

**CHARACTERIZATION OF ORGANOCHLORINE PESTICIDES AND
DETERMINATION OF POLLUTION LEVELS IN SURFACE WATER,
GROUND WATER AND SOIL SAMPLES: INCLUDING FIVE DISTRICTS
OF BOLU**

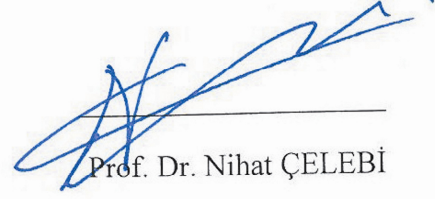
by

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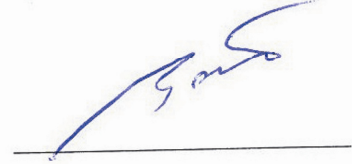
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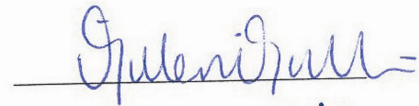


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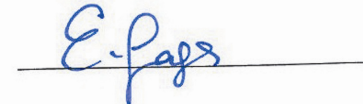
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ABSTRACT

CHARACTERIZATION OF ORGANOCHLORINE PESTICIDES AND DETERMINATION OF POLLUTION LEVELS IN SURFACE WATER, GROUND WATER AND SOIL SAMPLES: INCLUDING FIVE DISTRICTS OF BOLU

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In this study, totally 75 ground and surface water, 54 surface soil samples were collected from the five districts of Bolu in summer season of 2009. In autumn season, 17 surface and ground water and 17 soil samples were collected just in the city center to observe the seasonal changes of organochlorine pesticides (OCPs). Ground and surface water samples were extracted by using solid phase extraction and soil samples were ultrasonically extracted. Concentrations of 19 OCP compounds were detected by gas chromatography-electron capture detector (GC-ECD). Method validation was performed to determine 19 OCP compounds. However, 13 OCP compounds can be observed in the samples. The concentrations of most OCPs were higher in samples taken in the summer than that in the autumn. The

most observed pesticides were endosulfan sulfate and 4, 4' DDT in ground water samples, α -HCH in surface water samples, endosulfan sulfate in soil samples. Endosulfan sulfate also belonged to the highest average concentration in water and soil samples. Although the highest total concentration in soil samples and surface water samples were detected in Mudurnu, the highest total concentration in ground water was detected in Seben. The concentrations in soil and water samples had lower concentration values than literature values. Spatial distribution of OCPs were evaluated by the help of contour maps in the five districts of Bolu. Generally, agricultural processes affected the water and soil quality in the region. However, nonagricultural areas were also affected by pesticides. The concentrations of pesticides were not exceeded the legal limits of European directives for each pesticides.

Keywords: Organochlorine pesticides, Ground water, Surface water, Soil, Solid Phase Extraction, Ultrasonic extraction, GC-ECD, Mapping, Statistical evaluation

ÖZET

ORGANOKLORLU PESTİSİTLERİN BELİRLENMESİ VE YÜZEY SUYU, YERALTI SUYU VE TOPRAK ÖRNEKLERİNİNDE KİRLİLİK SEVİYELERİNİN TAYİNİ: BOLU İLİ BEŞ İLÇESİNDE

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Bu çalışmada, toplam 75 yeraltı ve yüzey suyu ile 54 toprak örneği 2009 yılının yaz mevsiminde Bolu İli'nin beş ilçesinden toplanmıştır. Organoklorlu pestisitlerin mevsimsel değişimlerini gözlemek için 2009 yılının sonbahar mevsiminde 17 yüzey ve yeraltı suyu ve 17 toprak örneği sadece şehir merkezinden toplanmıştır. Yeraltı ve yüzey sularının ekstraksiyonu katı faz ekstraksiyon düzeneği ile yapılmıştır ve toprak örnekleri ultrasonik yöntemi kullanılarak ekstrakte edilmiştir. 19 OCP bileşiğinin konsantrasyonları gas kromatografisi-elektron yakalama dedektörü ile belirlenmiştir (GC-ECD). 19 OCP bileşiğinin belirlenmesi için metot validasyonu yapılmıştır. Fakat örneklerde 13 OCP bileşiği gözlemlenmiştir. Yaz mevsiminde alınan örneklerde birçok OCP bileşiğinin konsantrasyonu sonbahar mevsimindekinden yüksek çıkmıştır. Yeraltı sularında

endosülfan sülfat ve DDT, yüzey sularında α -HCH ve toprak örneklerinde endosülfan sülfat en fazla gözlemlenen pestisitlerdir. Ayrıca endosülfan sülfat su ve toprak örneklerinde en yüksek ortalama konsantrasyona sahiptir. Toprak ve yer altı suyu örneklerinde en yüksek toplam konsantrasyon Mudurnu ilçesinde gözlemlenmesine rağmen, yüzey suyu örneklerinde en yüksek konsantrasyon Seben ilçesinde gözlenmiştir. Toprak ve su örnekleri literature değerlerinden daha düşük değerlere sahiptir. Kontur haritalarının yardımıyla Bolu İli'nin beş ilçesinde OCP'lerin mekansal dağılımları değerlendirilmiştir. Genellikle, bu bölgede tarımsal uygulamalar su ve toprak kalitesini etkilemektedir. Fakat tarımsal olmayan alanlar pestisitlerden etkilenmiştir. Pestisit konsantrasyonları, her bir pestisit için Avrupa'da belirlenen yasal limitleri aşmamıştır.

Anahtar Kelimeler: Organoklorlu pestisitler, Yeraltı suyu, Yüzey suyu, Toprak, Katı faz ekstraksiyon, Ultrasonik ekstraksiyon, GC-ECD, Haritalandırma, İstatistiksel değerlendirme

*Dedicated to my family
and my nephew Deniz Dikenoglu*

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CHAPTER 1

INTRODUCTION

Persistent organic pollutants (POPs) are toxic chemicals which have the ability to persist in the environment, to bioaccumulate in fatty tissues and food chains, to be transported long distance and deposited far from the place where they were released (Jones and Voogt, 1999). Although many of these chemicals are useful for pest and disease control, crop production, and industry, they have had unexpected effects on human health and the environment. Therefore, in Stockholm Convention, 90 countries agreed to reduce or eliminate the production, use, and/or release of 12 key POPs. These dirty dozen contains 8 kinds of pesticides (aldrin, chlordane, endrin, dieldrin, dichlorodiphenyl trichloroethane (DDT), hexachlorobenzene, mirex, toxaphene, heptachlor) (Anonymous 1, 2011).

Pesticides are any substance or mixture of substances intended for preventing, destroying or controlling any pest. While a pesticide kills or affects any pest such as insects, mice and other animals, unwanted plants (weeds), fungi, microorganisms, it can also cause harm to humans, animals, or the environment (Anonymous 2, 2011). On the other hand, their costs are low and they have versatile property in industry, agriculture and public health. These are the reasons why some developing countries are still using these compounds (Tanabe et al., 1994) and why these countries have

some environmental problems related with these toxic chemicals (Guruge and Tanabe, 2001).

Pesticides can contaminate surface water directly as spray drift or run-off and drainage from the treated soil because of their application. Their accumulative property and presence help to transport these compounds in many parts of the hydrosphere (Vega et al., 2005). The hydrosphere is one part of the environment which contains Earth's water. There is relatively small percentage of the total water on Earth which is actually used in terrestrial, atmospheric, and biological processes. These water circulates through environmental processes in the atmosphere, in underground as groundwater, and in streams, rivers, lakes, ponds, and reservoirs as surface water (Manahan, 2000). For this reason, pesticide usage is a risk for water quality since they can contaminate ground and surface water in agricultural areas.

