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GEBZE TECHNICAL UNIVERSITY
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THE USE OF SEMI-PERMEABLE MEMBRANE DEVICES (SPMD) FOR THE SAMPLING OF MICROPOLLUTANTS IN SEA WATER AND RIVER BASIN

ZEHRA RANA İKİZOĞLU
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GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

DENİZ VE NEHİR ORTAMINDA GERÇEKLEŞTİRİLEN MİKROKİRLETİCİ ANALİZLERİNDE YARI GEÇİRGEN MEMBRAN SİSTEMLERİN (SPMD) KULLANILMASI

ZEHRA RANA İKİZOĞLU
YÜKSEK LİSANS TEZİ
ÇEVRE MÜHENDİSLİĞİ ANABİLİM DALI

DANIŞMANI
PROF. DR. MELEK ÖZKAN

EŞ DANIŞMANI
DR. OLTAN CANLI

GEBZE
2020

GEBZE TEKNİK ÜNİVERSİTESİ	**YÜKSEK LİSANS JÜRİ ONAY FORMU**

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 15/01/2020 tarih ve 2020/04 sayılı kararıyla oluşturulan jüri tarafından 13/02/2020 tarihinde tez savunma sınavı yapılan Zehra Rana İKİZOĞLU'nun tez çalışması Çevre Mühendisliği Anabilim Dalında YÜKSEK LİSANS tezi olarak kabul edilmiştir.

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SUMMARY

In this study, effiency of Semi-Permeable Membrane Devices (SPMD) which was used for sampling at Yeşilırmak Basin was investigated. Semi-permeable membrane devices, are becoming an important sampling techonologies in our country and the world. The triolein contained in the sampler enables the sampler to move like fat tissue, allowing us to get similar results to live metabolism. Thanks to semi-permeable samplers, presence of lower pollutant concentrations can be detected as compared to standard sample analysis methods. Amasya, Turhal, Samsun L-1, Samsun L-2, Toros and Gümenek samplings at Yeşilırmak Basin was performed as five sampling intervals for different sampling periods. Concentrations for Persistent organic pollutants in water environment (POPs) which are; Polycyclic Aromatic Hydrocarbons (PAH), Polychlorinated Bifenyls (PCB) and Pesticides; were calculated for per SPMD. The sampling points were Samsun, Çorum, Amasya and Tokat in Yeşilırmak Basin. The most concentrated pollutant group in the region has been identified as Polycyclic Aromatic Hydrocarbons.

Key Words: Semipermeable Membrane Devices (SPMD), Micropollutants, Passive Sampling, Yesilirmak.

ÖZET

Bu çalışmada, Yeşilırmak Havzası'ndan örnekleme için kullanılan yarı geçirgen membran örnekleyiciler'in (Semipermeable Membrane Devices - SPMD) kullanım potansiyeli ortaya konmuştur. Yarı geçirgen membran örnekleyiciler ülkemizde ve dünyada son dönemde önem kazanan örnekleyici türlerindendir. Örnekleyici içerisinde bulunan triolein, örnekleyicinin yağ dokusu gibi hareket etmesini sağlayarak canlı metabolizmasına benzer sonuçlar almamızı sağlar. Yarı geçirgen örnekleyiciler sayesinde, standart numune analiz yöntemlerine göre daha düşük kirletici konsantrasyonlarının varlığı tespit edilebilmektedir. Yapılan çalışmalar; Yeşilırmak havzasındaki Amasya, Turhal, Samsun L-1, Samsun L-2, Toros ve Gümenek örnekleme noktalarında beş örnekleme dönemi boyunca farklı örnekleme sürelerinde gerçekleştirilmiştir. Su ortamındaki kalıcı organik kirleticilerden (KOK); Polisiklik Aromatik Hidrokarbonlar (PAH), Poliklorlu Bifenilller (PCB) ve Pestisit'lerin; SPMD başına olan konsantrasyonları hesaplanmıştır. Örnekleme yapılan noktalar Yeşilırmak Havzasında bulunan Samsun, Çorum, Amasya ve Tokat illeridir. Bölgede en yoğun olarak bulunan kirletici grubu Polisiklik Aromatik Hidrokarbonlar olarak tespit edilmiştir.

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Anahtar Kelimeler: Yarı Geçirgen Membran Örnekleyici (SPMD), Mikrokirletici, Pasif Örnekleme, Yeşilırmak.

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LIST of ABBREVIATIONS and ACRONYMS

Abbreviations and Acronyms		**Explanations**
µg	:	Microgram
mL	:	Milliliter
AA-EQS	:	Annual Avarage Environmental Quality Standarts
ATSDR	:	Agency for Toxic Substances and Disease Registry
CAS-No	:	Chemical Abstracts Service Number
DCM	:	Dichloromethane
EDC	:	Endocrine Disrupting Compounds
EEA	:	European Environmental Agency
EQS	:	Environmental Quality Standarts
EPA	:	Environmental Protection Agency
GC - ECD	:	Gas Chromatography Electron Capture
GC-MS	:	Gas Chromatography-Mass Spectrometry
MAC-EQS	:	Maximum Acceptable Concentration Environmental Quality Standards
ND	:	Not Detected
OCL	:	Organochlorine Pesticides
PAH	:	Polycyclic Aromatic Hydrocarbons
PCB	:	Polychlorinated Biphenyls
ppb	:	Part Per Billion
PPCP	:	Pharmaceuticals and Personal Care Products
ppm	:	Part Per Million
POP	:	Persistent Organic Pollutants
RPM	:	Rounds Per Minute
SPMD	:	Semi Permeable Membrane Devices

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1. INTRODUCTION

Industrialization and growth of population have brought many problems threatening health of world as a whole. With the increase of the population, the need for consumption has increased which resulted in growing of different industries continuously. With the increase in industrialization, some environmental problems have emerged unintentionally.

Industrial products or by-products; started to create pollution in the sense of environment. Pesticides are one of the most important chemical group polluting environment. Some of them were banned due to their hazard to the environment (For example, substances such as Dieldrin and Lindane, which have been used in the 1950's as agricultural pesticides, have been banned) [Demli ve ark., 2018]. The first concerns and researches on the risks of insecticide use for the environment began in the 1940's with the discovery of synthetic pesticides. For example, Cottam and Higgins studied the direct and indirect impact of DDT on fish and wildlife in 1946. However, the risks posed by the use of pesticides in the environment waspublished for the first time in 1962 in the "Slient Spring" by the American writer Rachel Carson [Yıldız ve ark., 2005]. Although the use of these substances are prohibited, we still find them in the ecosystem due to their long half-lives and their persistency. As the area of use of these substances is agriculture, they contaminate the soil; groundwater and surface waters. In addition to these substances, polycyclic aromatic hydrocarbons (PAHs), another pollutant caused by industrialization resulting from combustion reactions, contaminate the water bodies as a result of releasing into the air. These substances, which are mentioned as persistent organic pollutants (POPs), are kept under control by regulations and directives.

Although it is controlled by the directives, there is a great deal of responsibilities for both the institutions and individuals against these pollutants in order to protect the environment.

The institution setting and implementing directives for regulating the use of persistent organic pollutants worldwide is Environmental Protection Agency (EPA) and European Environmental Agency (EEA) for Europe; in our country it is the Ministry of Environment and Urbanization. One of the standards developed to protect the environment from pollutants is Environmental Quality Standards (EQS). EQSs specify the levels for annual avarage concentrations (AA-EQS) and Maximum Acceptable Concentration (MAC-EQS) specifies the level of contaminants for the river and marine environment that should not be exceeded [White House Environment Agency, 2012].

The remediation of polluted water bodies is both cost-effective and time-consuming. For this reason, industrial organizations must comply with the directives, and people should not use prohibited substances that harm the environment in their own interests.

The micropollutants is a novel measurement methods used for micropollutants are as important as themselves. A measurement method developed for micropollutants, usually present in low concentrations in the water column is semi-permeable membrane devices (SPMD). SPMDs are brand new technology for our country and also in the world. This system enables to measure very low pollutant concentrations; which makes it a suitable sampler for micropollutant measurements. In this thesis, will examine the effectiveness of use of SPMDs for micropollutant measurment in the Yeşilırmak Basin.

1.1. Purpose of the Thesis

The aim of the study is to detect PAH, pesticides and polychlorinated biphenyls (PCB) in Yeşilırmak Basin by using semi-permeable membrane devices and calculating the true concentrations of pollutants of pollutants by with the external calculation method for each semi-permeable membrane device. It is expected that by using semi-permeable membrane devices we can measure lower concentrations of the micropollutants which can not be detected by standart environmental sampling methods.

In this study semi-permeable membrane devices (SPMD) were used for sampling water from the specific points in Yeşilırmak basin. Sampling periods of the studies ranged from 3 to 30 days. Sampling points are Amasya, Turhal, Toros, Samsun Port 1, Samsun Port 2 and Gümenek in the basin. After the stations were determined, sampling was repeated during the year in four different times in these points. Sampling points include both sea and river stations. The collected samples were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) in accredited laboratories of

TÜBITAK Marmara Research Center, Environment and Cleaner Production Institute. Use of SPMD enabled accumulation of micropollutants which are usually found in the water bodies at undetectable quantities. By this study, difference between the use of SPMD and standard sampling method for determination of PAH, PCB and pesticides can be interpreted. Sources of pollutants in the basin can also be determined.

1.2. Micropollutants

Micropollutants are caused by use of products such as personal care products (PPCPs), industrial chemicals, pesticides, pharmaceuticals and hormones. Residue from such products contaminate water bodies. Different groups of chemical based compounds are in this category such as pesticides, PAHs, PCBs, flame retardants, perfluorinated compounds, pharmaceuticals and personal care products. Recent studies have indicated the often detection of these compounds in the aquatic environment [Stasinakis and Gatidou, 2010]. They normally reach the wastewater treatment plants (WWTPs). Various other sources of these micropollutants are surface run-off from agricultural areas, industrial discharge and stormwater run-off from the cities. Although the figures could vary in different parts of various countries, household use contributes 70% of the pharmaceutical residue found in the wastewater. 20% of these residues is attributed to livestock farming. 5% is is caused by hospital effluent, and the other 5% is due to runoff from non-specific sources [Web 1, 2018]. The continuous input of these organic micropollutants into water resources is an important environmental problem.

Micropollutants reach the water resources as they are persistent and non-biodegradable. It means that when released into the environment they pass through the soil and reach the groundwater. Even if they reach the WWTPs, a major portion of these micropollutants can not be treated and reach the surface water [Luo et al., 2014]. Many of the micropollutants have been determined to be highly hazardous to ecosystem including animals, aquatic species, as well as human beings because they are non-biodegradable and bioaccumulative. They can lead to mutagenicity, estrogenicity, and genotoxicity. An evident example is the feminization of male fish, caused due to the fish population being exposed to endocrine disrupting compounds (EDCs). Even at low concentrations, the continuous release of EDCs into the environment may cause reproductive and developmental abnormalities on sensitive species.

Another example is the increase of antibiotic-resistant organisms in the environment, which is an important risk to the microbial ecosystems. The vigorous usage of antibiotics to treat animals and humans has resulted in accumulation of antibiotic-resistant genes in different environmental matrices. As a result of population explosion and higher reliance of modern societies on pharmaceuticals, the release of micro-pollutants into the ecosystem is anticipated to increase in the future. In addition, exposure to complex mixtures is more serious than single compound because of their possible synergistic effects.

1.3 Persistent Organic Pollutants (POPs)

Since the Second World War, scientists have identified certain chemical contaminants which are toxic and persistent in the environment. Important characteristics of them are being bioaccumulative, being able to atmospheric migration and deposition, and expected to impose serious health effects on humans, wildlife, and marine biota. These chemical pollutants are referred to as persistent organic pollutants (POPs) [Ashraf, 2015]. POPs are very difficult to remove from environment because of their long half-life. Water, air, sediment and soil mixed with these pollutants are harmful for living organisms. These chemicals can be added to food chain and stored in fat tissue. PCBs, chlorine and heptachlor polychlorinated dibenzo-β-dioxins, and 12 chemical or chemical classes, including furan and DDT, are the most common persistent organic pollutants worldwide.

POPs can occur as a result of different types of burns or uses. Examples to these are; POPs resulting from volcanic combustion and forest fires; Dioxin and Dibenzofurans; POPs due to chemical use in industry; Polychlorobiphenyls combustion; diode and furans DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, toxaphene, mirex and hexachlorobenzene, hexachlorobenzene, brominated compounds and perfluorinated compounds, by-products POPs produced by industrial processes.

Many countries agree on prohibition of POPs due to the fact that POPs can be transported by air from thousands of kilometers away from the exit point. The researchers suggested first in 1974 that POPs could migrate as atmospheric gases and aerosols, and could be concentrated in low-temperature regions [Wania and Mackay, 1996].

The Stockholm Convention is the first global and legally binding agreement to protect the environment from POPs [UNEP, 2009]. Reason for mentioning Persistent Organic Pollutants in the Stockholm Convention; to control the use and destruction of the production of toxic chemicals and to protect the environment and human health on this occasion. The contract, as approved, addresses a “dirty dozen” chemical group that stays in the environment for a long time, is toxic and accumulates in living things - an unacceptable threat to human health and the environment [Web 2, 2019]. The contract creates a science-based process to identify and eliminate POPs worldwide.

1.3.1. Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are carbon and hydrogen containing permanent organic pollutants with more than two benzene rings.

PAHs are abundant in the earth. There are two main sources of PAHs in the environment; natural and anthropogenic. Natural sources are related to the incomplete combustion of organic matter. PAHs can also be produced geologically when organic sediments are chemically transformed into fossil fuels such as oil and coal. Therefore, natural PAHs originate mostly from volcanic eruption, plant emissions, and fires [Hussar et al., 2012]. Anthropogenic PAHs sources mainly categorized under combustion of materials for energy supply and waster minimalization [Li, 2019] [German Environmental Agency, 2016].

After the experimental analyses, scientist understand that PAHs are carcinogenic and toxic compounds. The ability of PAH-containing mixtures to induce human cancer has been known since 1775, when the British surgeon Sir Percival Pott demonstrated a correlation between the exposure of chimney sweeps to soot and the incidence of scrotal cancer [WHO-IARC, 2010].

PAHs are moderately to highly lipophilic pollutants that are widely distributed in the environment. They are present in the atmosphere from various sources such as emissions from gasoline and diesel-powered vehicles, municipal and commercial incinerators, combustion of fuels such as coal, wood, gas and oil. Some PAHs have carcinogenic properties related to the increasing size of the molecule (species with compounds of four or more benzene rings being especially carcinogenic) and their metabolic transformation to reactive dihydrodiol epoxides (Table 1.1) [Söderströma et al., 2005].

Table 1.1: PAHs and Physical Properties.

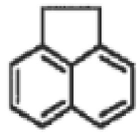
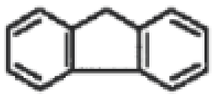
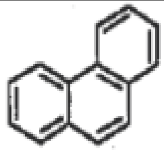
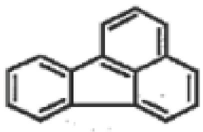
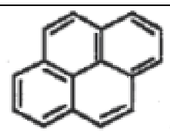
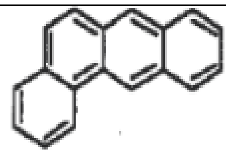
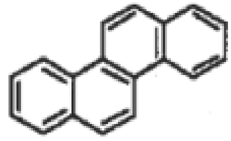
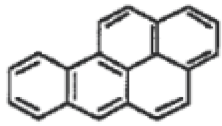
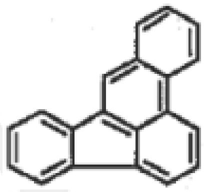
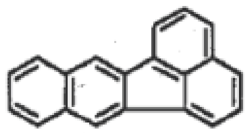
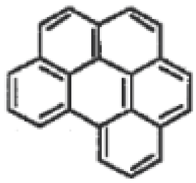
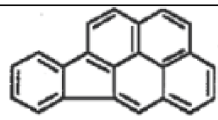
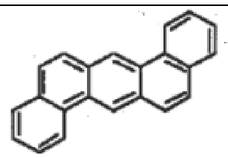
Compound Name	**Number of Rings**	**Chemical Formula**	**Molecular Weight (g/mole)**	**Molecular Structure**
Naphthalene	2	$C_{10}H_8$	128,17	
Acenaphthylene	3	$C_{12}H_8$	152,2	
Acenaphthene	3	$C_{12}H_{10}$	154,21	
Fluorene	3	$C_{13}H_{10}$	166,22	
Phenanthrene	3	$C_{14}H_{10}$	178,23	
Anthracene	3	$C_{14}H_{10}$	178,23	
Fluoranthene	4	$C_{16}H_{10}$	202,26	
Pyrene	4	$C_{16}H_{10}$	202,26	

Table 1.1: Continues.

