluent the lower was under the LOD and LOG for the period of February and March, the removal efficiency of Naphtahalene was looked low with 34,8 %, but the removal efficiency was widely varying between 100% to -315%; about Fluoranthene, the average concentration value of influents was 22 ng/L, the concentration for the period of November looked under the LOD and LOQ, for effluent was 12 ng/L more of the concentration were under LOD and LOQ (October, November and February), the average removal efficiency was 45,7% with removal ranged between 60% to -3%. The Benzo[b]fluoranthene showed with the average concentration of 23,9 ng/L of influent and effluents was 19,2 ng/L, most of the period had a concentration value under LOD and LOQ, Benzo[b]fluoranthene had the low removal efficiency with 19,6% in general. The Benzo[k]fluoranthene had a concentration of 9,8 ng/L in influent and 6,5 ng/L in the effluent and 33% removal efficiency, but only two months of the result of influents and effluents were above of the LOD and LOQ, About Benzo(a)pyrene, the concentration identified was 69,2 ng/L the influent and 59,3 ng/L the effluent with the removal efficiency of 14,4%. Indeno[1,2,3-cd] pyrene had a concentration average of 118,6 ng/L in influent and 36,8 ng/L effluent with removal of 69 %; however the Benzo[g,h,i] perylene showed the concentration of 42,4 ng/L of influent and 18,8 ng/L of effluent, with removal of 55,6 %. Summarizing, the Karabekir's CWs removed quite PAHs micro-pollutants, especially the Naphtahalene, Benzo[b] fluoranthene, Benzo[k] fluoranthene, Benzo (a) pyrene; mentioned also, the pollutants Benzo[b] fluoranthene, Benzo[k] fluoranthene and Benzo[g,h,i] perylene were none existed in winter related to the activities of the city, and then, looking the removal of PAHs in the figure the season not affected the removal efficiency of the PAHs.

The performance of removal of the Pharmaceutical Active Compounds are among the tested on this study, only Diclofenac, Carbamazapine had a concentration above of LOD and LOQ for 17 $\alpha$ -ethinyloestradiol, 17 $\beta$ -estradiol no concentration had got in the analysis; for Diclofenac the influent concentrations was 1034 ng/L and effluent was 695,8 ng/L, the removal efficiency of Diclofenac was low with 32,7%;

over hand, Carbamazepine removal efficiency was 46,9 % the better for PhCAs study, the concentration of the influent was 659,1 ng/L and effluent was 350 ng/L. Summarizing, most of the PhACs were existed in low quantity and not detected by the detector of the GC-MS, excepted the Diclofenac; looking the influent of the PhACs existing, it seems affected the activated used of the population of City in winter, in winter low of non some PhACs micro-pollutants were not detected in the discharged; and observing the removal of Diclofenac, it related to the season, in winter the removal efficiency was diminished.

Compared to others CWs is the same but different system of literatures from other countries with the same climate condition. Even other results of some micro pollutants seem to be low in removal efficiency, the Karabekir's CWs is able to remove nutrients, organic matters and micro pollutants from the Karabekir's City. Most of the results are under tolerate limit of the environment pollution rate. And this CW is a response to the criteria of small community wastewater treatments with its capacity to receive all the wastewater in the influent and ability to treat and give the water effluent available to the environment condition.

It is a recommended proposal to improve the future capacity of Karabekir's CWs and the others CWs in Turkey.

As the CWs of Karabekir's is a new CW, the results showed that CWs is available for the small community and its activity works very well and the removal efficiency in general is satisfying. Only some recommendation is necessary to improve its capacity of removal. In this study, different process is recommended; many options with diversity in parameters aren't yet known about this CW.

It is suggested to take the effluent samples follow the Hydraulic retention time (HRT), on this study, some parameters showed the negative removal efficiency like Nickel for heavy metals and Naphthalene and Fluoranthene for PAHs. Those results are supposed caused of same time of taking sample of influent and effluent. And it is better to study the HRT from influent to effluent of HSSF Karabekir's CWs.

As the relation between many factors are important, it is recommended to realize that the research in the factors, including the biomass, potential end-uses and the availability of land, climate as this allows the main effect of the CW in these factors.

If it is possible also, it needs for more research about micro-pollutants accumulation in sediment and their behaviors, plant up take and harvested plant biomass.

Studying the Pharmaceutical removal mechanisms in Karabekir's CWs is important to know well the removal of PhACs. It is recommended to study the process like sorption/adsorption, Dongqing Zhang and al (2014) reported that the fate of pharmaceuticals in CWs can be strongly influenced by their adsorption to soil and sediment. Adsorption influences the distribution of substances between aqueous phase and solid surfaces, these can be identify the real mechanisms affected the removal of PhACs and can be able to ameliorate or avoid the main problems of removal of PhACs.

For PAHs recommendation, the research about Biodegradation and biological degradation are very important processes. The PAHs absorbed into CW bed media also are recommended.

Suggestions are also made for the following research of metal removal mechanisms like sorption, precipitation, sedimentation and plant up take. Various removal mechanisms are necessary for different observations.

And the following study could show full results of the plant effect. If this study was done between planting and growth of the plant, then that would not show the right difference between both of them.

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**YAYINLAR**