1.1. Water System

Water, with a simple chemical formula of H_2O , is a vitally important substance in all parts of the environment. About 70% of Earth's surface is covered with water. It is found in all the spheres of the environment such as in the oceans as saltwater, on land as surface water, underground as groundwater, in the atmosphere as water vapor, in the polar icecaps as ice, and in many parts of the anthrosphere. Furthermore, water is an essential part of all living systems and is the medium from which life evolved and in which life exists (Manahan, 2000).

The world's water supply is found in the five parts of the hydrologic cycle (Figure 1.1). About 97% of Earth's water is found in the oceans. Another fraction is present as water vapor in the atmosphere (clouds). Some water is found in the solid state like ice and snow in snowpacks, glaciers, and the polar ice caps. Whereas

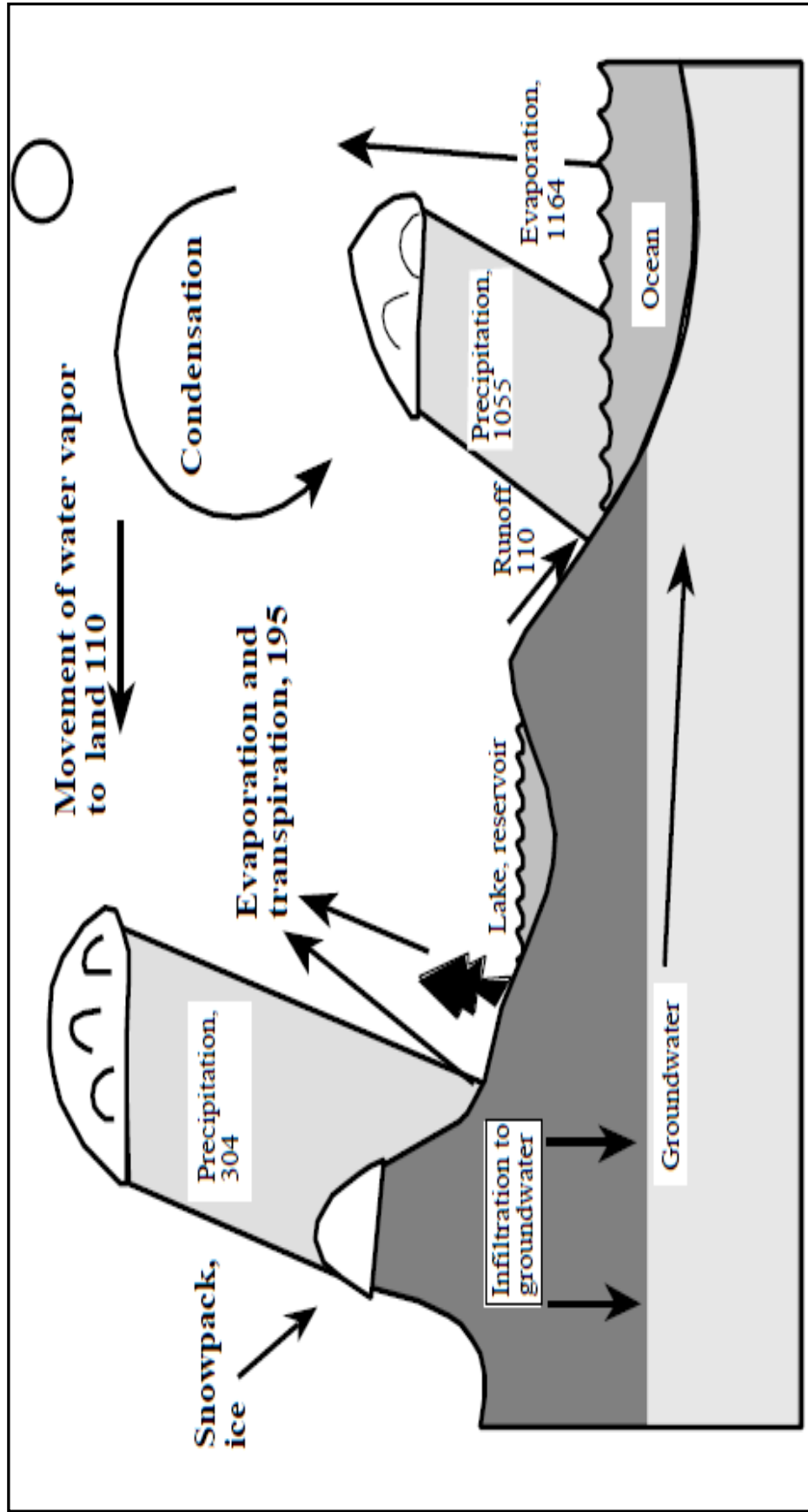


Figure 1.1. The hydrologic cycle, quantities of water in trillions of liters per day (Manahan, 2000).

surface water is found in lakes, streams, and reservoirs, groundwater is located in aquifers in underground. In addition, there is a strong connection between the hydrosphere, where water is found, and the lithosphere, the part of the geosphere easily obtainable to water. Human activities affect both lithosphere and hydrosphere. Humans use water primarily as fresh surface water and groundwater.

1.2. Water Pollution

Water pollution is a contamination of water that affects usefulness of water to humans (Anonymous 3, 2011). Water supply in the earth remains constant but humans have an ability to change the hydrological cycle. Increasing population and living standards, industrial and economic growth damages the natural environment. As a result, man-made activities affect the quality and quantity of natural water sources.

There are many sources of water pollution. These are direct discharges by industry, sewage, leaking underground storage tanks, and landfills. Another source is the pollution from the air which falls to the water. But a major source of pollution comes from nonpoint sources (Calhoun, 2005). It is hard to control because of the seasonality, inherent variability, and multiplicity of origins of this kind of pollution (Spiro and Stigliani, 2003). These nonpoint sources include run-off that contains fertilizers, herbicides, and pesticides from agricultural lands and drainage from paved surfaces and big drains (Calhoun, 2005).

Transfer of pesticides to surface run-off during precipitation or irrigation is a major concern associated with non-point-source pollution. It means that a pesticide can be transported to surface-water bodies (National Academy of Sciences, 2000). This is the reason why pollution of pesticides is important.

1.3. Soil and the Effect on the Water Quality

The geosphere, or solid earth, is that part of the earth which humans live and extract their food, minerals, and fuels. The most important part of the geosphere for life on earth is soil (Manahan, 2000). Soil is a mixture of minerals, organic matter, and water which is capable of supporting plant life on the surface of the earth (Thayer, 1999). It is the receptor of large quantities of pollutants for food production. Materials which are applied to soil like fertilizers and pesticides may cause water and air pollution. As a result, soil is also an important part of the environmental chemical cycles (Manahan, 2000).

Humans use geosphere to increase industrialization and live with increasing population. Therefore, those usages force to protect water sources because of the contamination of mining, agricultural, chemical, and radioactive wastes with surface water and groundwater. After the application to crops, soil may contain enormous quantities of pesticides as an inevitable result. The degradation and fate of these pesticides on soil has an effect on environmental fate of them. The sorption of pesticides by soil, leaching of the pesticide into water are the factors which is related with the water pollution. Adsorption by soil is an important point for pesticide degradation. The degree of adsorption and the speed are influenced by the factors solubility, volatility, charge, polarity, and molecular structure and size (Manahan, 2000).

1.4. Pesticides

Pesticides are any substance or mixture of substances intended for preventing, destroying or controlling any pest (Anonymous 2, 2011). Humans have been used pesticides from the ancient times. The usage of pesticides began before 1000 B.C.