Compound Name	**Number of Rings**	**Chemical Formula**	**Molecular Weight (g/mole)**	**Molecular Structure**
Benz[a]anthracene	4	$C_{16}H_{12}$	228,29	
Chrysene	4	$C_{18}H_{12}$	228,29	
Benzo[a]pyrene	5	$C_{20}H_{12}$	252,32	
Benzo[b]fluoranthene	5	$C_{20}H_{12}$	252,32	
Benzo[k]fluoranthene	5	$C_{20}H_{12}$	252,32	
Benzo[g,h,I]perylene	6	$C_{22}H_{12}$	276,34	
Indeno[1,2,3-cd]pyrene	6	$C_{22}H_{12}$	276,34	
Dibenzo[a,h]anthracene	6	$C_{22}H_{14}$	278,35	

PAHs belong to a diverse family of hydrocarbons with over one hundred compounds known, each containing at least two aromatic rings in their structure. Due to hydrophobic nature, PAHs tend to accumulate in the aquatic sediments, leading to bioaccumulation and elevated concentrations over time. In addition to their well-manifested mutagenic and carcinogenic effects in humans, they pose severe detrimental effects to aquatic life [Behera et al., 2018] [Alver ve ark., 2012].

Although PAH includes hundreds of compounds; the total contents of 16 PAHs, categorized as priority pollutants by US EPA [Chen et al., 2005] [. Those PAHs are; Acenaphtylene, Acenaphthene, Anthracene, Benzo (a) pyrene, Benz(a)anthracene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chyrsene, Dibenz(a,h)anthracene, Fluorene, Fluoranthene, Indeno(1,2,3-cd)pyrene, Naphtalene, Phenanthrene and Pyrene.

1.3.2. Polychlorinated Biphenyls (PCBs)

PCBs are synthetic organic compounds with the empirical formula $C_{12}H_{10}$-xClx (x=1–10) (Figure 1.1.). There are 209 congeners of PCBs, numbered PCB 1 to PCB 209 based on the number and position of chlorine atoms around the biphenyl rings [Ballschmiter and Zell, 1980]. Commercial production of PCBs began in the early 1920s, and PCBs were marketed in the US under the trade name Aroclor and with various trade names in other countries [Silberhorn et al., 1990]. When added to a material, PCBs impart plastic and fire retardant properties. They are also very good coolants and lubricating agents. For these properties, PCBs were valuable chemicals in the industrial development of the twentieth century. Examples of PCB-containing products are transformers, capacitors, microwave ovens, air conditioners, fluid-cooled motors and electromagnets, electrical light ballasts, hydraulic and heat transfer fluids, switches, voltage regulators, circuit breakers, vacuum pumps, electric cables, inks, lubricants, waxes, flame retardants, adhesives, electrical and thermal insulating materials, pesticides, dyes, paints, asphalts, caulks, sealants and many more [AIHA, 2013], [ATSDR, 2000], [ATSDR, 2011], [IARC, 2013]. The commercial production of PCBs was banned in many countries since the late 1970s. However, PCB legacy materials and new materials containing PCBs from pigments continue to be a source of environmental release even today [Hu and Hornbuckle, 2010], [Shanahan et al., 2015]. PCBs, which are not found in the nature, they are human-made chemicals. They are water soluble, odorless, fire resistant hydrocarbons with good solubility in oil. They are used in the production of transformers, electrical cables, hydraulic systems, heat transfer systems, pesticide production, adhesives and fire retardants. PCBs in the group of persistent organic pollutants are analyzed because of the possibility of mixing with water and soil ecosystem as a result of industrial and agricultural activities in basin. PCBs are mixed in the natural environment as a result of spillage or burning during transport, production or disposal.

Although PCBs are hydrophobic, they can accumulate in the hydrosphere and in the organic fraction of the soil, due to their low vapor pressures. At the same time the oceans are also capable of keeping this contaminant, although they are hydrophobic. As the water pressure in the ocean increases with depth, the PCBs become heavier than water and begin to accumulate in the sediment. At the same time, PCBs have air transport characteristics. Because of these features, they can spread for miles [Ballschmiter, 1992].

While in the water environment, PCBs tend to be stored in fat tissues due to their lipophilic structure and hydrophobic properties.

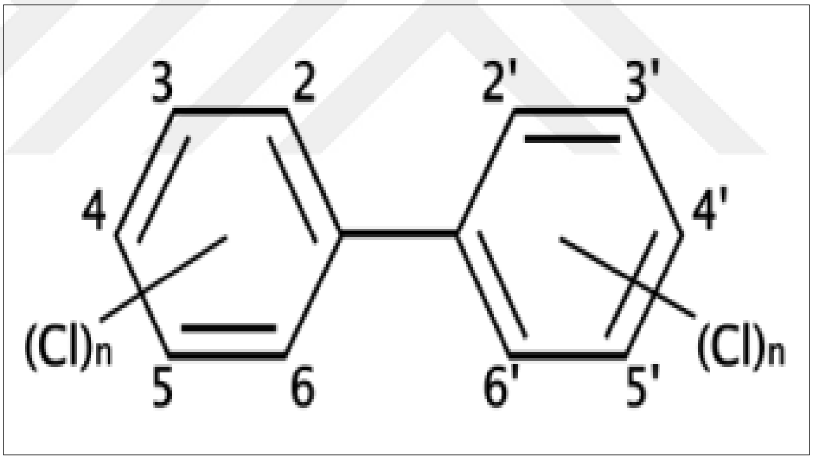
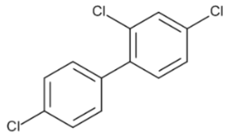
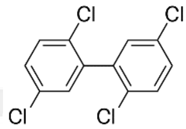
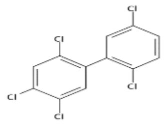
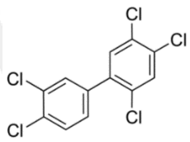
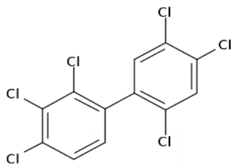
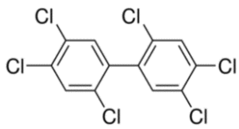
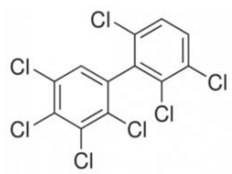


Figure 1.1: Chemical structure of PCBs.

In this study, indicator PCBs and PCB 118 pollutants were investigated. The analyzed PCB compounds and their properties are given at the Table 1.2.

Table 1.2: PCBs and Their Properties.

Compound Name	Moleculer Weight (g/mole)	Molecular Structure
2,4,4,'-Trichlorobiphenyl (PCB 28)	257,55	
2,2',5,5'-Tetrachlorobiphenyl (PCB 52)	291,99	
2,2',4,5,5'-Pentachlorobiphenyl (PCB 101)	326,44	
2,3',4,4',5-Pentachlorobiphenyl (PCB 118)	326,44	
2,2',3,4,4',5'-Hexachlorobiphenyl (PCB 138)	360,88	
2,2',4,4',5,5'-Hexachlorobiphenyl (PCB 153)	360,88	
2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB 180)	395,32	

1.3.3 Organochlorinated Pesticides (OCLs)

Organochlorine pesticides are toxic and has hydrogen, chlorine and complex substances of carbon atoms. Organochlorines were the first synthetic organic pesticides to be used in public health and in agriculture. These pesticides are often accumulate and persist in the environment and results showed that OCLs were hydrofobic and also lipophilic.

Although it is very easy to reach all kinds of commodities in a globalizing world; a problem that would be caused by a plant pathogen may trigger global food supply crises. In today's world where human and commercial goods movements are very fast, the spread of such disease factors from one area to another is also rapid.

It is necessary to combat the diseases, pests and weeds in the fruit and vineyard areas for supply of healthy products. Combating with these factors includes cultural measures, physical and chemical struggles. The most important and the most preferred application is undoubtedly chemical struggle. Although pesticides used as chemical control have been known and used for thousands of years, pesticides in today's perception started to be used after World War II [Kaymak ve Serim, 2005].

Health problems and environmental problems are the result of chemical use at production. In the face of these problems, the use of pesticides was questioned. Pesticides were started to be used in 1945 in Turkey. Together with the appearance of damage caused by pesticide use, restrictions were started to be applied since 1983. After the researches on demage of pesticides, use of most of the OCLs was banned and restricted in Turkey as in many countries because of persistent contamination of the environment. However, some OCLs (like chlorpyrifos and endosulfans) are currently used [Odabasi ve ark., 2008]. Developing countries still use pesticide to prevent malicious organisms emitting malaria, such as mosquitoes.

Pesticides can be grouped according to their origin: Inorganic substances, Natural organic substances (Vegetable substances, Petroleum oils, etc.) and Synthetic organic substances (Organochlorines, Organic phosphorous, other synthetic organic substances).

Organochlorine pesticides are toxic and has hydrogen, chlorine and complex substances of carbon atoms. These compounds, which are miscible to the food chain by bioaccumulation are resistant to degradation. Darko founded out that the levels of most of the residues in fish were higher than those found in water. Darko showed that organochlorine pesticide residues in the lake are likely to originate from nonpoint sources via runoff, atmospheric deposition, and leaching due to agricultural applications and vector control practices and the lake sediments act as a sink for the persistent contaminants, whose resuspension during the lake's mixing may increase pesticide bioavailability and accumulation in the fish [Ecobichon, 2001]. Results showed that OCLs were hydrofobic and also lipophilic [Darko et al., 2008]

Organochlorine pesticides examined within the scope of the thesis are given in the table below (Table 1.3).

Table 1.3: Organochlorine Pesticides Examined Within the Scope of the Thesis.

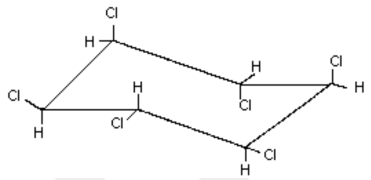
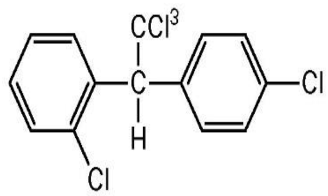
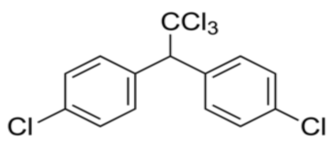
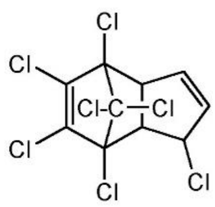
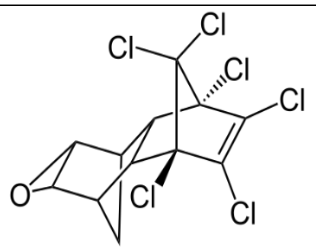
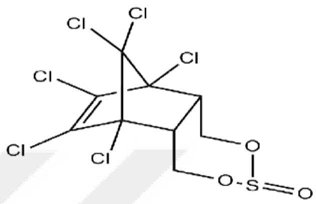
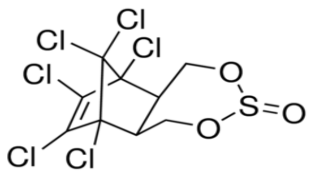
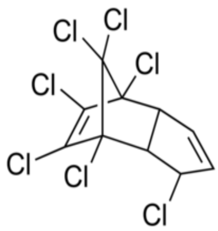
Compound Name	**Molecular Weight (g/mol)**	**Molecular Structure**
Lindane	290,81	
o,p' DDT	354,48	
p,p' DDT	354,48	
Heptaclor	373,30	

Table 1.3: Continues.

Compound Name	Molecular Weight (g/mol)	Molecular Structure
Dieldrin	380,91	
Endosulfan-I	406,93	
Endosulfan-II	406,93	
cis-Chlordane	409,78	

1.4. Semi-Permeable Membrane Devices (SPMD)

Passive samplers are new technology products that are formed by placing tubic trioleine films in polyethenyl membranes and can be used to monitor trace amounts of organic pollutants in air, water and sediment [EPA, 2012]. For most of the organic pollutants, gas chromatography and mass spectrometry (GC-MS) or electron capture (GC-ECD) methods are applied, as is known. For hydrophobic contaminants, the extraction process must be carried out prior to analysis. This process; where the concentration of the pollutant is too low, it requires a large volume sample and the results of the analysis are likely to be affected by the concentrations of particulate and colloidal substances. The concentration measured in this case increases the probability that there is no concentration directly exposed to living things. Another advantage of this technique is that much less use of solvents, such as expensive and hazardous substances, is used. With the passive sampling technique, it is possible to reduce the role of various external factors and to reflect the temporal changes more accurately.

Semi-permeable membrane devices (SPMD) are a passive sampler designed to simulate chemicals dissolved in water by imitating the accumulation of organic pollutants in fatty tissues of organisms [Huckins et al., 1990]. SPMDs consist of a thin-walled (70-90 µm) membrane tube made of low density polyethylene (LDPE) with triolein (1,2,3-tris-cis-9-octadecenoyl glycerol). A standard SPMD; It is 2.54 cm wide, 106 cm long and contains 1 mL of triolein. SPMDs can be used at different sizes and contents in field studies by considering certain rates (Figure 1.2).

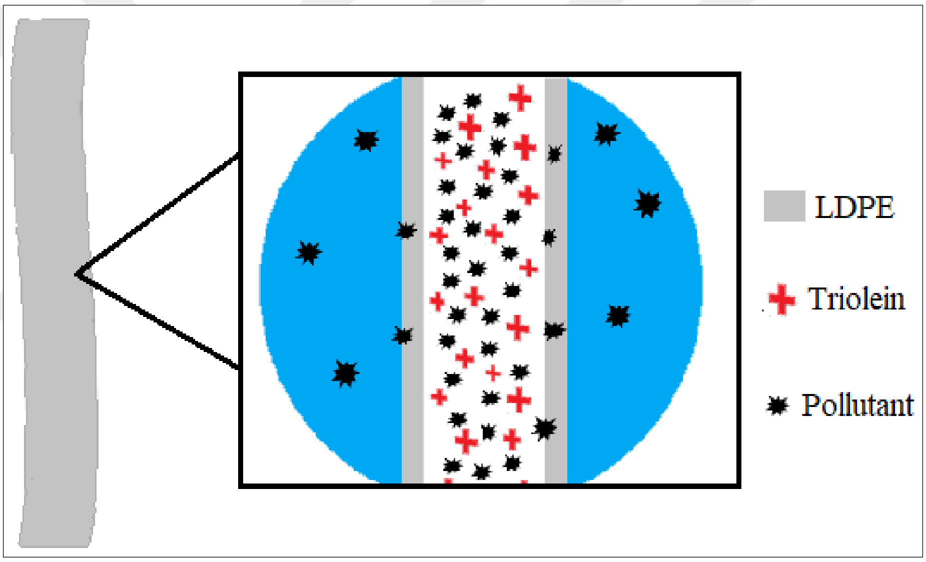


Figure 1.2: A simple figure of semipermeable membrane devices.

For SPMDs, the sampling period is usually one month, however, depending on the scope of the study, samplings can be take days or month. While placing SPMDs to the sampling points, they are placed in special metal cages to protect them from damage from living things and other factors.

In the samples made in the water environment, SPMDs are placed with the buoys so that they are all in the water together with the cage. Organic pollutants, which are found to be dissolved in very low concentrations in water, are accumulated over time by passing through the triolein phase due to the small pores on the low density polyethylene surface of SPMD.

In the early 1990s, SPMDs were used to detect metal contamination in water environments, and many hydrophobic organic pollutants could be sampled, including polyaromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo dioxins, polychlorinated dibenzofuranes and organochlorinated pesticides [Huckins et al., 2006]. SPMDs are more advantageous than other passive samplers, since they are only available for bioavailable portions and very low concentrations of contaminants, commercially available, widely used in research and literature.

Nowadays, it is seen that SPMDs are widely used for sampling various chemical compounds in water, air and sediment environments including salt water [Harman et al., 2010], [Marucci, 2013], [Metcalfe et al., 2011], fresh water [Blahova et al., 2012], [Rosen et al., 2010], [Scott et al., 2012], groundwater [Berho et al., 2011], [Koci et al.,2009] and wastewater [Clark et al., 2010], [Gillis et al., 2013]. In addition, several studies have been carried out on the sampling of organic compounds in the air environment [Piccardo et al., 2010], [Zouir et al., 2010].

SPMDs are widely used in the sampling of various chemical compounds in water, air and sediment environments. In addition, several studies have been carried out on the sampling of organic compounds in the air environment [Piccardo et al., 2010], [Zouir et al., 2010]. The way to use SPMD is different for air and water sampling. In water operations, steel cages are often used to protect devices from damage caused by water flow, while protection for air sampling is not required (Figure 1.3). In both cases, it is recommended that the SPMD be protected from sunlight to prevent the deterioration of photosensitive compounds. Usually 15-30 days of sampling times are used for water. Sampling of pollutants by SPMDs is severely affected by environmental variables. Although there is no major change in pollutant sampling from water in different salinity, pH or organic matter composition, temperature and flow rates are factors that directly affect absorption rates.

In the light of the literature studies carried out in order to ensure the application of passive sampling technique (semi-permeable membrane sampler, SPMD), which has been used intensively in recent years, the sampling equipment was carried out by US EST LAb. Company. Passive samplers; It consists of a carrier canister, a semi-permeable membrane (SPMD), a carrier module for SPMDs and semi-permeable membrane assemblies [Huckins et al., 2000].

Figure 1.3: SPMDs in steel cage.

There are two types of commercially available SPMD in the markets, with and without internals. The ones with the internals includes C^{13} deuterium which is helper for obtaining quantitative results. In order to calculate the pollutant concentrations in water, the performance reference compounds are used. These compounds are C^{13} isotopes of pollutants whose levels are to be determined and these compounds are not found in nature. During the sampling, there is a balance mechanism between the pollutants in the water environment and the sampler. Organic pollutants dissolved in sea water begin to accumulate in SPMD over time, while performance reference compounds that are not found in nature pass into the water environment simultaneously. At the end of the sampling, quantitative results are calculated using the PRB concentrations remaining in the SPMDs. SPMDs without internals has no C^{13} deuterium and used for obtaining qualitative reasults. Within the scope of the thesis, semi-qualitative analysis has been done and the results have been converted to quantitative with the help of Estimator.

1.5. Information About Yeşilırmak Basin

Yeşilırmak Basin located in the Black Sea region hosts the provinces of Amasya, Bayburt, Çorum, Erzincan, part of Giresun province, Gümüşhane, Ordu, Samsun, Tokat and Sivas. Yesilirmak Basin has an area nearly 5% of Turkey's area. The basin area is 39.000 km^2 and the length of Yesilirmak River is 2.470.617 km. As a life source in the basin, the interest in livestock and industry is intense.

Important part of agriculture and animal husbandary in Turkey are made in Yeşilırmak Basin. Food, non-metallic mineral products, plastic and rubber, metal industry are intensive sectors in the basin. At this research samplings were made in Samsun, Tokat and Amasya provinces (Figure 1.4) [Web 3, 2020].

Figure 1.4: Yeşilırmak Basin's Location at Turkey.

Table 1.4: Agricultural Land Datas for 2018 Taken from Turkish Statistical Institute.

Cities	Area of cereals and other crop products			Area of vegetable gardens	Area of fruits, beverage and spices	Ornamental Plants Area
	Total land	Sown area	Fallow land	As Decare		
TR83 (Samsun, Tokat, Çorum, Amasya)	14295017	9941647	2314825	548199	1489286	1060
TR831 Samsun	3753923	2201886	205753	167336	1178 314	634
TR832 Tokat	3040304	2360159	359643	175397	144679	426
TR833 Çorum	5218079	3583906	1437838	105207	91128	-
TR834 Amasya	2282711	1795696	311591	100259	75165	-

Livestock in the provinces within the borders of the basin has an important contribution to the economy of the provinces. In these provinces, cattle, sheep, poultry, aquaculture and beekeeping are carried out (Table 1.4).

Besides farming, agricultulture is another important contribution to the economy at the basin. Agriculture provides new working areas and it is an important economical support for the people. While agriculture has that much positive effects, there is one harmful effect of it, which is pesticide using.

1.6. Pollutant Sources of Yeşilırmak Basin

Yesilirmak River basin make up 5% of Turkey's land area, is an important source for Turkey's economy. The biggest share in the basin economy belongs to the services sector with a rate of 60,6%, agriculture is 20% and the industry sector is around 19,4%. It has been determined by The Union of Chambers and Commodity that it has 255 industrial activities in Yeşilırmak basin. 4 organized industrial zones in Amasya, 3 organized industrial zones in samsun, 5 organized industrial zones in slap; There are wastewater treatment plants belonging to the city in Amasya and Samsun.

There are different industrial companies operating in different parts of the basin. Within the scope of previous studies, the industrial establishments for the basin are as follows;

For Tokat Province; Manufacture of other electronic and electric wires and cables; Manufacture of oils and fats; Cutting, shaping and finishing of stone; Manufacture of other wearing apparel and accessories; Quarrying of ornamental and building stone, limestone, gypsum, chalk and slate; Manufacture of other food products n.e.c.

For Amasya Province; Manufacture of office and shop furniture; Manufacture of refined petroleum products; Herbal oil, Organic Fertilizer, Quarrying of ornamental and building stone, limestone, gypsum, chalk and slate PVC Window, LPG and Electric, Exterior coating.

For Samsun Province; Manufacture of machinery for mining, quarrying and construction; Manufacture of cocoa, chocolate and sugar confectionery; Metalware industry; Manufacture of ovens, furnaces and furnace burners; Manufacture of doors and windows of metal; Manufacture of medical and dental instruments and supplies; Manufacture of other electronic and electric wires and cables; Manufacture of industrial gases; Manufacture of ceramic sanitary fixtures; Manufacture of corrugated paper and paperboard and of containers of paper and paperboard; Manufacture of office and shop furniture; Manufacture of other pumps and compressors; Manufacture of other fabricated metal products n.e.c.; Manufacture of fertilisers and nitrogen compounds, Manufacture of electricity distribution and control apparatus; Manufacture of mattresses; Manufacture of central heating radiators and boilers; Manufacture of wire products, chain and springs; Manufacture of non-electric domestic appliances; Manufacture and processing of other glass, including technical glassware; Manufacture of refined petroleum products; Manufacture of plastic plates, sheets, tubesand profiles; Manufacture of other parts and accessor ies for motor vehicles; Manufacture of non-domestic cooling and ventilation equipment; Manufacture of engines and turbines, except aircraft, vehicle and cycle engines; Manufacture of prepared feeds for farm animals; Manufacture of weapons and ammunition; Manufacture of grain mill products; Manufacture of other general-purpose machinery n.e.c.; Manufacture of ceramic tiles and flags; Manufacture of basic iron and steel and of ferro-alloys; Manufacture of glues [Erdem, 2018]. As a result of certain industrial activities, environmentally harmful pollutants ocur [Web 4, 2018] [Web 5, 2020] [Web 6, 2020]. Pollutants and their sources are given in the table (Table 1.5).

Table 1.5: Pollutants and Their Sources.

Pollutants	**Sources**
cis-Chlordane	Control termites and as a broad-spectrum insecticide on a range of agricultural crops.
Dieldrin	Control termites and textile pests, dieldrin has also been used to control insect-borne diseases and insects living in agricultural soils.
Lindane	Used as insecticide for seed and soil treatment, foliar applications, tree and wood treatment and against ectoparasites in both veterinary and human applications.
Heptaclor	Used to kill soil insects and termites, malaria-carrying mosquitoes.
o-p' DDT	It was used during World War II to protect soldiers and civilians from malaria, typhus, and other diseases spread by insects. After the war, continued to be used to control disease, and it was sprayed on a variety of agricultural crops, especially cotton.
p-p' DDT	
Endosulfan beta	Endosulfan is an insecticide still in widespread use in many countries, on crops like cotton, soy, coffee, tea and vegetables.
Endosulfan alpha	
Naphthalene	Incomplete combustion.
Acenaphthylene	Fumes from vehicle exhaust, coal, coal tar, asphalt, wildfires, agricultural burning and hazardous waste sites are all sources of exposure.
Acenaphthene	Detected in fumes from vehicle exhaust, coal, coal tar, and at hazardous waste sites.

Table 1.5: Continues.

Pollutants	**Sources**
Fluorene	Vehicle exhaust, coal, coal tar, asphalt, wildfires, agricultural burning and hazardous waste sites are all sources of exposure.
Phenanthrene	Combustion of fossil fuels, traffic and exhausts from industry. It can be detected, e.g. in tobacco smoke, smoked, charbroiled and contaminated foods and drinking water. It is used in the production of dyes, drugs, pesticides and explosives.
Anthracene	Fumes from vehicle exhaust, coal, coal tar, and at hazardous waste sites. Since anthracene has been found in cigarettes, you can be exposed by breathing cigarette and tobacco smoke.
Fluoranthene	Produced water, drilling fluids, seepages from storage, transportation activities, working decks.
Pyrene	Incomplete combustion.
Benz[a]anthracene	Incomplete combustion.
Chrysene	Gasoline, diesel, and aircraft turbine exhausts; coal combustion and gasification; emissions from coke ovens, wood burning stoves, and waste incineration; and various industrial applications such as iron, aluminum, and steel production.
Benzo[b]fluoranthene	Present in coal, coke oven emissions and petroleum products.
Benzo[k]fluoranthene	Primarily found in gasoline exhaust, cigarette smoke, coal tar, coal and oil combustion emissions, lubricating oils, used motor oils and crude oils.
Benzo[a]pyrene	Wood burning, coal tar, in automobile exhaust fumes (especially from diesel engines).
Indeno[1,2,3-cd]pyrene	Incomplete combustion.
Dibenzo[a,h]anthracene	Gasoline exhaust, tobacco smoke, coal tar, soot and certain food products, especially smoked and barbecued foods.
Benzo[g,h,I]perylene	Incomplete combustion.
PCB 28, 52, 101, 118, 138, 153, 180	Industrial uses as dielectrics in transformers and large capacitors, as heat exchange fluids, as paint additives, in carbonless copy paper and in plastics.

2. MATERIAL AND METHODS

2.1. Sampling Points and Sampling Times

At five periods, SPMD sampling was carried out in the river and sea water in Yeşilırmak River Basin with the experience obtained from this thesis study. In the determination of the stations, 2 seaports were selected as the sampling point in Samsun Port, where the port activities were carried out, and one point in the Tekkeköy coast where industrial activities were intense. Amasya, Turhal and Gümenek were selected as river water sampling stations. Table 2.1 shows the stations and the coordinates of which passive samplings are performed.

Table 2.1: Sampling Stations and Station Coordinates.

Station	Location	Coordinate
Samsun L-1 (Sea Station)	Samsun Port	41°17'55.53"N
		36°20'10.43"E
Samsun L-2 (Sea Station)	Samsun Port	41°18'19.53"N
		36°20'29.03"E
Toros (Sea Station)	Tekkeköy Coasts	41°14'52.25"N
		36°27'25.48"E
River-1 (River Station)	Amasya Province	40°39'25.85"N
		35°50'3.98"E
River-2 (River Station)	Gümenek / Tokat Province	40°21'20.1"N
		36°05'47.9"E
River-3 (River Station)	Turhal / Tokat Province	40°26'50"N
		36°05'47.9"E

The periods and times of passive sampling studies are presented in Table 2.2.

Table 2.2: The Periods and Times of Semipermeable Membrane Sampling Studies.

Sampling Period	**SPMD Sampling Dates**	**Stations**	**Sampling Days**
1	20th September 2017 – 10th October 2017	Samsun L-1 Samsun L-2 Toros (Lost) Amasya Turhal	20
2	11st October 2017 – 2nd November 2017	Samsun L-1 (Lost) Toros Amasya Gümenek Turhal	22
3	17th May 2018 – 30th May 2018	Samsun L-1 Toros (Lost) Amasya Turhal	13
4	14th September 2018 – 17th September 2018	Amasya Turhal	3
5	14th September 2018 – 20th September 2018	Amasya Turhal	6

The necessary permissions were obtained from Samsun Governorate, Coast Guard Black Sea Region Command, Samsunport and Toros Tarım Port Operations Directorate in order to ensure the safe operation of the coastal waters. During the field studies, all three institutions / enterprises provided significant support to the study (Figure 2.1).

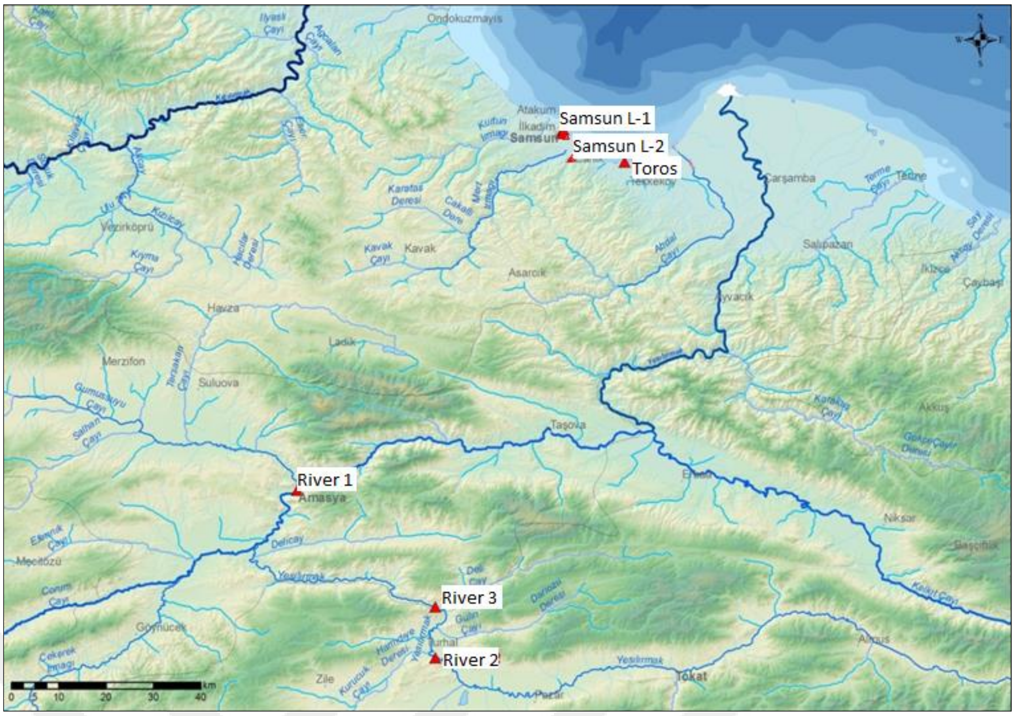


Figure 2.1: Sampling points figuration on map.

The passive samplers found at Toros Port and Samsun Port were lost due to strong harbor activities and strong currents. Gümenek, one of the river stations, had only one sampler left due to the high probability of loss of the sampling system. The collected samples were stored at -20 ^{o}C and carried to TÜBİTAK MAM Laboratories.

2.2. Overwiev of Sampling Points

Samsun L-1 and Samsun L-2 (Sea Station) is an international port point. . The depth of sea water at this point is 6.5 meters. SPMDs are positioned 1 meter below the surface in order to prevent the formation of biofilm on the SPMD. SPMDs are allowed to sampling with cage system. An SPMD was lost at this point due to the flow (Figure 2.2).

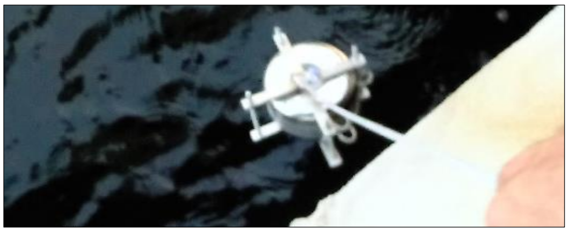


Figure 2.2: Perspective of Samsun L-1 and L-2 points.

Toros (Sea Station) is the port point of an industrial chemical agricultural support production facility. SPMDs are allowed to sampling with cage system. The depth of this point is 20 meters and the SPMD is located 1 meter below the surface (Figure 2.3).

Figure 2.3: Perspective of Toros point.

River-1 (River Station - Amasya Province) is a point located in the city center. Touristic hotels are available around. SPMDs are located in the river with a pedestal system. The height of the SPMD from the bottom is 1.5 meters due to the shallow water. Membranes are located 0.5 meters below the surface (Figure 2.4).

Figure 2.4: Perspective of River-1 (Amasya) point.

River-2 (River Station - Gümenek / Tokat Province) is a point near by forest area and outside the city of Tokat. The height of the SPMD from the bottom is 1.5 meters due to the shallow water. Membranes are located 0.5 meters below the surface (Figure 2.5).

Figure 2.5: Perspective of River-2 (Gümenek / Tokat Province) point.

River-3 (River Station - Turhal / Tokat Province) is a spot outside the city of Tokat. Located next to the hydroelectric power plant construction, and at this point the river flow is higher than other locations. Pedestal systems are also used here too. The height of the SPMD from the bottom is 1.5 meters; The SPMD position from the surface is 0.5 meters (Figure 2.6).

Figure 2.6: Perspective of River-3 (Turhal / Tokat Province) point.

2.3 Sampling and Analysis of SPMDs

The SPMDs, were taken from the Est. LAb which is pioneer in the field of laboratory and passive sampling in the United States of America. They were preserved at -20 °C until the analysis stage. Ordered SPMDs are standart samplers which is is 2.54 cm wide, 91 cm long and contains 1 mL of triolein in polyethylene tubes. SPMDs without C13 deuterius were used in the thesis and the results are not quantitative, but with the "SPMD Water Concentration Estimator v4-1" all results can be convert to quantitative results (µg per Liter) [Alvarez, 2010] [Alvarez, 2010].

SPMDs were left to the sampling point with the help of special cages made of stainless steel which is shown in the Figure 2.7. Samplers fixed to the field environment with the help of a stationary pedestal or according to the field condition.

Figure 2.7: SPMD in a stainless cage.