Until the seventh century, humans used sulfur and arsenic as insecticides. In the seventh century, the first natural pesticide, nicotine, was used as an insecticide. Before the middle of the nineteenth century, systematic scientific methods began for agricultural pests. Although synthetic organic pesticides were used in the 1930s, the first manufactured pesticide was DDT. It was also the most widely used single insecticide in the world. In 1940s, the other pesticide type, organophosphorous pesticides were produced. In 1960s, humans attracted attention on the effect of pesticides for the environment and human health (Waxman, 1998). Despite understanding the toxic effects of the pesticides, humans still use pesticides.

Different kinds of pesticides having different chemical nature are currently used for agricultural purposes all over the world (Sankararamakrishan et al., 2005). They are divided into many classes according to target organism, mode of action and chemical structure (Arias-Estévez et al., 2008). The most important classes are organochlorine and organophosphorous compounds (Sankararamakrishan et al., 2005).

1.4.1. Organochlorine Pesticides (OCPs)

Organochlorine pesticides are one of the most persistent organic micropollutants present in water (Dong et al., 2005). They are also classical examples of persistent organic pollutants. Because of OCPs' persistence property, bioaccumulation and having negative effect on humans and wildlife, they have great concern (Zhang et al., 2007).

Organochlorine pesticides have been widely used in agricultural purposes. The usage of pesticide helps to increase crops outputs, improve quality of products and decrease the incidence of illnesses propagated by insects (Pardo and Marañón, 1997; Krauthacker et al., 2001). They are characterized by three kinds of chemicals.

These are DDT analogs, Benzenehexachloride (BHC) isomers, and cyclodiene compounds. DDT is the most persistent one. It is effective in different families of insects and related organisms. BHC is also active against a great variety of pests. Cyclodiene compounds like endosulfan, dieldrin, endrin, chlordane, heptachlor, aldrin, toxaphene are used when contact action and long persistence are needed (Tadeo et al., 2008).

1.4.1.1. Molecular Structure of OCPs and Their Physical and Chemical Properties

One of the criteria for the concentration and type of pesticides found in water samples are the physical and chemical properties of pesticides (Carabias et al., 2003). The chemical structures of the common pesticides are shown in Figure 1.1.

Low solubility in water, high solubility in lipid materials such as animal fat are the common characteristic properties of OCPs. Because of the low solubility in water, they cling to soil particles. Therefore they can dissolve in rainwater very little and then migrate into water bodies or groundwaters. In addition, they have an ability to reach the Arctic with global distillation, because cold climates prevent their degradation (Hill, 2004). The physical and chemical properties of pesticides are shown in Appendix II.

Aldrin and Dieldrin

Aldrin is the most common name for the substance composed of at least 95% of the chemical 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1,4-endo-5,8-dimethanonaphthalene. Dieldrin is a stereoisomer of endrin and it has been typically produced by the epoxidation of aldrin with peracetic or perbenzoic acid. In their “pure” formulations, both aldrin and dieldrin have densities greater than water, and

Table 1.1. Chemical structures of some OCPs

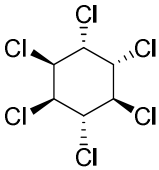
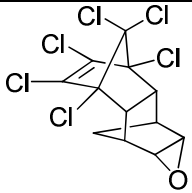
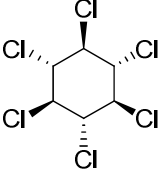
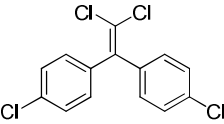
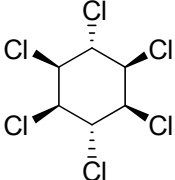
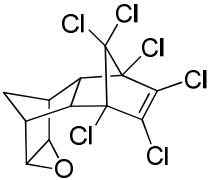
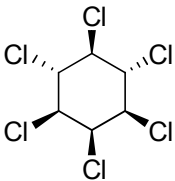
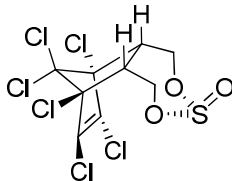
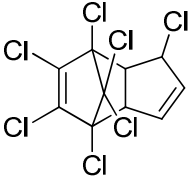
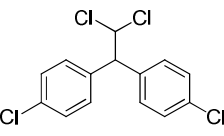
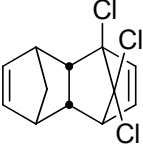
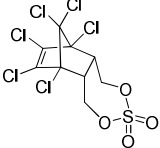
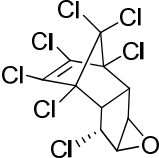
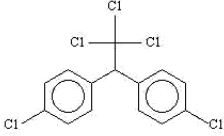
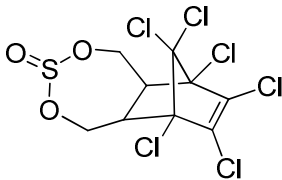
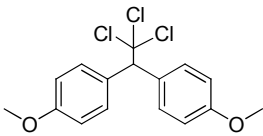
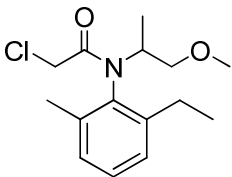
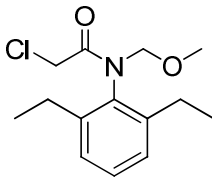
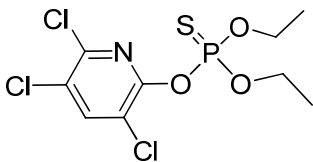
Compound	Chemical structure	Compound	Chemical structure
α -HCH		Dieldrin	
β -HCH		4,4'-DDE	
γ -HCH (Lindane)		Endrin	
δ -HCH		Endosulfan II	
Heptachlor		4,4'-DDD	
Aldrin		Endosulfan sulfate	
Heptachlor- epoxide		4,4'-DDT	

Table 1.1. Chemical structures of some OCPs (continued)

Compound	Chemical structure	Compound	Chemical structure
Endosulfan I		Methoxychlor	
Metolachlor		Alachlor	
Chlorpyrifos			

have both low volatilities and aqueous solubilities. These chemicals are stable in the presence of organic and inorganic alkalines and soft acids. Under most environmental conditions, aldrin is largely converted to more persistent dieldrin by biological and/or abiotic mechanisms. After the application, significant volatilization between aldrin and dieldrin is possible. Dieldrin is extremely apolar and it has a high affinity for organic matter (USEPA, 2003).

Endrin

Endrin is very insoluble in water and has low volatility. Endrin can be transformed by heat to endrin ketone, with small amounts of endrin aldehyde. In turn, endrin aldehyde and endrin ketone react photochemically with hydroxyl radicals in the atmosphere. The half life of endrin aldehyde and endrin ketone is only

a few days (Agency for Toxic Substances and Disease Registry, 1996). Endrin is very insoluble in water; endrin ketone and aldehyde are slightly more soluble than endrin (Office of Environmental Health Hazard Assessment, 1999).

Hexachlorohexane isomers

Hexachlorocyclohexane (HCH) is a name used collectively for the isomers of 1,2,3,4,5,6-hexachlorocyclohexane. It has eight isomers. The most important ones are α -, β -, γ - and δ - isomers (Agency for Toxic Substances and Disease Registry, 1989). β -HCH has a much lower vapor pressure, much higher melting point and bioconcentration factor in human fat (BCF) as compared to the α -isomer. These properties are largely related with the axial and equatorial positions of the chlorine atoms on each molecule. As shown in Table 1.1, all of the chlorines on β -HCH are in the equatorial positions. This position gives the greatest physical and metabolic stability to this isomer and this stability is also seen in the environmental and biological persistence. The δ -isomer has three chlorines in axial positions (Buser and Muller, 1995). It is found that the γ -isomer can be isomerized to the α -form by UV radiation in laboratory studies. However, it has not been proven in environment (Malaiyandi et al., 1984). In general, isomers of HCH are stable to light, high temperatures, hot water, and acid; however, they are dechlorinated by alkaline compounds (Deo et al., 1994). Compared to other organochlorines (such as DDT), HCH isomers are generally more water soluble and volatile, which explain why HCHs are now detected in all environmental compartments including water, sediments, air, and animals (Willett et al., 1998).