2.3.1. Preparation of Calibration Points and Internal Standards

PCB (Polychlorinated Biphenyls) No: 29 and PAH Mix were used as internal standarts. All standarts purchased from the brand name to Dr. Ehrenstorfer GmbH (Table 2.3).

Ten different concentrations of the calibration standards, 1 ppm, 500 ppb, 250 ppb, 100 ppb, 50 ppb, 25 ppb, 10 ppb, 5 ppb, 2 ppb and 1 ppb were prepared in hexane solvent. Internal standards are prepared in hexane solvent with 500 ppb for PAH, PCB and Pesticides (Table 2.4). Recoveries range from 20 to 200%. Internal standarts help us to understand positive and negativie mistakes of caused by change in pollutant concentration in the sample.

Table 2.3: Calibration Standarts, Their Solvent and Brand Name.

Calibration Standarts	Solvent	Trademark
PCB Mix No. 21	10 μg/mL in Cyclohexane	Dr. Ehrenstorfer GmbH.
PAH Mix No. 9	100 μg/mL in Cyclohexane	Dr. Ehrenstorfer GmbH.
Organochlorine Pesticide Mix No. 2	2000 μg/mL in Toluene/Hexane	Dr. Ehrenstorfer GmbH.

Table 2.4: Internal Standarts, Their Solvent and Brand Name.

Internal Standarts	Solvent	Trademark
PCB No. 198	10 μg/mL in Isooctane	Dr. Ehrenstorfer GmbH.
PCB No. 29	10 μg/mL in Isooctane	Dr. Ehrenstorfer GmbH.

2.3.2 Chemicals used and their properties

All solvents are allowed to be used for liquid and gas chromatography. All solid chemicals are purified at 500 ^{o}C in drying-oven.

Table 2.5: Solid Chemicals, Cas-No and Their Trademarks.

Chemical Name	Cas-No	Trademark
Aluminium Oxide	1344-28-1	Sigma-Aldrich Chemie GmbH
Silica Gel 60 (0.063-0.0200 mm)	7631-86-9	Merck KGaA
Sodium Sulfate	7757-82-6	Merck KGaA
Supelclean™ ENVI™ - 8SPE Tubes 6 cc/1.0 g	-	Supelco Analytical

Table 2.6: Liquid Chemicals, Cas-No and Their Trademarks.

Chemical Name	Cas-No	Trademark
Cyclohexane	110-82-7	Merck KGaA
Toluene	108-88-3	Merck KGaA
n-Hexane	110-54-3	Merck KGaA
Dichloromethane	75-09-2	Merck KGaA
Methanol	67-56-1	Merck KGaA
Acetonitrile	75-05-08	Merck KGaA
Water	7732-18-5	Merck KGaA

All the solid chemicals and their properties are given at Table 2.5 and all the liquid chemicals and their properties are given at Table 2.6.

2.3.3 SPMD's Analyzing Steps

They passed through four basic preparation stages before being analyzed in the instrument. These are extraction, evoparation, 1st stage pretreatment and 2nd stage pretreatment. Each material used was cleaned with Toluene before starting the analysis. SPMDs from sampling points (Figure 2.8) were brought to TÜBİTAK MAM Laboratories at -20 ° C and kept at the same temperature in the same laboratory.

Figure 2.8: SPMDs view after sampling.

At the extraction phase, SPMDs removed from the freezer were cut into small pieces and placed into 250 mL erlenmeyer using tweezers. Cyclohexane, which must have a total volume of 100 mL, was added to the flask and the tweezers (to obtain the triolein remaining on the scissors and tweezers) (Figure 2.9).

Figure 2.9: SPMDs are cutting into little pieces.

The 500 μL of 500 ppb concentration PAH internal was then add onto the sample and cyclohexane in the Erlenmeyer to use in the calculation phase. Samples left on shaker at 120 RPM for 24 hours (Figure 2.10).

Figure 2.10: Samples on shaker.

At the evaporation stage, the samples were taken from the shaker and passed through 5 grams of Sodium Sulphate column. Water in the sample is removed after the sample get through Sodium Sulphate column to erlenmeyer; Erlenmeyerler was washed with 60 mL of cyclohexane and transferred to Zaymark Turbovaps tubes against the possibility of sample residence. In these tubes, a volume reduction is carried out at a temperature of 40 °C to a sample volume of 0.5 mL (Figure 2.11).

Figure 2.11: Sodium Sulphate column and volume decreasing at Zaymark Turbovaps.

For the first stage of the pretreatment, Silica, Aluminum Oxide (97 g Aluminum Oxide, activated with 3 mL of distilled water) and Sodium Sulphate purified at 500 ^{o}C were added on glass column as 10 g, 5 g and 2 g respectively. Dichloromethane (DCM) and Hexane, which are mixed in an equal ratio (1: 1) to 60 mL in order to activate the column, were transferred to the column. The 0.5 mL sample from the volume reduction process was then added to the column without allowing the column to dry (Figure 2.12). The inner walls of the Zaymark Turbovaps sample tubes were washed three times and added to the column, with a total volume of 100 mL of 1: 1 DCM / Hexane. The column content was collected in Zaymark Turbovaps tubes once again to make a volume reduction. The collected sample was reduced to 1 mL.

Figure 2.12: Silica, Aluminum Oxide and Sodium Sulphate column.

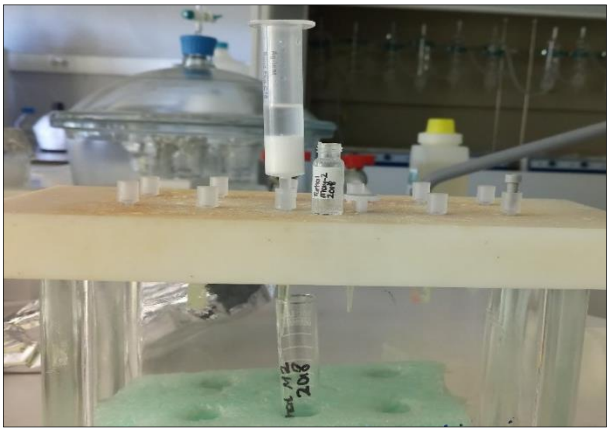


Figure 2.13: Activated C18 columns.

In the second pre-treatment step (Figure 2.13)., which is the final preparation step, by adding 0.5 mL of acetonitrile onto the samples the volume was increased to 1 mL; Samples were passed through the C18 column activated with 10 mL of methanol, 10 mL of DCM and 10 mL of distilled water.

After passing the samples through the column, in the same way, the walls of the tubes were cleaned with 3.3 mL acetonitrile and transferred to the column. After this, the samples volume was reduced to 0.5 mL for phase change and 1 mL of DCM was added. After repeating this process 3 times, samples which pass into DCM phase were taken to vials (Figure 2.14).

Figure 2.14: Volume decreasing of the sample and take it to the vials.

2.3.4 GC-MSMS Thermo Conditions

After the SPMD samplers has been clean-up beyond the process, the samplers were analyzed at GC-MSMS Thermo device. The column's features are 30 meters, 0.25 mm ID, TG-5SILMS GC column with 0.25 μm film properties.

2.3.5 Method of Calculating SPMD Results

Results from the GC-MSMS device were evaluated according to the recovery rate of internal standards. The recovery rates for internal standards including Chrysene D12, Acenapthene-D10, Napthalene-D8, Perylene-D12 and Phenathrene-D10 deuteriums range from 20% to 200%. This range shows the recovery of the micropollutants in the samples. Internal standards are the isotopes of the micropollutants which can not be found in nature. At the beginning of the analysis, internal standards were added to the samples and range of the decrease or increase of the internal standarts shows that if any kind of contamination or loss happened. If internal ranges higher than 100%, it means there was a contamination; if internal standart recovery ranges smaller than 100% it means there is a loss beyond the analysis. This range doesn't effect the results directly but gives us a vision for explain of the uncertainity in the results.

The results were calculated as "SPMD Water Concentration Estimator v4-1" by Est LAb. and calculated in ng per SPMD and converted to µg per SPMD. The table shows stations where SPMDs were located, and preserved temperatures and days in laboratory conditions. In the laboratory study, the micropollutant holding capacity of SPMDs at 10, 18 and 26 centigrade degrees was determined as externally. The temperature values at the sampling points were measured separately for periods of sampling and the temperature values are given in the table (Table 2.7).

Table 2.7: Temperatures, Dates and Sampling Times of Sampling Points.

Periods	Stations	Temperature	Sampling Dates	Sampling Period
1	Samsun L-1	18	20 September – 10October 2017	30
	Samsun L-2	18		
	Toros (Lost)	-		
	Amasya	10		
	Turhal	10		
2	Samsun L-1 (Lost)	-	11 October – 2 November 2017	22
	Toros	18		
	Amasya	10		
	Gümenek	10		
	Turhal	18		
3	Samsun L-1	18	17–30 May 2018	13
	Toros (Lost)	-		

Table 2.7: Continues.

Periods	Stations	Temperature	Sampling Dates	Sampling Period
3	Amasya	18	17–30 May 2018	13
	Turhal	18		
4	Amasya	26	14–17 September 2018	3
	Turhal	18		
5	Amasya	26	14–20 September 2018	6
	Turhal	18		

The external calculation is made for the SPMDs as ng per SPMD. The mass of the SPMD, the amount of lipid in the SPMD, the volume of the membrane and the volume of the SPMD are constant for the standard SPMD and are included in the table. The figure shows the view of the calculator. According to the results, amount of pollutants (OCL, PCB and PAH) /SPMD were determined (Figure 2.15).

At the end of calculations by using software seen in above figure, an analyte can appear "not found" although it was measured in GC-MS analysis in SPMD sample (in other word, standards and calculations was designed to serve removing errors in measurements). These analytes are Naphthalene, Anthracene, Fluorene, Chrysene, alpha-Hexachlorocyclohexane, beta-Hexachlorocyclohexane, delta-Hexachlorocyclohexane, 4,4'- DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD, Aldrin and Endosulfan-I were found in SPMD for each temperature. This can be considered a positive error.

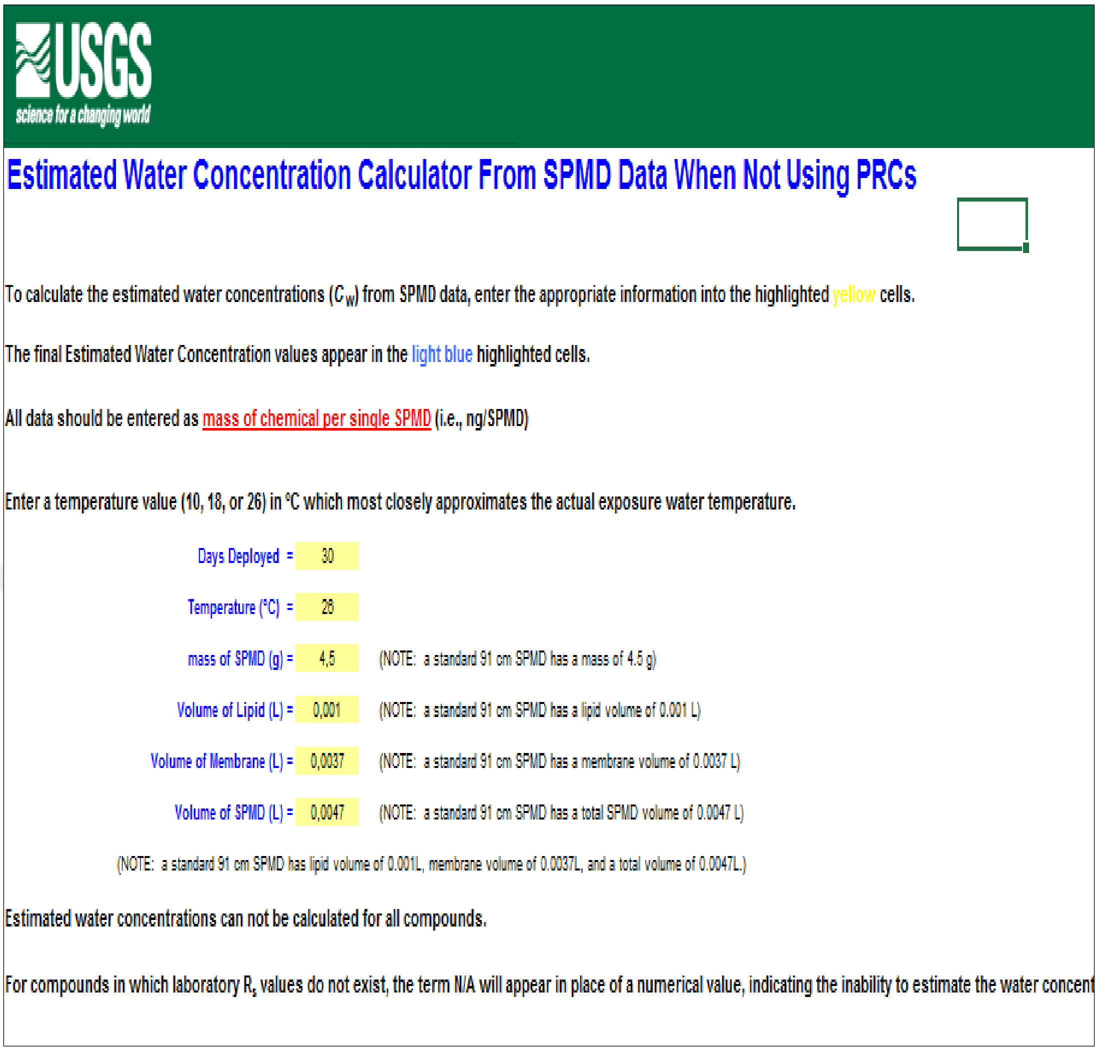


Fig 2.15: "SPMD Water Concentration Estimator v4-1" appearance.

3. RESULTS AND DISCUSSION

SPMD sampling was carried out in the river and sea water in Yeşilırmak River Basin for five periods as described in Materials and Methods Section. In accordance with the analysis of the state of river and surrounding activities, the micro pollutants to be measured were decided. They are PAHs; Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene and Benzo[g,h,I]perylene. PAHs that emit pollutants into the environment in any combustion reaction are on the list of substances that must be controlled under the Water Framework Directive.

Yeşilırmak Basin is the region where agriculture and animal husbandry activities are mostly conducted. Especially in Amasya and Tokat, the livelihood that keeps the economy alive is agriculture. Agricultural pesticides and pharmaceutical active substances used in agriculture are stored in soil, water and sediment and have the risk of mixing with groundwater. In the light of this information, organochloro pesticide pollutants were also examined as a result of the sampling in the region. These pollutants; Endosulfan-alpha, o-p’ DDT and p-p’ DDT.

Polycyclic Biphenyls; PCB 101, PCB 153, PCB 28, PCB 52, PCB 138, PCB-28/31, PCB 180 and PCB 118 were examined.

Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene, Benzo[g,h,i]perylene were examined in Yeşilırmak sampling as PAHs.

All results are given in µg/L and no sampling period or either point has exceeded the AA-EQS or MAC-EQS values.

3.1. Evaluation of Amasya Sampling Point Results

Amasya province is located in northern Turkey.In this region, livelihood is provided through agriculture and livestock. The main sectors for the province of Amasya are foodstuff production facilities, cement, domestic wastewater, slaughterhouses and integrated meat plants and domestic wastewater treatment plants. The results of the SPMD sampling studies in Yeşilırmak River in Amasya are given in Table 3.1. All results are given as µg/L.

Table 3.1: Concentration of Micropollutants in SPMD's at Amasya Point (µg/L).

Pollutant Name	Amasya Sept. 17	Amasya Oct. 17	Amasya May 18	Amasya Sept. 1/18	Amasya Sept. 2/18
cis-Chlordane	0,0004	ND	ND	ND	ND
Endosulfan alpha	ND	ND	ND	ND	ND
Dieldrin	0,0059	ND	ND	ND	ND
Lindane	ND	ND	ND	ND	ND
Heptaclor	0,00006	ND	ND	ND	ND
o-p' DDT	0,0015	ND	ND	ND	ND
p-p' DDT	0,005	ND	ND	ND	ND
Endosulfan beta	ND	ND	ND	ND	ND
Naphthalene	ND	ND	ND	ND	ND
Acenaphthylene	0,0445	0,0013	0,0001	0,00012	0,00013
Acenaphthene	0,0447	0,0002	4,5E-05	7,7E-05	5,6E-05
Fluorene	ND	ND	0,00038	0,0003	0,00025
Phenanthrene	0,6518	0,0034	0,00146	0,00128	0,00123
Anthracene	ND	ND	6,1E-05	7,5E-05	0,00011
Fluoranthene	0,0656	0,0003	0,00021	8,9E-05	0,0001
Pyrene	0,0585	0,0003	0,00021	9,4E-05	0,00011
Benz[a]anthracene	0,0028	0,00001	7,4E-06	4,1E-06	5,1E-06
Chrysene	ND	ND	ND	1,8E-05	2,4E-05
Benzo[b]fluoranthene	0,0015	0,00002	7,8E-06	ND	3E-06
Benzo[k]fluoranthene	2E-07	7E-09	ND	ND	6E-09

Table 3.1: Continues.

Pollutant Name	**Amasya Sept. 17**	**Amasya Oct. 17**	**Amasya May 18**	**Amasya Sept. 1/18**	**Amasya Sept. 2/18**
Benzo[a]pyrene	4E-07	5E-09	ND	4,5E-09	1,7E-09
Indeno[1,2,3-cd]pyrene	1E-07	1E-09	ND	ND	5E-10
Dibenzo[a,h]anthracene	3E-08	5E-10	ND	ND	ND
Benzo[g,h,I]perylene	6E-08	ND	ND	ND	2,2E-09
PCB 28	0,0008	0,00003	ND	ND	ND
PCB 52	0,0003	0,00003	ND	ND	ND
PCB 101	1E-07	ND	ND	ND	ND
PCB 118	6E-08	ND	ND	ND	ND
PCB 138	2E-07	ND	ND	ND	ND
PCB 153	2E-07	ND	ND	ND	ND
PCB 180	ND	ND	ND	ND	ND

When Amasya point sampling studies are examined in detail, polycyclic aromatic hydrocarbons are frequently encountered among measured micro pollutants. Although the polycyclic aromatic hydrocarbon called Phenanthrene was the most abundant pollutant in the environment during sampling studies, it did not exceed the maximum and annual average EQS values (Figure 3.1), (Figure 3.2), (Figure 3.3), (Figure 3.4), (Figure 3.5).

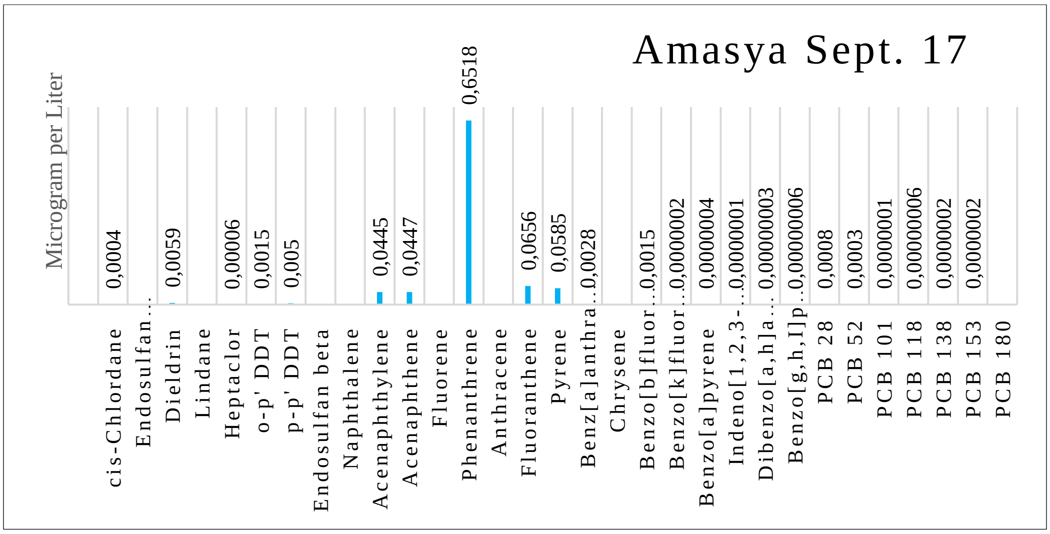


Figure 3.1: Results of Amasya sampling at September 2017.

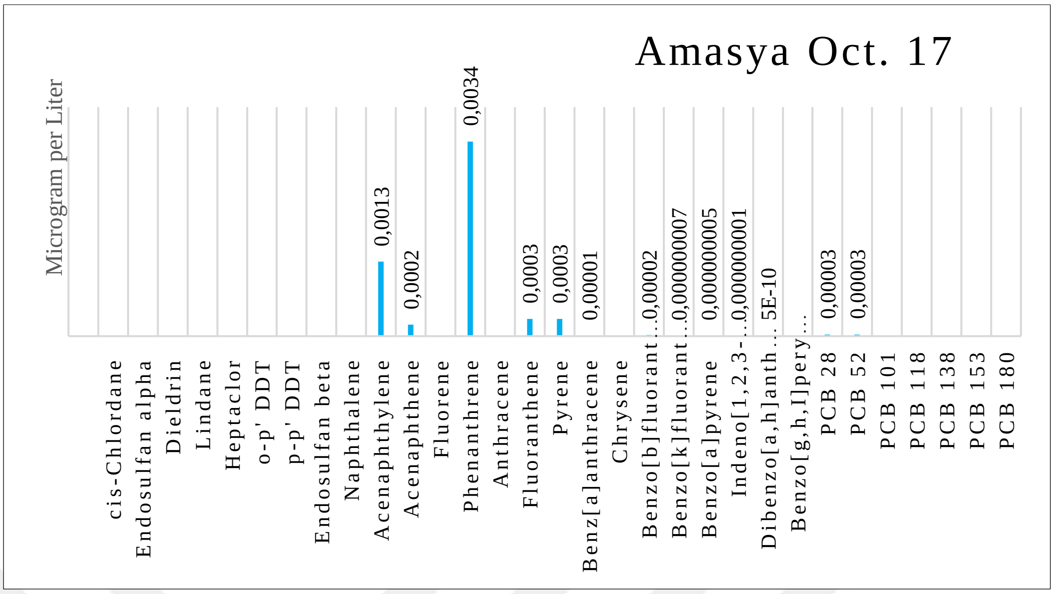


Figure 3.2: Results of Amasya sampling at October 2017.

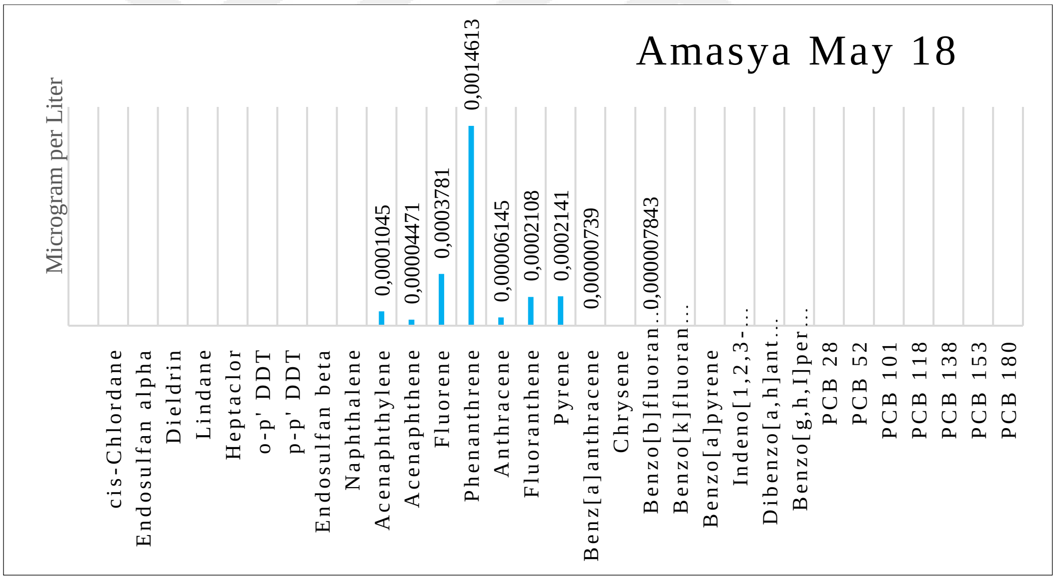


Figure 3.3: Results of Amasya sampling at May 2018.

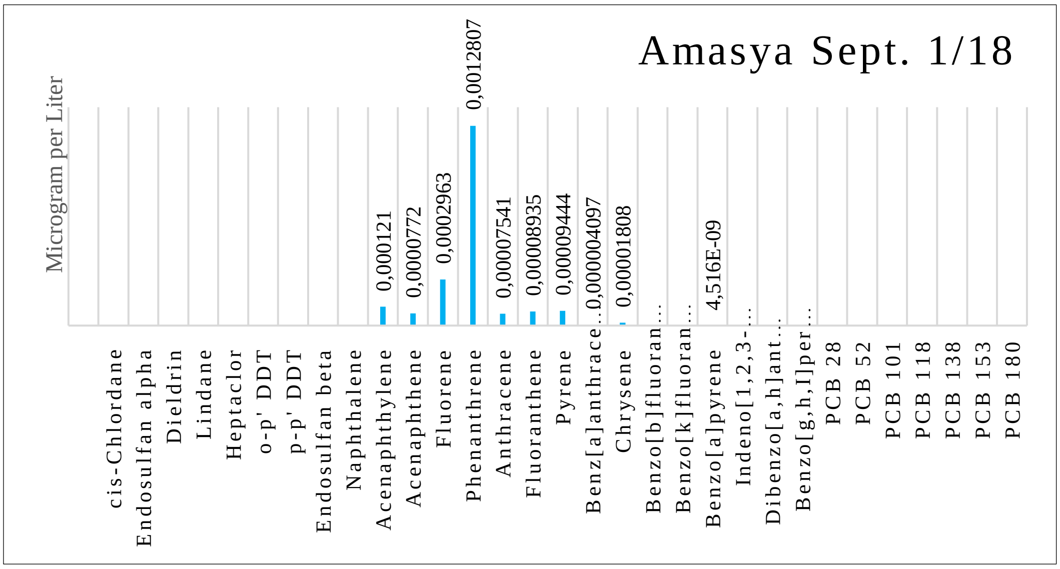


Figure 3.4: Results of Amasya sampling at September/1 2018.

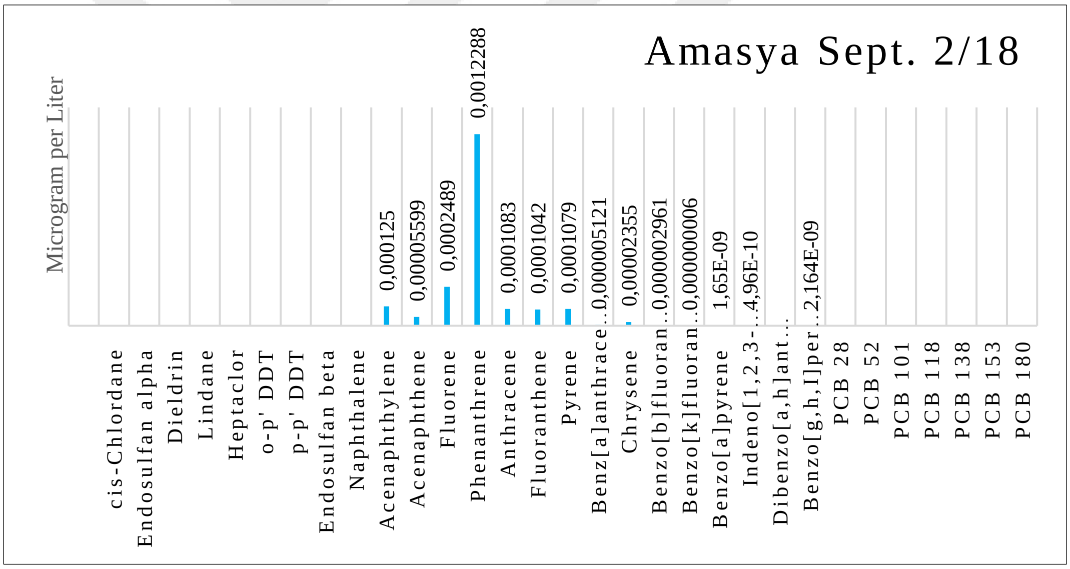


Figure 3.5: Results of Amasya sampling at September/2 2018.

3.2. Evaluation of Turhal Sampling Point Results

Turhal sampling point as the point at which one of the most intensive agriculture and animal husbandry in Turkey. Other predominantly sectors for Tokat; food production, metal processing plant and domestic wastewater facilities. The results of the SPMD sampling studies are given in Table 3.2. All results are given as µg/L.

Table 3.2: Concentration of Micropollutants in SPMD’s at Turhal point (µg/L).

Pollutant Name	**Turhal Sept. 17**	**Turhal Oct. 17**	**Turhal May 18**	**Turhal Sept. 1/18**	**Turhal Sept. 2/18**
cis-Chlordane	0,0013	ND	ND	ND	ND
Endosulfan alpha	0,0097	ND	ND	ND	ND
Dieldrin	0,0134	ND	ND	ND	ND
Lindane	ND	ND	ND	ND	ND
Heptaclor	ND	ND	ND	ND	ND
o-p' DDT	0,0202	ND	ND	ND	ND
p-p' DDT	0,0318	ND	ND	ND	ND
Endosulfan beta	ND	ND	ND	ND	ND
Naphthalene	ND	ND	ND	ND	ND
Acenaphthylene	0,1283	0,0006	6,44E-05	7,21E-05	8,43E-05
Acenaphthene	0,1007	0,0002	1,62E-05	2,71E-05	9,15E-05
Fluorene	ND	ND	0,000135	0,000185	0,000254
Phenanthrene	1,8622	0,0022	ND	0,000507	0,000633
Anthracene	ND	ND	0,000802	0,000019	0,000028
Fluoranthene	0,1147	0,0002	0,000136	4,87E-05	7,15E-05
Pyrene	0,1521	0,0002	7,84E-05	4,45E-05	6,44E-05
Benz[a]anthracene	0,0096	0,000006	2,6E-06	1,4E-06	1,9E-06
Chrysene	ND	ND	1,15E-05	4,7E-06	ND
Benzo[b]fluoranthene	0,0052	0,000005	3,5E-06	1,32E-06	1,74E-06
Benzo[k]fluoranthene	0,00003	0,00002	ND	ND	ND
Benzo[a]pyrene	0,000002	9E-10	ND	ND	ND

Table 3.2: Continues.

Pollutant Name	Turhal Sept. 17	Turhal Oct. 17	Turhal May 18	Turhal Sept. 1/18	Turhal Sept. 2/18
Indeno[1,2,3-cd]pyrene	9E-07	ND	ND	ND	ND
Dibenzo[a,h]anthracene	9E-08	1E-10	ND	ND	ND
Benzo[g,h,I]perylene	2E-07	ND	ND	ND	ND
PCB 28	0,0034	0,00001	ND	ND	ND
PCB 52	0,0018	0,00002	ND	ND	ND
PCB 101	4E-07	0,00005	ND	ND	ND
PCB 118	2E-07	ND	ND	ND	ND
PCB 138	7E-07	ND	ND	ND	ND
PCB 153	8E-07	ND	ND	ND	ND
PCB 180	0,000003	ND	ND	ND	ND

The Turhal sampling station is located far from the city, close to the construction of the hydroelectric power plant. Periodic pollutant concentrations are given below at Figure 3.6, Figure 3.7, Figure 3.8, Figure 3.9 and Figure 3.10.

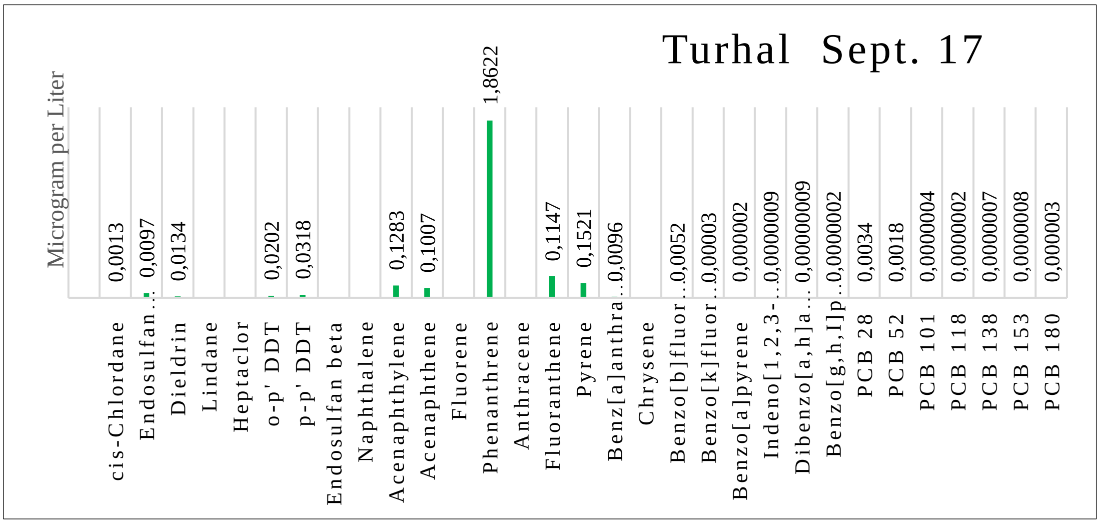


Figure 3.6: Results of Turhal sampling at September 2017.