4,4' DDT and its Breakdown Products (4,4' DDD and 4,4' DDE)

4,4' Dichloro diphenyl trichloroethane (4,4' DDT) is highly insoluble in water and is soluble in most organic solvents. It is semi-volatile and can be expected to partition into the atmosphere. As a result, its presence is ubiquitous in the environment and residues have even been detected in the Arctic. It is lipophilic and partitions readily into the fat of all living organisms and has been demonstrated to bioconcentrate and biomagnify. The breakdown products of 4,4' DDT, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (4,4' DDD or TDE) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (4,4' DDE), are also present virtually everywhere in the environment and are more persistent than the parent compound (EPA, 1993; EPA, 1998).

Endosulfan and Endosulfan Sulfate

Endosulfan is a chlorinated hydrocarbon insecticide and acaricide of the cyclodiene subgroup. It does not easily dissolve in water, and has a very low solubility. The technical product is a mixture of endosulfan I and II. The two isomers are different from each other related with the exo- and endo-positions of the sulfite group. The chemical name for endosulfan is 6,7,8,9,10,10-hexachloro-1,5,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide (Brooks, 1974; Whetstone, 1972). The vapour pressures of two isomers are similar, while endosulfan sulfate is 4-fold lower. Interestingly, the aqueous solubility of the endosulfan II isomer is markedly higher than the endosulfan I (10-fold). As a result the endosulfan II has a lower Henry's Law constant. Both the endosulfan II and the sulfate are likely to experience relatively higher vapour scavenging from the atmosphere by precipitation than the endosulfan I (Chan et al., 1994).

Heptachlor and Heptachlor Epoxide

Heptachlor is an organochlorine cyclodiene insecticide. It is first isolated from technical chlordane. An important metabolite of heptachlor is heptachlor epoxide. It is an oxidation product formed from heptachlor by many plant, and animal species. It has solubility in water of 0.056 mg/l at 25 to 29°C (Metcalf, 1955). The chemical name for heptachlor is 1,4,5,6,7,8,8- heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene. It is produced by means of a Diels-Alder addition reaction by joining cyclopentadiene to hexachlorocyclopentadiene. Technical grade heptachlor is a mixture of approximately 73 percent heptachlor, 21 percent trans (gamma) chlordane, 5 percent nonachlor, and 1 percent chlordene isomers (Martin, 1972). In general, heptachlor is quite stable to chemical reactions such as dehydrochlorination, autooxidation, and thermal decomposition. However, in the environment, heptachlor decomposes numerous microbial, biochemical, and photochemical reactions (Anonymous 4, 2010).

Methoxychlor

Methoxychlor, 2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane, is a bicyclic aromatic chemical related to DDT. Like other halogenated aromatics, methoxychlor is lipophilic, only slightly soluble in water and is poorly volatile. It binds rather tightly to soil. Because of its short environmental half-life, the slow volatilization and distribution around the globe has been documented (Wania and Mackay, 1996).

Chlorpyrifos

Chlorpyrifos, [0,0-diethyl 0-(3,5,6-trichloro-2-pyridinyl)-phosphorothioate], is a broad-spectrum, chlorinated organophosphate insecticide. It was first registered in 1965. Technical chlorpyrifos is a white crystalline solid. Chlorpyrifos is stable in

neutral and acidic aqueous solutions. However, its stability decreases with increasing pH. Chlorpyrifos is insoluble in water, but is soluble in most organic solvents. It is not particularly volatile. Because it has low vapor pressure. It has a half-life in the field of less than 60 days. Chlorpyrifos appears to degrade slowly in soil under both aerobic and anaerobic conditions. The environmental fate of the major chlorpyrifos degradate, 3,5,6-trichloropyridinol (TCP), indicates that it is mobile in soils and persistent in soils when it is not exposed to light. Like OCPs, chlorpyrifos has been detected in fish tissues and aquatic birds (USEPA, 2002).

Metolachlor

Metolachlor is widely used as a chloracetanilide herbicide. Chemical name is 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide. Technical metolachlor is an odorless and colorless liquid. Metolachlor appears to be stable to hydrolysis for a broad pH range. The aqueous photolysis half-life is estimated as 200 days. It is possible that a majority of the soil-applied metolachlor reaching ground and surface waters through leaching and surface runoff. The soil photolysis half-life of metolachlor with natural sunlight was 8 days. The low soil/water partitioning of metolachlor shows that most of the metolachlor run-off will dissolve in run-off water (Anonymous 5, 2010).

Alachlor

Alachlor is an herbicide. Technical alachlor is a colorless to white crystalline solid with a melting point of 39.5-41.5°C and a specific gravity of 1.133 g.mL⁻¹ at 25°C. At 25°C alachlor is soluble in water at 242 ppm. Alachlor is soluble in ether, acetone, benzene, alcohol, and ethyl acetate, and is slightly soluble in hexane. In an acceptable study, [¹⁴C] Alachlor (carbonyl labeled) applied at 50 ppm was relatively

stable in sterile commercial pH 3, 6, and 9 buffer solutions, natural lake water, and deionized water that were incubated in the dark at 25°C for 30 days. Alachlor has a vapor pressure of 2.2×10^{-5} mm Hg at 25°C. Since this value is relatively low, volatility may not be an important route of dissipation for alachlor (EPA-RED, 1998).

The information about the usage and ban of the OCPs was summarized in Table 1.2 to be used in the next sections for discussion.

Table 1.2. Usage of OCPs and information for ban

Pesticides	Usage	Ban	
		USEPA	Turkey
Aldrin and Dieldrin	Insecticides used on crops such as corn and cotton; also used for termite control.	1987	1979
Lindane	Insecticides used as a seed treatment on six agricultural crops: barley, corn, oats, rye, sorghum, and wheat.	1987	1985
DDT	Insecticide used on agricultural crops, primarily cotton, and insects that carry diseases such as malaria and typhus.	1972	1985
Endrin	Insecticide used on crops such as cotton and grains; also used to control rodents.	1984	1979
Heptachlor	Insecticide used primarily against soil insects and termites. Also used against some crop pests and to combat malaria.	1989	1979
Methoxychlor	Insecticides used to control cockroaches, mosquitoes, flies and chiggers, as well as various arthropods that attack field crops, vegetables, fruits, ornamentals, stored grain, livestock, and domestic pets.	In use	In use
Endosulfan	Insecticides used on squash, eggplant, cantaloupe, sweet potato, broccoli, pears, pumpkins, cotton, cantaloupe, tomatoes and potatoes.	In use	In use

1.4.1.2. Toxicity and Carcinogenicity of OCPs

Organochlorine insecticides are highly lipophilic, well absorbed across intact skin, and capable of inducing hepatic microsomal enzymes. During a poisoning,

organochlorines cause seizures, respiratory failure, and death. Organochlorines can be absorbed from the gut, by the lung and across the skin in varying degrees. Whereas hexachlorocyclohexane, including lindane, the cyclodienes like aldrin, dieldrin, endrin, chlordane, heptachlor and endosulfan are efficiently absorbed across the skin, dermal absorption efficiencies of DDT are substantially less (Echobichon, 1996).

Organophosphorous pesticides generally have an effect in nervous system. They inhibit acetylcholinesterase in the nervous system with subsequent accumulation of toxic levels of acetylcholine (Anonymous 6, 2010). Chlorpyrifos is moderately toxic to humans (USEPA, 1989). Poisoning from chlorpyrifos may damage the central nervous system, the cardiovascular system, and the respiratory system. It is also a skin and eye irritant. Studies in humans suggest that skin absorption of chlorpyrifos is limited (Gallo and Lawryk, 1991). While alachlor is recognized as a Group B-2 carcinogen, as well as a suspected endocrine disrupter; and the toxicities of many of its breakdown products have yet not been clearly established (Graham et al., 2000), metolachlor acts by inhibiting protein synthesis, high-protein crops can be adversely affected by metolachlor applications (Wilkinson, 1981).

1.5. Sources of Pesticides

Pesticides are applied to agricultural crops and special land for the management of those areas for best yield. In agriculture, the pesticides used are determined by the crops grown and the pests related with those crops (Thomas and Wardman, 1999). Long distance aerial deposition of pesticides around the globe can also affect the pesticides pollution in the land (Wania and Mackay, 1993).

Climate is probably the most important factor in determining the types of crops that are grown within a particular location (MAFF, 2000). It also affects the type of pesticide use (Bloomfield et al., 2006). Although many pesticides are involatile or semivolatile, there is a transition from solid phase, sorption on surfaces or aqueous solution to vapour phase. It is dependent on the ambient temperature. Greater volatility allows transporting pesticide away from the place of application. Any difference in ambient temperatures, change the proportion of pesticides in the gas and soil phase. With increasing temperature, the distribution rate of a pesticide also increases. The transport of pesticides which includes evaporation in the region with higher temperature and condensation in the region with lower temperatures is explained by global distillation (Wania and Mackay, 1993).

Increasing atmospheric oxidation rates affect the removal of pesticides. When the atmospheric oxidation rates increase, removal of pesticides oxidation products from the atmosphere to the Earth's surface is more rapid and the effective transport distance decreases from the sources.

1.6. Chemical Fate and Transport of Pesticides

When a pesticide is used in the environment, it distributes between water, air, soil and biota (living organism). Figure 1.2 summarizes partitioning between these major compartments. The fraction of the chemical that moves into each compartment is also governed by the physico-chemical properties of that chemical.

Pesticides can distribute in the environment by physical processes such as sedimentation, adsorption, and volatilization. After these processes, they can be degraded by chemical and/or biological processes. Chemical processes generally

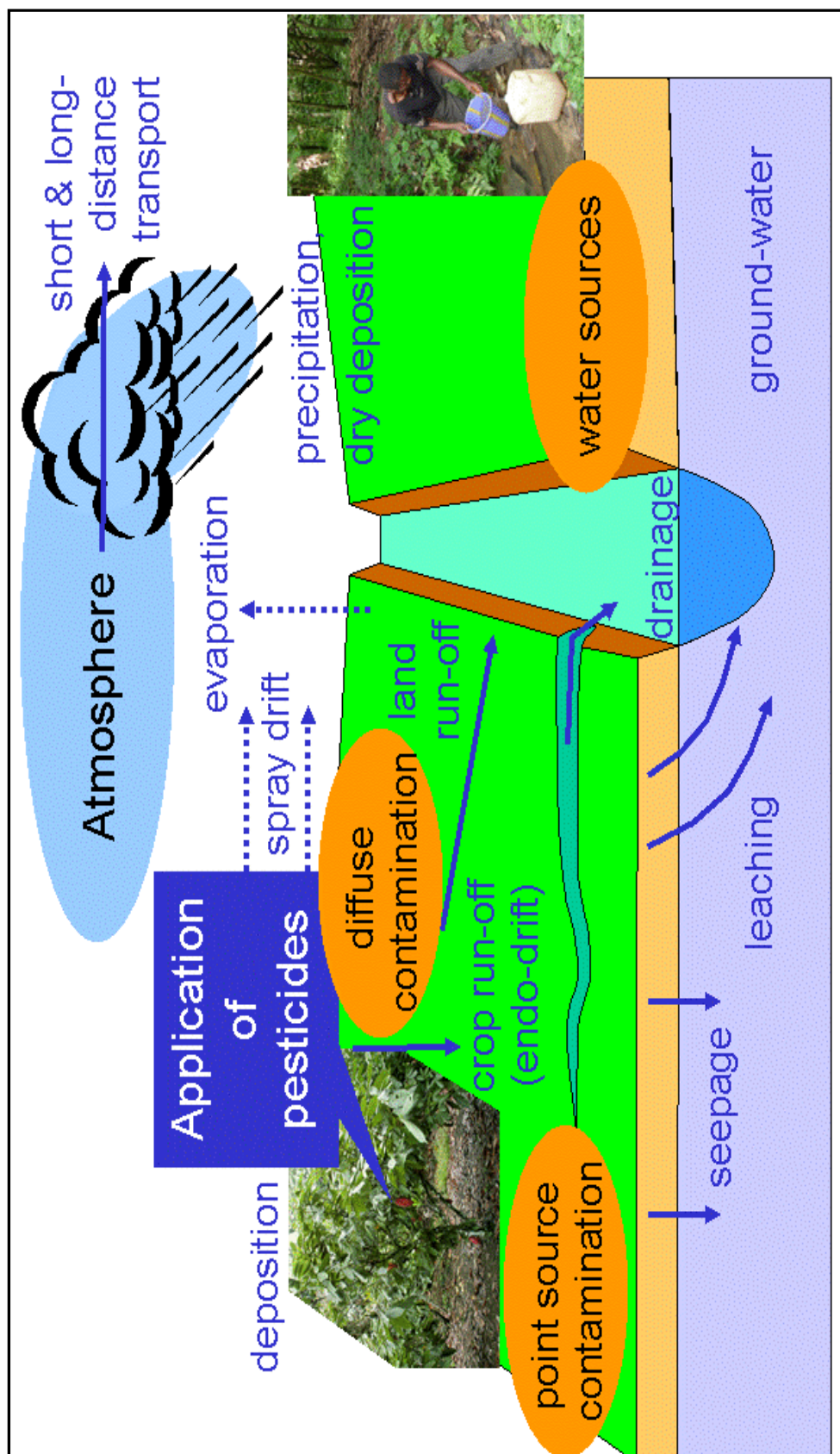


Figure 1.2. Environmental fate of pesticides (Anonymous 7, 2010)

occur in water or the atmosphere. Degradation process is governed by the compartment in which the pesticide is distributed. This physical and chemical process depends on the physico-chemical properties of individual compounds. These are solubility, octanol/ water partition coefficient (K_{ow}), hydrolysis, soil adsorption coefficient (K_{oc}/K_d), bioconcentration factor (BCF), Vapor Pressure (P_{vp}), Henry's Law Constant (H'), volatilization, photolysis and microbial metabolism (Linde, 1994). After application, pesticide may be lost from the soil, water, and air system to atmosphere in two stages. Pesticide residues in the soil or on the crop and these molecules dissipate into the atmosphere by diffusion and turbulent mixing (Taylor, 1995). Volatilization losses can change from a few percent to 50% of applied dose (van den Berg et al., 1999). These losses also depend on properties of pesticides. Remaining part in the soil will be partitioned between the soil and soil water. The ratio of the concentration in the soil to the concentration in the water is called the soil sorption coefficient (Bloomfield et al., 2006).

A pesticide is changed into a different compound by transformation processes. These compounds often refer to degradation product or metabolite. This transformation can occur due to different processes such as oxidation, hydrolysis, photolysis and biodegradation. Generally, biodegradation is the most important transformation process in soil (Bloomfield et al., 2006).

1.7. Methods and Analysis of Samples, Theory of Instruments

Studies which determine OCPs in environmental matrices often deal with sample containing low analyte concentrations and a high number of interferent compounds. Thus, simple and highly sensitive and selective analytical methods are required (Dong et al., 2005).