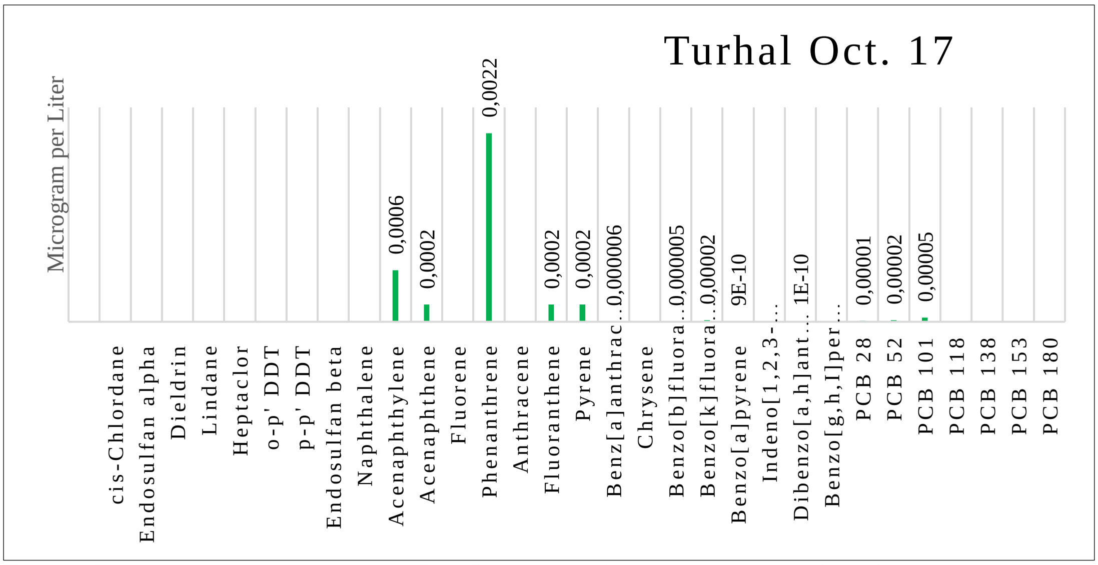


Figure 3.7: Results of Turhal sampling at October 2017.

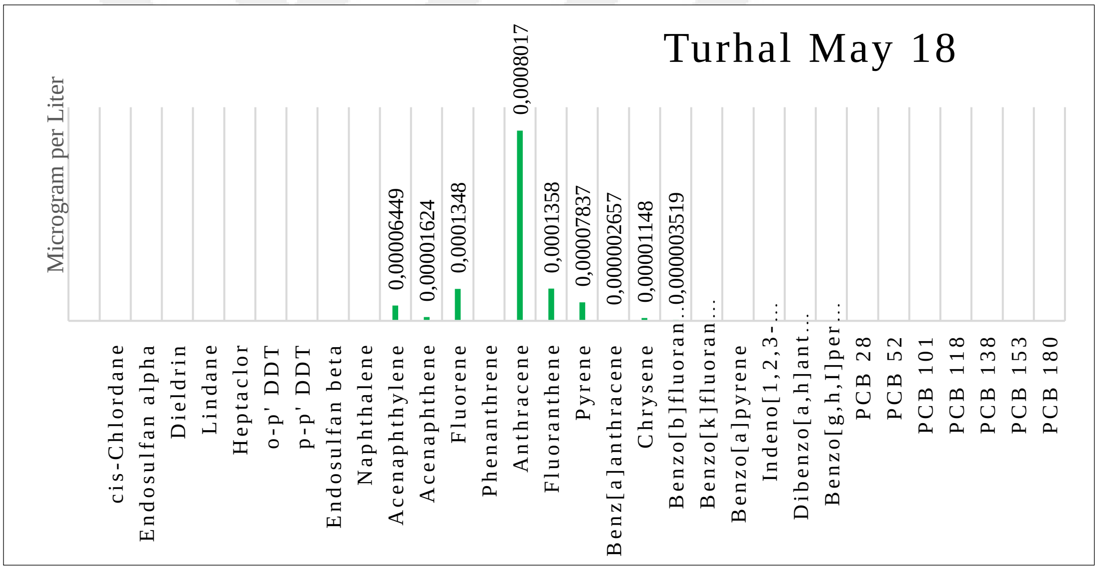


Figure 3.8: Results of Turhal sampling at May 2018.

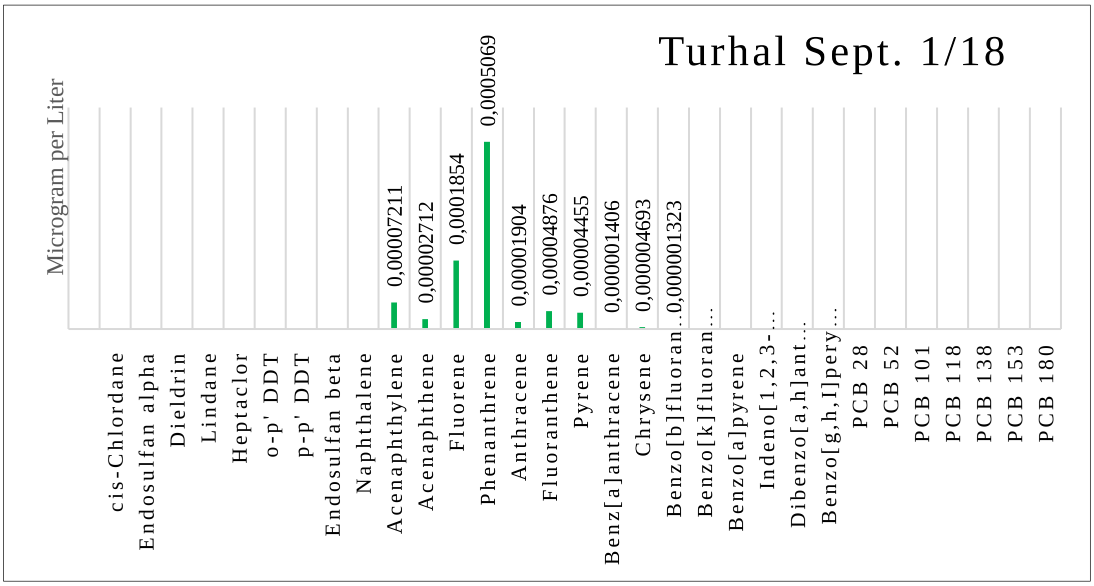


Figure 3.9: Results of Turhal sampling at September/1 2018.

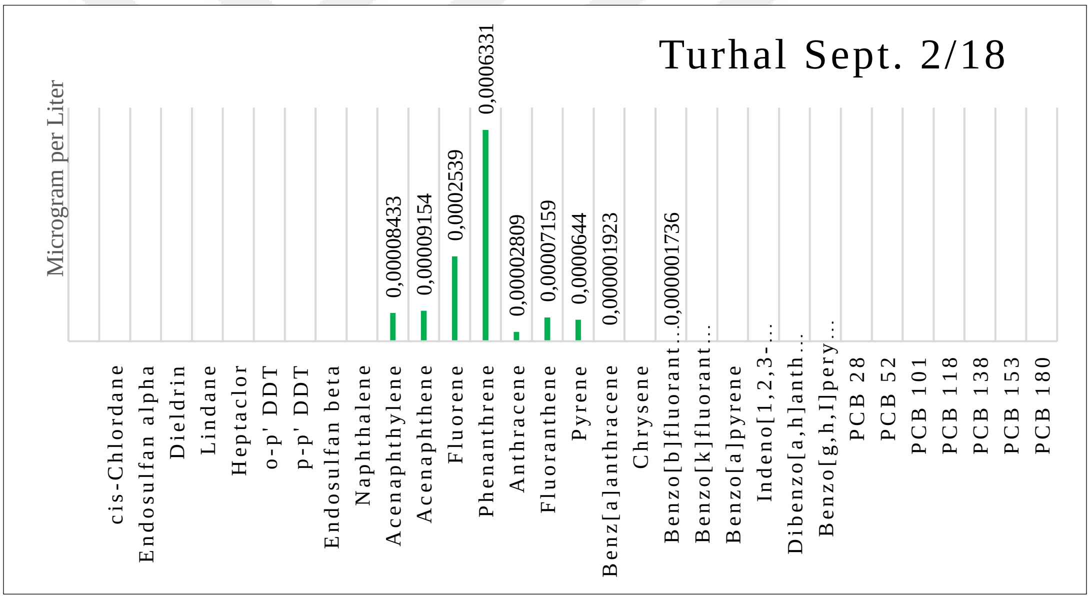


Figure 3.10: Results of Turhal sampling at September/2 2018.

3.3.Evaluation of Samsun L1 and Samsun L2 Sampling Points Results

In Samsun, there are slaughterhouses, oil filling facilities, domestic wastewater facilities, milk and milk products facility, flour and pasta production facility and non-ferrous metal production facilities in order to ensure economic livelihood. The ports, which are considered as one of the important livelihoods of the city and also seen as one of the permanent sources of pollution, also occupy an important place in Samsun.

The results of the SPMD sampling studies are given in Table 3.3. All results are given as µg/L.

Table 3.3: Concentration of Micropollutants in SPMD's at Samsun L1 and Samsun L2 Points (µg/L).

Pollutant Name	Samsun L1 Sept. 17	Samsun L1 May 18	Samsun L2 Sept. 17
cis-Chlordane	0,0003	ND	0,0003
Endosulfan alpha	ND	ND	ND
Dieldrin	ND	ND	ND
Lindane	0,0305	ND	0,0924
Heptaclor	ND	ND	ND
o-p' DDT	0,00002	ND	0,0005
p-p' DDT	0,0004	ND	0,0022
Endosulfan beta	ND	ND	ND
Naphthalene	ND	ND	ND
Acenaphthylene	0,0369	7,3E-05	0,0648
Acenaphthene	0,0339	ND	0,0193
Fluorene	0,1317	0,00028	0,0962
Phenanthrene	0,5739	0,00068	0,4633
Anthracene	0,0364	1,7E-05	0,035
Fluoranthene	0,0683	5,4E-05	0,0655
Pyrene	0,0529	4E-05	0,0362

Table 3.3: Continous.

Pollutant Name	Samsun L1 Sept. 17	Samsun L1 May 18	Samsun L2 Sept. 17
Benz[a]anthracene	0,0025	1,6E-06	0,0025
Chrysene	0,0066	6E-06	0,0069
Benzo[b]fluoranthene	0,0043	4,1E-06	0,002
Benzo[k]fluoranthene	ND	ND	ND
Benzo[a]pyrene	9E-07	ND	ND
Indeno[1,2,3-cd]pyrene	7E-07	ND	ND
Dibenzo[a,h]anthracene	2E-07	ND	ND
Benzo[g,h,I]perylene	2E-07	ND	ND
PCB 28	ND	ND	ND
PCB 52	ND	ND	ND
PCB 101	ND	ND	ND
PCB 118	ND	ND	ND
PCB 138	ND	ND	ND
PCB 153	ND	ND	ND
PCB 180	ND	ND	ND

Samsun L1 and Samsun L2 points are sampling stations located at two different coastal points of an international port in Samsun. While Samsun 1 was monitored in two different periods, sampling was conducted for Samsun 2 in one monitoring period. The fact that the two points were close to each other brought about the fact that the sampling results were very close to each other (Figure 3.11), (Figure 3.12), (Figure 3.13).

SPMD sampling data obtained as a result of the studies found below the EQS values, cis-Chlordane, Endosulfan alpha, Dieldrin, Lindane, Heptaclor, o-p 'DDT, p-p' DDT, polyaromatic hydrocarbons and PCBs (28, 52, 101, 118, 138, 153 and 180) are among the pollutants encountered in sampling studies. Since the sampling point is a point within the port and the agricultural Yeşilırmak River is poured around the sampling point by current, the pollutants in the sampling point are among the expected pollutants.

With the sampling, non-PCBs were found during SPMD sampling in the present study. Phenantrene as polyaromatic hydrocarbon was detected at the highest level in each period; In September 2017, Dibenzo [a, h] anthracene and Benzo [g, h, I] perylene in May 2018, Benz [a] anthracene was found to be the lowest pollutant.

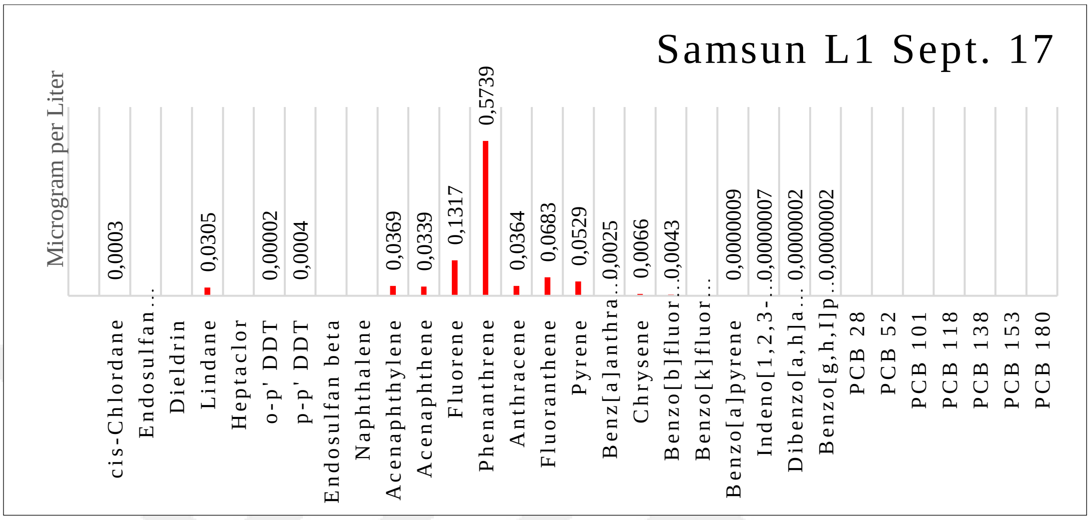


Figure 3.11: Results of Samsun L1 sampling at September 2017.

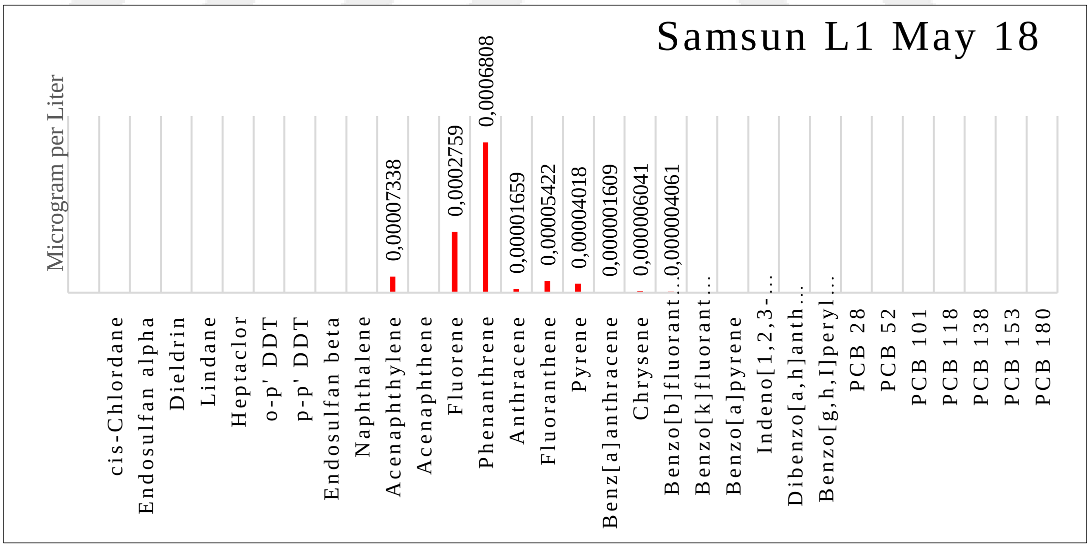


Figure 3.12: Results of Samsun L1 sampling at May 2018.

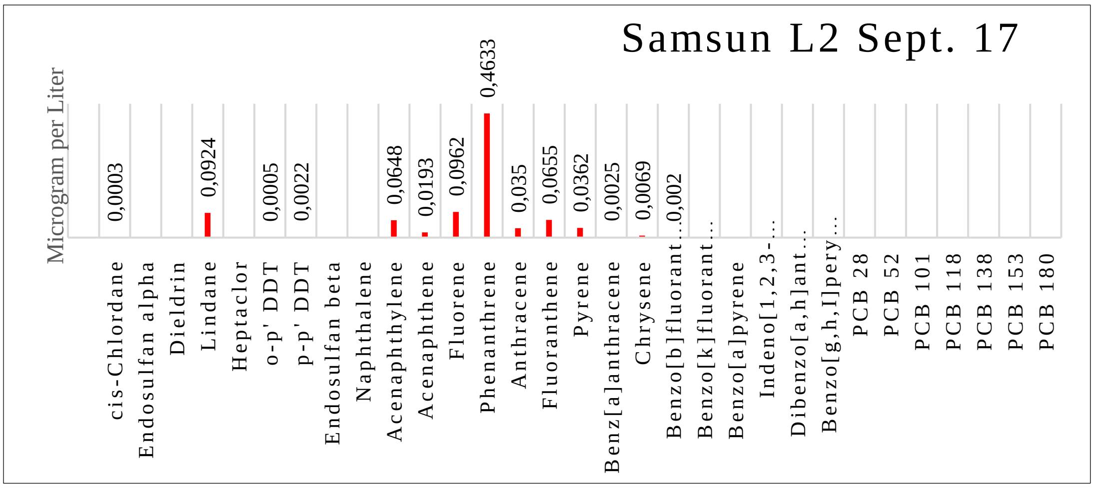


Figure 3.13: Results of Samsun L2 sampling at September 2017.