1.7.1. Extraction

The main aim of any extraction process is to isolate the analytes which are to be determined from the selected sample by using an appropriate solutions (Tadeo, 2008). It helps to convert the analyte into a suitable form for the detection, to remove the interferences from the sample, and to increase the concentration of the sample (Smith, 2003). Generally, a liquid extract has been obtained and it needs a cleanup step (Tadeo, 2008). This step is usually performed by SPE because of the less contamination (Dong et al., 2005).

1.7.1.1. Solid Phase Extraction

Solid phase extraction (SPE) is a fast preparation method that occurs in a syringe filled with a solid. Before the analysis of GC and HPLC, it helps to obtain purer analyte and extract an analyte from the matrix. There are two main formats of SPE materials. These are a cartridge and a disk format.

SPE is increasingly useful sample preparation technique. With SPE, solvent use and laboratory time are decreased. It is used most often to prepare liquid samples and extract semivolatile or nonvolatile analytes. They are available in a wide variety of adsorbents, and sizes. Selecting the most suitable products for each application and sample is important.

After the selection of the proper SPE cartridge or disk, the procedure includes conditioning, adsorption, washing and elution step. Before the addition of the sample, conditioning process should be done to remove any impurities on the SPE cartridge. The cartridge should be prevented from drying. Sample is loaded to a cartridge and when it is finished the loaded one is washed with a suitable solvent again to remove unwanted, weakly retained materials. Lastly, the compounds of

interests are eluted from SPE cartridges. This procedure is shown in Figure 1.3 (Supelco technical resources, 1998).

1.7.1.1.1. Properties of SPE Sorbents

After the selection of suitable SPE sorbent, some compounds can be hold in the cartridge because of the adsorption property of the sorbent (Figure 1.4). Selected components are hold by the sorbent while the sample passes through the tube. If there is any impurities hold by the tube, it should be washed with solutions which are strong enough to remove this impurities but weak enough to affect the compounds of interests. Lastly, adsorbed compounds are eluted by a solvent which is strong enough to remove from the tube (Supelco technical resources, 1998).

1.7.1.2. Ultrasonic Extraction

One of the techniques which is fast and simplify sample treatment is ultrasonic extraction. When ultrasonic energy imparts to solutions, it causes acoustic cavitation like bubble formation and subsequent implosion (Suslick et al., 1999; Suslick et al., 1988; Hua and Haufman, 1997). A collision of bubbles created by the sonication of solutions create extremely high local temperature and pressure gradients in the generation. This can be called as hot spots. On a timescale of about 10^{-10} s, effective local pressures and energies of about 105 atm and about 1 eV, respectively, are generated under sonochemical conditions (Suslick et al., 1999). Sonication can also help for preparing samples directly within the sample container. Therefore, it prevents sample losses and minimizes the likelihood of sample contamination (Demange et al., 1990).

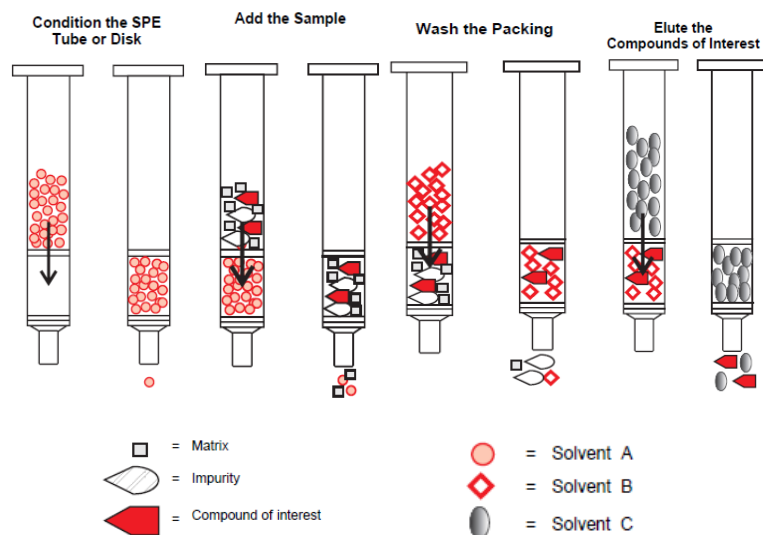
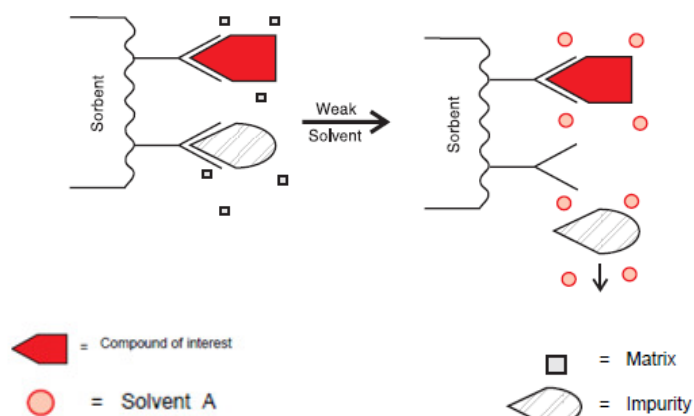
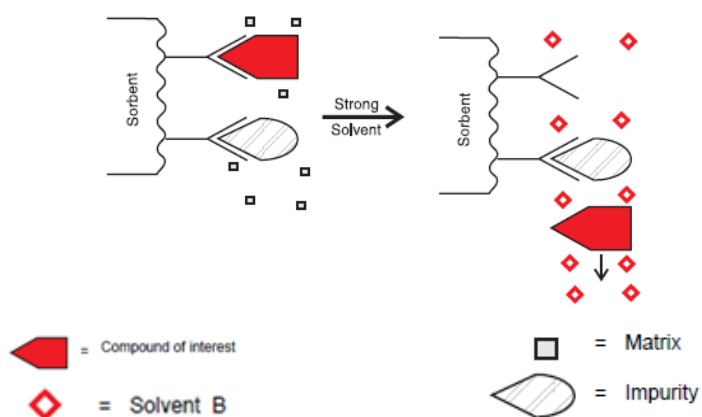


Figure 1.3. The application of SPE in a cartridge (Supelco technical resources,1998).



Selection of washing



Selection of elution

Figure 1.4. Properties of sorbent (Supelco technical resources, 1998)

1.7.2. Chromatography

Chromatography is a technique for separating components of a mixture based on partitioning difference between stationary and mobile phase. While the stationary phase is fixed in a place like column or planar, mobile phase moves over or through the stationary phase. Chromatographic methods fall into three categories based on the mobile phase. These are gas, liquid and supercritical fluid chromatography.

1.7.2.1. Gas Chromatography

One of the most widely used techniques for qualitative and quantitative analysis is gas chromatography (GC) (Figure 1.5) (Skoog, 1996). After the preparation of samples of mixtures of volatile liquids such as the components of a petroleum oil fraction, mixed products of an organic synthesis procedure, lipid mixtures, etc., this sample is injected on the GC column with a syringe for separation and detection of analyte components. The mobile phase gas, called the carrier gas, is also introduced to the head of the column into an unpacked open space. The mobile phase is usually nitrogen, helium, or hydrogen and does not have significant interactions with analyte molecules. When the liquid mixture is injected, vaporized at the elevated oven temperature, and is swept along by the carrier gas. Its components subsequently are progressed more slowly, at different rates along the packed portion of the column, and the chromatographic separation is ensured. Lastly, a simple detector at the end of the column is produced a signal proportional to the amount of analyte in each eluting peak. Related with the electrical current, GC produces an electrical signal which gives a chromatogram. The GC detectors are often classified on the basis of their selectivity. Universal detectors respond to every component, and selective detectors to a group of compounds with similar characteristics.

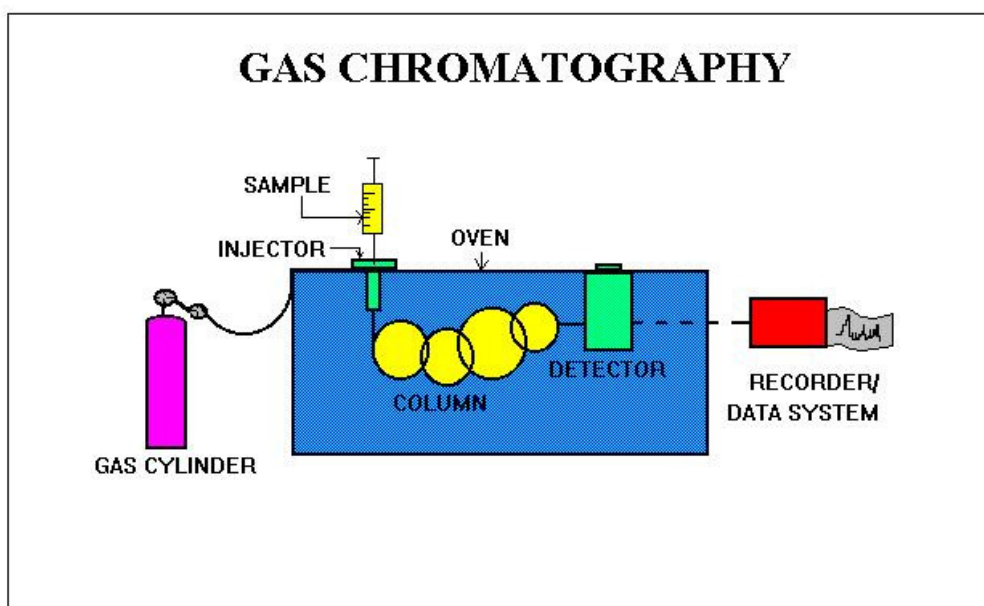


Figure 1.5. Gas Chromatography (Anonymous 8, 2010).

1.7.2.2. Electron Capture Detector (ECD)

The electron-capture detector (ECD) was the first selective detector. It is widely used for organochlorine pesticides. The principle of this detector is based on the reduction in conductivity (Figure 1.6).

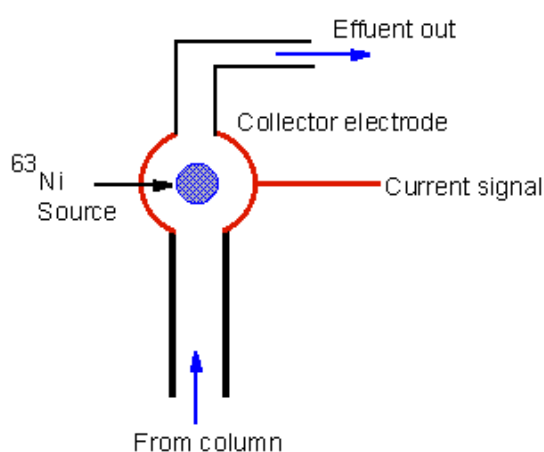


Figure 1.6. Schematic for an ECD (Anonymous 9, 2010)

The ECD selectively responds to halogen-containing compounds like pesticides. Therefore, it has become one of the most widely used detectors for environmental samples. In this detector, the sample is swept from the column is passed over a radioactive β -emitter. An electron from the emitter causes ionization of carrier gas and it produces a burst of electrons. The current decreases in the presence of organic molecules which contain electronegative functional groups, compounds such as halogens, peroxides, quionones, and nitro groups (Skoog, 1996).

Modern ECDs use ^{63}Ni sources. Because of its stability, this detector can be used at temperatures up to 400°C . In addition it can provide a linear range over a factor of 103. The sensitivity of the detector is lower for low halogenation levels, and it is not suitable for monochloro compounds. This detector is suitable for drinking water and ground water. However, when more complex matrices, such as surface water extracts, are injected, many organic compounds can interfere with ECDs response and they affect the selectivity of the detector.

1.8. Mapping

Geostatistics helps advanced methodology for quantifying the spatial distribution of pollution and its associated uncertainty in pollution assessments. These techniques widely used by environmental scientists to characterize contaminated sites.

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1.9. Objectives of the Study

The aims of this study are:

- to determine the pesticides in ground and surface water samples and in soil collected from the City center, Mudurnu, Göynük, Seben, Kıbrısık in Bolu,
- to study the general pattern of total organochlorine pesticide concentrations, together with their occurrences in Bolu surface and ground water and soil samples,
- to determine the levels of pesticide pollution in the region and to prepare the pollution maps,
- to study the seasonal trends in pesticide pollution.

CHAPTER 2

LITERATURE SURVEY

In the literature, pesticide studies involve the general information about the pesticide transformation, characterization, toxicity, environmental fate. In this study, the journal articles about the determination of OCPs in water samples and in soil samples from the different part of the world and Turkey will be summarized.

2.1. Literature Survey about the Water

2.1.1. Literature Survey around the World

2.1.1.1. Literature Survey Related with Europe

Every year over 200,000 tonnes of pesticides are released into the European environment. Unfortunately, the EU's use of insecticides has more doubled over the past decade. All of the EU's top 10 insecticides are described as hazardous by the World Health Organisation (WHO) (Anonymous 10, 2010). Those pesticides can also contaminate important water resources. According to a recent study, pesticide contamination in lowland river areas of Belgium, France, Netherlands and the UK is the most acute. In Germany, Denmark and the Netherlands pesticide pollution which is high from legal limits affects up to 10% of all groundwater resources (Anonymous 11, 2010).

In a study made in Portugal, pesticides used in agricultural areas were determined in surface and ground water samples. Whileas the surface water samples collected in three river basins from 1983 to 1999, the ground water samples collected from the wells of seven agricultural areas from 1991 to 1998. Samples were collected into 1 L amber bottle. Totally 27 pesticides were looked in water samples including lindane, α -BHC, β -BHC, δ -BHC, hexachlorobenzene, heptachlor, heptachlor epoxide, aldrin, p,p'-DDE, p,p'-DDD, endrin, dieldrin, endosulfan I and II. Different extraction methods were used like liquid-liquid extraction, solid phase microextraction, solid phase extraction. In addition different identification methods were used such as GC-ECD for OCPs, GC with γ -Nitrogen Phosphorous Detector (NPD) for organophosphorous pesticides (OPs) and high pressure liquid chromatography/ diode array dedector (HPLC- DAD) for chlorinated acid herbicides. The monitored pesticides for surface water samples were atrazine, chlorfenvinphos, endosulfan I and II, lindane, molinate and simazine. For each compound, the maximum values were 0.63, 31.6, 0.18, 0.18, 0.24, 48 and 0.3 $\mu\text{g L}^{-1}$, respectively. The pesticides used in agricultural area were monitored only for ground water samples. Those were alachlor, atrazine, metalochlor, metribuzine and simazine. Identification of pesticides was done with GC-NPD. The maximum concentration values were 13, 30, 56, 1.4 and 0.4 $\mu\text{g L}^{-1}$ respectively (Cerejeira et al., 2003).