3.4. Evaluation of Gümenek Sampling Point Results

Gümenek sampling point was sampled in October 2017 sampling period. The results of the SPMD sampling studies are given in Table 3.4. All results are given as µg/L.

Table 3.4: Concentration of Micropollutants in SPMD's at Gümenek Point (µg/L).

Pollutant Name	**Gümenek Oct. 17**
cis-Chlordane	ND
Endosulfan alpha	ND
Dieldrin	ND
Lindane	ND
Heptaclor	ND
o-p' DDT	ND
p-p' DDT	ND
Endosulfan beta	ND
Naphthalene	ND

Table 3.4: Continues.

Pollutant Name	**Gümenek Oct. 17**
Acenaphthylene	0,0004
Acenaphthene	0,00005
Fluorene	ND
Phenanthrene	0,0017
Anthracene	ND
Fluoranthene	0,0002
Pyrene	0,0001
Benz[a]anthracene	0,00001
Chrysene	ND
Benzo[b]fluoranthene	0,00001
Benzo[k]fluoranthene	0,00007
Benzo[a]pyrene	ND
Indeno[1,2,3-cd]pyrene	ND
Dibenzo[a,h]anthracene	ND
Benzo[g,h,I]perylene	ND
PCB 28	0,00002
PCB 52	0,00003
PCB 101	ND
PCB 118	ND
PCB 138	ND
PCB 153	ND
PCB 180	ND

As a result of the studies, none of the items exceeded the annual average or maximum EQS values (Figure 3.14).

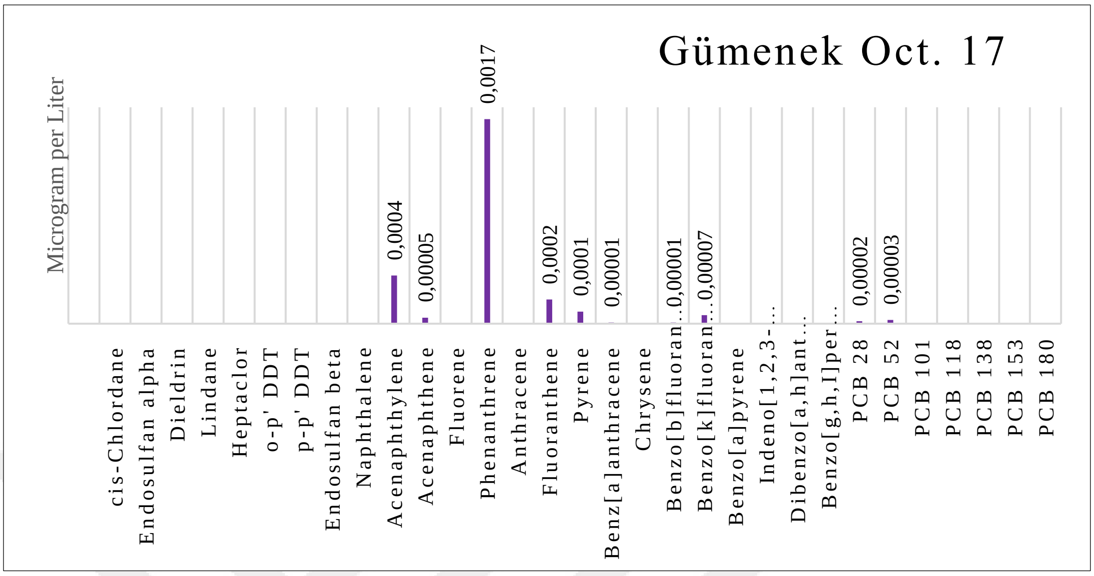


Figure 3.14: Results of Gümenek point sampling.

3.5. Evaluation of Toros Sampling Point Results

Toros sampling point was sampled in October 2017 sampling period. The results of the SPMD sampling studies are given in Table 3.5. All results are given as µg/L.

Table 3.5: Concentration of Micropollutants in SPMD's at Toros Point (µg/L).

Pollutant Name	**Toros Oct. 17**
cis-Chlordane	ND
Endosulfan alpha	ND
Dieldrin	ND
Lindane	0,00005
Heptaclor	ND
o-p' DDT	5E-06
p-p' DDT	6E-06

Table 3.5: Continues.

Pollutant Name	Toros Oct. 17
Endosulfan beta	ND
Naphthalene	ND
Acenaphthylene	0,0003
Acenaphthene	0,0001
Fluorene	0,0006
Phenanthrene	0,0019
Anthracene	0,00009
Fluoranthene	0,0004
Pyrene	0,0003
Benz[a]anthracene	0,00002
Chrysene	0,00006
Benzo[b]fluoranthene	0,00002
Benzo[k]fluoranthene	ND
Benzo[a]pyrene	6E-09
Indeno[1,2,3-cd]pyrene	2E-09
Dibenzo[a,h]anthracene	ND
Benzo[g,h,I]perylene	ND
PCB 28	ND
PCB 52	ND
PCB 101	ND
PCB 118	ND
PCB 138	ND
PCB 153	ND
PCB 180	ND

Napthalene and Acenaphthene pollutants for Toros point were determined by twister method in marine samples which were developed in parallel with passive sampling studies. From Napthalene and Acenaphthene detected in marine analysis, Napthalene was seen as a positive error during calculations, while Acenaphthene was detected as a pollutant in SPMD.

The micropollutant with the highest concentration was determined to be Phenanthrene, while Acenaphthene was the lowest concentrated one. As a result of the analysis, none of the items exceeded the annual average or maximum EQS values (Figure 3.15).

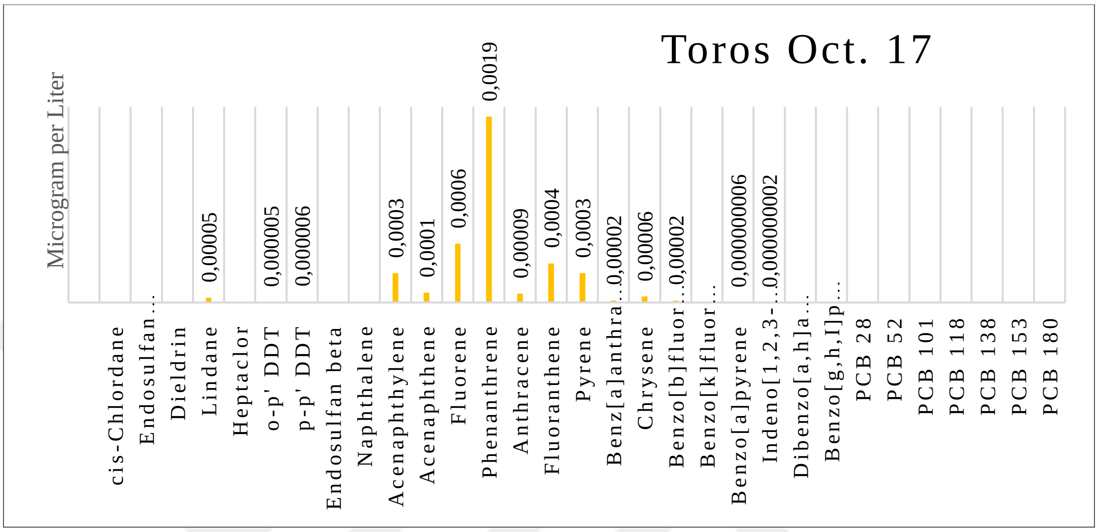


Figure 3.15: Results of Toros point sampling.

3.6. Results Assessments

In order to be able to measure very low concentrations in the receiving environment is very important for micropollutant analysis. SPMD's are important inventions for measurement of high or low concentrations of micropollutants depending on the sampling period.

In this study, SPMDs without deuterium were used and qualitative results were obtained. After measurement of micropollutant concentration in water bodies, the software was used for converting qualitative results to quantative ones. This software uses the result obtained from measurements of SPMD content and the other parameters such as temperature, date of sampling and estimates quantative results in the laboratory. With the help of this software positive erros were corrected (positive error: the micropollutant is detected however it is actually not present in the environment).

For each sampling time, results obtained at different sampling stations were summed up and average values were obtained (Figure 3.16).

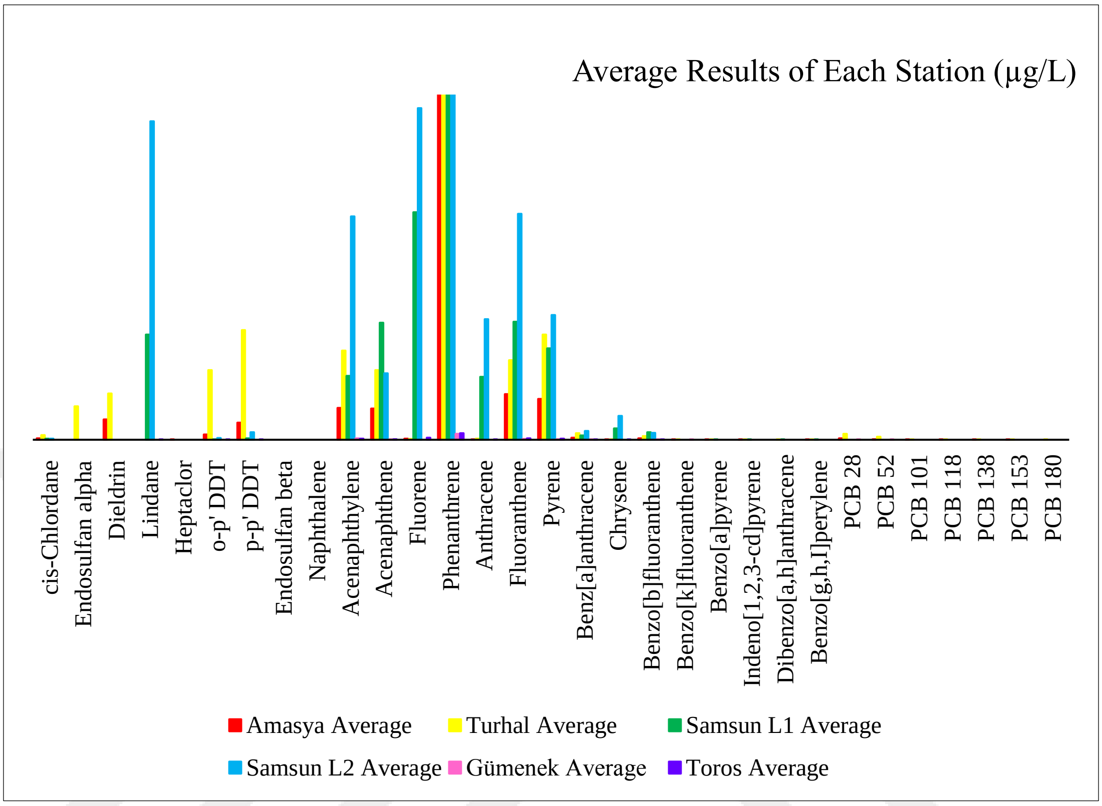


Figure 3.16: Average Results of Each Station (µg/L).

PAHs, which are known to occur as a result of industrial activities and natural burns, are the dominant pollutant group in the basin Pesticide and PCB contaminants were found extensively in the first analysis. Detailed result interpretation is as follows.

The highest pesticide concentrations for Amasya point were determined as Dieldrin and p-p’ DDT. Despite the restriction on the use Dieldrin and DDT has been brought, because of the long half-life is still seen in the territory of Turkey. Dieldrin has not been generally detected in all studies. Studies have found a lower concentration than other pollutants [Golfinopoulos et al., 2003]. Dieldrin was used to prevent termites and textile damage. DDT also was the highest pollutant in SPMD studies conducted in Marmara Region [Yılmaz ve ark.,, 2014]. It is known that Dieldrin is used in termite control and p-p’ DDT is used as an insect inhibitor. Considering that agricultural activities are intense in Amasya, the findings are indicative of the presence of pollutants whose half-life has not expired.

The highest PAH concentrations for Amasya point were determined as Phenanthrene and Fluorene. PAHs, which are among the POPs whose limit values are determined by the regulations, did not exceed EQS within the scope of the study. In the studies conducted in Macao harbor at the Pearl River Delta and Tounghi River in 2004, Phenantrene and Fluorene was determined as the highest concentration of pollutants in the area. [Luo et al., 2004], [Zhang et al., 2004]. Some of the industrial sources of Flourene and Phenanthrene are designated as recine, medicine, pigment, paint manufacture, pesticides and thermoset plastic. [Abdel-Shafy and Mansour, 2016]. Looking at the sectoral distribution of Amasya, the presence of pollutants detected due to the presence of the pesticide source, plastic production and Manufacture of refined petroleum products industries was an estimated result.

The highest PCB concentrations for Amasya point are determined as PCB 28 and PCB 52. None of the PCBs that are restricted to use have exceeded EQS. In studies previously conducted in Marmara Sea and Hartbeespoort Dam, similar results were found in the scope of the thesis and PCB 28 and PCB 52 were found predominantly [Amdany et al., 2014], [Yılmaz ve ark.,, 2014]. PCBs known to be used in paint, plastic and capacitor production; It is one of the pollutants expected to occur due to the industries such as LPG and Electric, PVC Window and Refined petroleum products manufacturing in the region.

The highest pesticide concentrations for Turhal point were determined as Endolsulfan-alpha and p-p’ DDT. Endosulfan-alpha was also found in a study at rivers of Northern Greece [Golfinopoulos et al., 2003]. Since p-p’ DDT takes about 40 years to go through surface waters, p-p’ DDT is still encountered in waters even if it is not used. In the previous study conducted in the Marmara region, p-p’ DDT findings were obtained [Yılmaz ve ark.,, 2014]. Prohibited use in Turkey since 2010, with the Endosulfan-alfa was detected trace amounts anyway. Endosulfan reaches surface waters as a result of direct deposition and runoff from agricultural use. Since the Endosulfan-alpha and p-p’ DDT was found as a disinfection in agriculture in the past years at Turhal point, which is close to the agricultural lands, it shows that they have been found as traces in the area in the current sampling period.

The highest PAH concentrations for the Turhal point are Phenanthrene and Fluorene, as in Amasya. In previous studies in Macao harbor at the Pearl River Delta and Tounghi River in 2004, Phenantrene and Fluorene was determined as the highest concentration of pollutants in that area [Luo et al., 2004], [Zhang et al., 2004]. Some of the industrial sources of Flourene and Phenanthrene are indicated as recine, medicine, pigment, paint manufacture, pesticides and thermoset plastic [Abdel-Shafy and Mansour, 2016]. For Turhal point Phenanthrene was not detected in the period of May 18. The reason for this is thought to be the sweep of the Phenanathrene pollutant in the SPMD due to the flow of the river. Looking at the sectoral distribution of Turhal, we can say that presence of pollutants detected due to the existence of the manufacture of other electronic and electric wires and cables, quarrying of ornamental and building stone, limestone, gypsum, chalk and slate and cutting, shaping and finishing of stone industries was an estimated result.

The highest PCB concentrations for Turhal point were determined as PCB 28 and PCB 52 as in Amasya point. None of the PCBs that are restricted to use have exceeded EQS. In studies previously conducted in Marmara Sea and Hartbeespoort Dam, similar results were found in the scope of the thesis and PCB 28 and PCB 52 were found predominantly [Amdany et al., 2014], [Yılmaz ve ark.,, 2014]. PCBs known to be used in the sector of paint, plastic and capacitor production are among the pollutants expected to be present at the sampling point due to the manufacture of other electronic and electric wires and cables sector in the region.

No pesticides have been detected for the Gümenek point. Phenanthrene and Acenaphthylene are detected as the PAH pollutants at the sampling point. Although the concentration of Acenaphthylene is very low compared to Phenantrene, it is the second highest pollutant detected at the sampling point. In previous studies conducted in China’s Tonghui River and Pearl River, it has been found that Phenanthrene has a much higher concentration than Acenaphthylene [Luo et al., 2004], [Zhang et al., 2004]. Considering PCB concentrations, PCB 28 and PCB 52, which have low permanence, were found. In studies previously conducted in Marmara Sea and Hartbeespoort Dam, similar results were found in the scope of the thesis and PCB 28 and PCB 52 were found predominantly [Amdany et al., 2014], [Yılmaz ve ark.,, 2014]. PCBs known to be used in paint, plastic and capacitor production are among the pollutants expected to be present at the sampling point due to the manufacture of other electronic and electric wires and cables sector in the region.

The pollutants detected in the highest concentrations in the samples of Samsun L-1, Samsun L-2 and Toros sampling points are the same. PCB pollutant was not found for all three points.

The highest concentration of PAH pollutants detected in Samsun L-1, Samsun L-2 and Taurus points are the same pollutants detected in Amasya and Turhal points and Phenanthrene and Fluorene. The same pollutants have been found in similar studies conducted in China before [Luo et al., 2004], [Zhang et al., 2004]. Considering that all three points are ports and are located close to the city, it can be thought that the impact of industrial activities in the city of Samsun on surface waters has been determined. Factories located in Samsun province and operating industrially as metalware industry, manufacture of ovens, furnaces and furnace burners, manufacture of other electronic and electric wires and cables, manufacture of industrial gases, manufacture of refined petroleum products, manufacture of plastic plates, sheets, tubesand profile, can be shown as a few of the sources of PAH pollutant present in surface waters.

The highest pesticide concentrations in Samsun L-1, Samsun L-2 and Taurus points are detected as o-p' DDT, p-p' DDT and Lindane (Gamma-hexachlorocyclohexane, γ-HCH) pollutants. In the studies conducted in Samsun, it was revealed that one of the most used pesticide species in the past was p-p' DDT and o-p' DDT [Erdoğan, 2010]. Thus, it became clear that DDTs detected at sampling points were residues. [Erdogan, 2010]. Lindane is a new pollutant encountered in sampling points. Lindane concentration was found to be much higher in DDT concentrations. The same situation can be seen in the study on the Pearl River [Luo et al., 2004]. Lindane is used in tree, seed and soil treatments. It is also used as an insecticide against ectoparasites in human applications. Another factor is the use of Lindane in care products (body lotion, shampoo, hand cream, etc.) [Web 6, 2020]. It is thought that Lindane passes to surface waters through domestic wastewater both with the use of agriculture and personal care products.

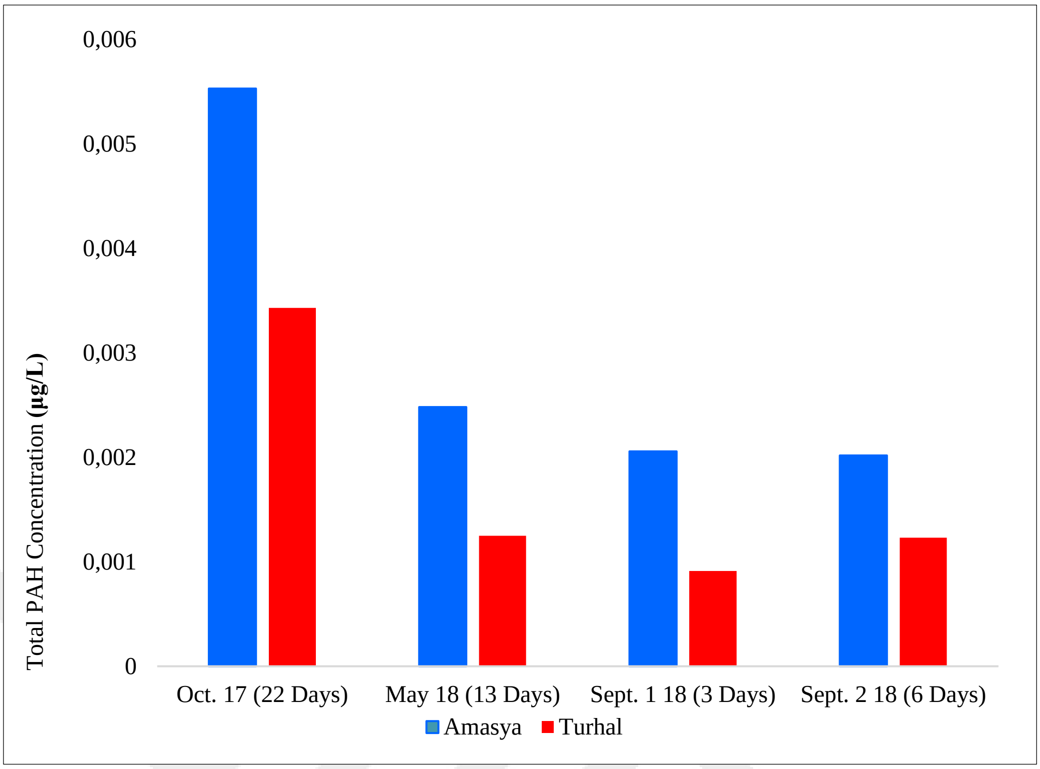


Figure 3.17: Total PAH Results for Amasya and Turhal samplings.

In the Figure 3.17, as a result of sampling studies carried out at Amasya and Turhal points, the total amount of PAHs in the SPMDs are given. In the calculations made separately for each period, it was observed that SPMDs kept more PAH pollutants in their body with the increase of sampling time.

Measurement of micropollutant levels in water environments which are protected with the frameworks and directives of EPA in the world, EEA in Europe and Department of Forestry and Water Affairs in Turkey, is very important. In our country, Surface Water Quality Directives states the highest concentrations of micropollutants which should not be exceeded. The list is divided into two environmental quality standard (EQS) as annual average (AA-EQS) and maximum acceptable concentration (MAC-EQS) values for inland and transitional waters [RezGaz 1, 2015].

MAC-EQS and AA-EQS values given in Table 3.6 and Table 3.7 were taken from Surface Water Quality Drectives presented in appendix Table 4 and Table 5. The average micropollutant concentrations at different sampling points were compared with these MAC EQS and AA-EQS values.

Table 3.6: Assesment of MAC-EQS and AA-EQS Values on Amasya Point (for Inland Surface Waters).

Pollutant Name		**MAC-EQS Inland Surface Waters (µg/L)**	**AA-EQS Inland Surface Waters (µg/L)**	**Amasya MAC of Each Sampling (µg/L)**	**Amasya Annual Average Results (µg/L)**
Pesticides	cis-Chlordane	42	42	0,0004	0,00008
	Endosulfan alpha	0,01	0,005	-	-
	Dieldrin	0,93	0,02	0,0059	0,00118
	Lindane	-	-	-	-
	Heptaclor	3E-04	-	6E-05	0,000012
	o-p' DDT	-	-	0,0015	0,0003
	p-p' DDT	-	-	0,005	0,001
	Endosulfan beta	0,01	0,005	-	-
PAHs	Naphthalene	130	2	-	-
	Acenaphthylene	-	-	0,0445	0,0092301
	Acenaphthene	66	6	0,0447	0,009015
	Fluorene	47	3,4	0,00038	0,000184
	Phenanthrene	11,2	1,4	0,6518	0,131834
	Anthracene	0,4	0,1	0,00011	4,9E-05
	Fluoranthene	0,12	0,063	0,0656	0,013260
	Pyrene	0,4	0,1	0,0585	0,0118432
	Benz[a]anthracene	-	-	0,0028	0,0005653
	Chrysene	1,9	19	8,3E0-6	8,3E0-6
	Benzo[b]fluoranthene	0,017	-	0,0015	0,0003061
	Benzo[k]fluoranthene	0,017	-	7E-09	4,26E-08
	Benzo[a]pyrene	0,27	1,7E-03	5E-09	8,2E-08
	Indeno[1,2,3-cd]pyrene	-	-	1E-07	2,029E-08
	Dibenzo[a,h]anthracene	-	-	3E-08	6,1E-09
	Benzo[g,h,I]perylene	8,20E-03	-	6E-08	1,24E-08
PCBs	PCB 28	0,02	0,01	0,0008	1,66E-04
	PCB 52	0,02	0,01	0,0003	6,6E0-5
	PCB 101	0,25	0,25	1E-07	2E-08
	PCB 118	0,02	0,01	6E-08	1,2E-08
	PCB 138	0,02	0,01	2E-07	4E-08
	PCB 153	0,02	0,01	2E-07	4E-08
	PCB 180	0,02	0,01	-	-

Table 3.7: Assesment of MAC-EQS and AA-EQS Values on Turhal and Gümenek Point (for Inland Surface Waters).

Pollutant Name		MAC-EQS Inland Surface Waters (µg/L)	AA-EQS Inland Surface Waters (µg/L)	Turhal MAC of Each Sampling (µg/L)	Turhal Annual Average Results (µg/L)	Gümenek MAC of Each Sampling (µg/L)
Pesticides	cis-Chlordane	42	42	0,0013	0,00026	-
	Endosulfan alpha	0,01	0,005	0,0097	0,2303	-
	Dieldrin	0,93	0,02	0,0134	0,00268	-
	Lindane	-	-	-	-	-
	Heptaclor	3E-04	-	-	-	-
	o-p' DDT	-	-	0,0202	0,00404	-
	p-p' DDT	-	-	0,0318	0,00636	-
	Endosulfan beta	0,01	0,005	-	-	-
PAHs	Naphthalene	130	2	-	-	-
	Acenaphthylene	-	-	0,1283	0,025824	4E-04
	Acenaphthene	66	6	0,1007	0,020206	5E-05
	Fluorene	47	3,4	-	0,000114	-
	Phenanthrene	11,2	1,4	1,8622	0,373108	1,7E-04
	Anthracene	0,4	0,1	8E-04	0,000169	-
	Fluoranthene	0,12	0,063	0,1147	0,02303	2E-04
	Pyrene	0,4	0,1	0,1521	0,030497	1E-04
	Benz[a]anthracene	-	-	0,0096	0,001922	1E-05
	Chrysene	1,9	19	1,15E-05	3E-06	-
	Benzo[b]fluoranthene	0,017	-	0,0052	0,001042	1E-05
	Benzo[k]fluoranthene	0,017	-	0,00003	0,00001	7E-05
	Benzo[a]pyrene	0,27	1,7E-03	2E-06	4,00E-07	-
	Indeno[1,2,3-cd]pyrene	-	-	9E-07	1,8E-07	-
	Dibenzo[a,h]anthracene	-	-	9E-08	1,8E-08	-
	Benzo[g,h,I]perylene	8,20E-03	-	2E0-7	4E-08	-
PCBs	PCB 28	0,02	0,01	0,0034	6,8E-04	2E-05
	PCB 52	0,02	0,01	0,0018	3,6E-04	3E-05
	PCB 101	0,25	0,25	5E-05	1E-05	-
	PCB 118	0,02	0,01	2E-07	4E-08	-
	PCB 138	0,02	0,01	7E-07	1E-07	-
	PCB 153	0,02	0,01	8E-07	1,6E-07	-
	PCB 180	0,02	0,01	3E-06	6E-07	-

Table 3.6 and Table 3.7 gives MAC and annual average concentrations for inland waters. For MAC-EQS result evaluation, the highest level of pollutants detected at sampling points was taken and recorded in the table. Thus, it is understood that the pollutants levels which do not exceed MAC-EQS are below the limit values in other sampling periods. For Amasya and Turhal points, annual average values and maximum acceptable concentration values were used. Only one sampling was performed in

Gümenek, then MAC was taken into account for Gümenek point. Neither MAC-EQS nor AA-EQS was exceeded in all the sampling points.

Table 3.8 gives MAC and annual average concentrations of transitional water bodies. For the evaluation of results in terms of MAC-EQS the highest concentration detected in the sampling points were taken into account and involved in the table. Thus no other concentrations exceeded MAC-EQS values for these waters. There was no annual monitoring for Samsun L-1, Samsun L-2 and Toros because of that maximum acceptable concentrations were used for these points.

Table 3.8: Assesment of MAC-EQS Values on Samsun L1 and Samsun L2 and Toros Points (for Transitional Water Bodies).

<table>
<tr><th colspan="2" rowspan="2">Pollutant Name</th><th>MAC-EQS</th><th>AA-EQS</th><th rowspan="2">Samsun L1 MAC of Each Sampling (µg/L)</th><th rowspan="2">Samsun L2 MAC of Each Sampling (µg/L)</th><th rowspan="2">Toros MAC of Each Sampling (µg/L)</th></tr>
<tr><th colspan="2">Transitional Water Bodies (µg/L)</th></tr>
<tr><td rowspan="8">Pesticides</td><td>cis-Chlordane</td><td>42</td><td>42</td><td>0,0003</td><td>0,0003</td><td>-</td></tr>
<tr><td>Endosulfan alpha</td><td>0,004</td><td>0,0005</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Dieldrin</td><td>0,93</td><td>0,02</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Lindane</td><td>-</td><td>-</td><td>0,0305</td><td>0,0924</td><td>5E-05</td></tr>
<tr><td>Heptaclor</td><td>3E-05</td><td>1E-08</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>o-p' DDT</td><td>-</td><td>-</td><td>2E-05</td><td>0,0005</td><td>5E-06</td></tr>
<tr><td>p-p' DDT</td><td>-</td><td>-</td><td>4E-04</td><td>0,0022</td><td>6E-06</td></tr>
<tr><td>Endosulfan beta</td><td>0,004</td><td>0,0005</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td rowspan="11">PAHs</td><td>Naphthalene</td><td>130</td><td>2</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Acenaphthylene</td><td>-</td><td>-</td><td>0,0369</td><td>0,0648</td><td>0,0003</td></tr>
<tr><td>Acenaphthene</td><td>66</td><td>6</td><td>0,0339</td><td>0,0193</td><td>0,0001</td></tr>
<tr><td>Fluorene</td><td>3,4</td><td>47</td><td>0,1317</td><td>0,0962</td><td>0,0006</td></tr>
<tr><td>Phenanthrene</td><td>11,2</td><td>1,4</td><td>0,5739</td><td>0,4633</td><td>0,0019</td></tr>
<tr><td>Anthracene</td><td>0,4</td><td>0,1</td><td>0,0364</td><td>0,035</td><td>9E-05</td></tr>
<tr><td>Fluoranthene</td><td>0,12</td><td>0,063</td><td>0,0683</td><td>0,0655</td><td>0,0004</td></tr>
<tr><td>Pyrene</td><td>0,4</td><td>0,02</td><td>0,0529</td><td>0,0362</td><td>0,0003</td></tr>
<tr><td>Benz[a]anthracene</td><td>-</td><td>-</td><td>0,0025</td><td>0,0025</td><td>2E-05</td></tr>
<tr><td>Chrysene</td><td>1,9</td><td>19</td><td>0,0066</td><td>0,0069</td><td>6E-05</td></tr>
<tr><td>Benzo[b]fluoranthene</td><td>0,017</td><td>-</td><td>0,0043</td><td>0,002</td><td>2E-05</td></tr>
</table>

Table 3.8: Continues.

Pollutant Name		MAC-EQS	AA-EQS	Samsun L1 MAC of Each Sampling (µg/L)	Samsun L2 MAC of Each Sampling (µg/L)	Toros MAC of Each Sampling (µg/L)
		Transitional Water Bodies (µg/L)				
PAHs	Benzo[k]fluoranthene	0,017	-	-	-	-
	Benzo[a]pyrene	0,027	1,7E-03	9E-07	-	6E-09
	Indeno[1,2,3-cd]pyrene	-	-	7E-07	-	2E-09
	Dibenzo[a,h]anthracene	-	-	2E-07	-	-
	Benzo[g,h,I]perylene	8,2E-04	-	2E-07	-	-
	PCB 28	0,02	0,01	-	-	-
	PCB 52	0,02	0,01	-	-	-
	PCB 101	0,25	0,01	-	-	-
	PCB 118	0,02	0,01	-	-	-
	PCB 138	0,02	0,01	-	-	-
PCBs	PCB 153	0,02	0,01	-	-	-
	PCB 180	0,02	0,01	-	-	-

As a result of the analysis, it is thought that the pollutants are mostly originated from agriculture and industry in the region. As a result of the study, considering factors such as rains, floods and flow rate in the sampling environment will affect sampling, it is foreseen to use deuterium SPMDs in future studies to obtain healthier results. No pollutant has exceeded EQS values within the scope of the study. Phenanthrene is the closest pollutant approach to EQS limit values. The persistence of permanent organic pollutants in surface waters raises a suggestion for sampling more frequently. Yeşilırmak basin is a basin where agricultural and industrial activities are intense, and the most intense pollutant group in the region has been identified as PAHs. The pollutants present in the basin, although its use has been banned in the past years, show the difficulty of dissolution permanent organic pollutants from nature. It is understood that, with the use of SPMDs, one of the passive sampling methods, by using less chemicals, results with lower concentrations can be obtained.

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BIOGRAPHY

Zehra Rana İkizoğlu was born on 23th of December 1993 in Istanbul, Turkey. She started his Bachelors Degree in Environmental Engineering of Sakarya University in 2011. After her graduation from BSc in 2016, she started Master of Science education in Environmental Engineering program of Gebze Technical University. In the spring of 2020, she graduated from MSc with this thesis.

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APPENDICES

Appendix A: Abstracts from this Thesis Study

İkizoğlu Z. R., Avaz G., Canlı O., Öktem Olgun E., Özkan M., (2018), “Using Passive Sampling Technologies at Sea Water and River Basin: A Case of Black Sea and Yeşilırmak Basin Sampling with Semipermeable Membrane Devices (SPMD)” 10th IWA Eastern-European Young Water Professionals, Zagreb.

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