In Spain, a total number of 44 substances were found in waters of the Ebro river basin. Most of the pesticide sampling points are located in the sections of this river and it can transport run-off waters from various agricultural areas shortly before opening out onto the main river (the Ebro). Surface water samples were prepared for the analysis with a solid-liquid extraction. Then, analysis was done with gas

chromatography/mass spectrometry (GC-MS). Pesticides most frequently found and having greater concentrations in the waters of the Ebro river basin were 3, 4-dichloroaniline, molinate, desethylatrazine, dimetoate, simazine, atrazine, metolachlor and chlorpyrifos. The other compounds such as 4-isopropylaniline, ametryn, β -HCH, δ -HCH, aldrin, isodrin, dieldrin, heptachlor epoxide, endosulfan and endosulfan-sulfate were not detected or their concentrations were below the quantification limit (Claver et al., 2006).

147 compounds in surface river waters from northeastern Greece near Greek/Bulgarian/Turkish borders were monitored during 1999–2007 by Vryzas et al., (2009). Eight sampling points were determined along the rivers Ardas, Evros and Erythropotamos based on agricultural usage. Totally, 88 sampling were done from 1999 to 2007. Pesticides were extracted by solid-phase extraction (SPE) and analyzed by gas chromatography–mass spectrometry (GC–MS) using a multiresidue in-house analytical method. The 28 compounds (pesticides, metabolites and caffeine) applied to Greece soil was detected in surface waters of northeastern Greece. High pesticide concentrations were detected within 2 months of their application. In addition, in the beginning of the irrigation season or just after high rainfall events extreme pesticide concentrations were detected. Generally, low levels of pesticide residues were found in the Greek/Bulgarian borders of all rivers. However, o',p'-DDT, o',p'-DDE and γ -HCH were mainly detected in this sampling point regarded as crossboundary contamination (Vryzas et al., 2009).

2.1.1.2. Literature Survey Related with America

Generally, pesticides are used for agriculture purposes in USA. Usage of pesticides in agriculture is greater over five times the amount used by industry and

government, and nearly seven times that applied to lawns and gardens. (Anonymous 12, 2010).

Samples collected from rural and urban streams in the City of Denton, Texas, USA. Those water samples were analyzed for the organophosphorus pesticides diazinon and chlorpyrifos. Monitoring stations were selected and samples were collected monthly from March through August. Totally, 308 samples and 311 samples collected during 2001 and 2002, respectively. Concentrations of pesticides were determined using commercially available enzyme-linked immunosorbent assays (ELISA) specific for each pesticide. The difference in concentration after the ban of chlorpyrifos was determined. The concentrations of chlorpyrifos were significantly decreased when comparing the before the ban and after the ban. This indicated that the contamination of chlorpyrifos will decrease after the ban during 2002 (Banks et al., 2005).

Argentina is a main area of soybean production. In a study located nearby soybean fields, chlorpyrifos, cypermethrin and endosulfan concentration were determined in sediments, suspended particles and water. Water samples were prepared with SPE. Analysis of water samples was done with GC-ECD and gas chromatography-flame photometric dedector. Suspended particles, runoff sediment and bottom sediment samples were extracted twice with methanol in an ultrasonic bath and then passed through C₁₈ columns by using SPE system. Highest concentrations in suspended particles were 318 $\mu\text{g kg}^{-1}$ for endosulfan in the stream Horqueta, while 226 $\mu\text{g kg}^{-1}$ chlorpyrifos and 13.2 $\mu\text{g kg}^{-1}$ cypermethrin were measured in the stream Brown. In the Horqueta stream 150 and 53 $\mu\text{g kg}^{-1}$ chlorpyrifos and cypermethrin were detected in runoff sediments, respectively. For water, the highest chlorpyrifos concentration in floodwater was 0.45 $\mu\text{g L}^{-1}$ in Brown

stream. However, endosulfan was not detected in the water phase. In runoff water the highest concentrations measured were $0.3 \mu\text{g L}^{-1}$ for chlorpyrifos in Horqueta stream and $0.49 \mu\text{g L}^{-1}$ for cypermethrin in the Brown stream (Jergentz et al., 2005).

2.1.1.3. Literature Survey Related with Asia

In 1997, Food and Fertilizer Technology Center (FFTC) and the Asian Productivity Organization (APO) prepared a regional survey of the production and use of agricultural chemicals in the region. The results showed changes in patterns of pesticide use in recent decades. This means that chemical use in Asian countries may still be immature. For this reason, there is a need for pesticides data. In addition, technical grade pesticides are produced in Japan and India. Korea and Taiwan also produce technical grades. The other countries in the region import technical grades and apply them locally into required formulations (Anonymous 13, 2010).

In a study, for screening 31 pesticides (α -HCH, β -HCH, γ -HCH, δ -HCH, hexachlorobenzene (HCB), aldrin, heptachlor, endosulfan I and II, p,p'-DDD, o,p'-DDT, p,p'-DDT, p,p'-DDE, endrin aldehyde, endosulfan sulphate, methoxychlor, heptachlor epoxide, α -chlordane, γ -chlordane, dieldrin, endrin, dicofol, acetochlor, alachlor, metolachlor, chlorpyrifos, nitrofen, trifluralin, cypermethrin, fenvalerate, deltamethrin) which are potential or suspected endocrine disrupting, water and surface sediments samples were collected. Thirty one pesticides in water and surface sediment samples from Beijing Guanting reservoir were analyzed. To prepare samples for the analysis SPE technology was used. A multiresidue analysis method based on gas chromatography with electron capture detection (GC/ECD) was developed. The relevant mean recoveries were 70–103% for water and sediment, respectively. Relative standard deviations (RSD) are 2.0, 7.0%, for water and sediment, respectively. Concentrations of pesticides ranged from 48.8 to 890 ng L^{-1}

for water samples, with a mean of total pesticides concentration 295 ng L^{-1} in water. The highest concentration was observed for o,p'-DDT in water (161 ng L^{-1}) and in sediment (9610 pg g^{-1}). These results showed the need to improved environmental protection measures (Xue et al., 2005).

In a survey undertaken in Kanpur, northern India, the presence of high concentrations of both organochlorine and organophosphorous pesticides in the surface and ground water samples were found. In this study, pesticides determined with liquid–liquid extraction followed by GC-ECD technique. Surface water samples were collected from the River Ganges in Kanpur and high concentrations of γ -HCH ($0.259 \text{ } \mu\text{g L}^{-1}$) and malathion ($2.618 \text{ } \mu\text{g L}^{-1}$) were detected. In the ground water samples collected from agricultural and industrial areas, γ -HCH and malathion, dieldrin were detected. The maximum concentration values of γ -HCH, malathion and dieldrin were 0.900 , 29.835 and $16.227 \text{ } \mu\text{g L}^{-1}$, respectively. The concentration of malathion was found higher than water quality standards in the groundwater samples from industrial area. Pesticides like DDE, DDT, aldrin, ethion, methyl parathion and endosulfan were not detected in both the surface and groundwater samples (Sankararamakrishnan et al., 2005).

The Pearl River Delta (PRD) is an rapid industrialization and urbanization and also agricultural area in China. Water samples were collected from eight major riverine runoff outlets of the Pearl River Delta (PRD). The concentrations of 21 OCP components and sum of 20 PCB congeners were determined by using GC-MS. There was a possibility of new input sources in the study area because of the compositional distributions of DDTs. Total OCPs concentration was in the range $2.57\text{--}41.2 \text{ ng L}^{-1}$. In general, the levels of DDTs and HCHs were at the high end of the global range. When a comparison was made between the annual inputs and total

usage in this agricultural area, riverine runoff is the major mode carrying OCPs from the PRD to the coastal ocean following open seas (Guan et al., 2009).

2.1.2. Literature Survey Related with Turkey

Pesticide usage is low in Turkey if a comparison is made with developed countries in unit area. Whileas pesticide usage per hectare in France, Germany, Italy, Holland, Greece and Belgium is 4.4, 7.6, 17.5, 6 and 10.7 kg, respectively, pesticide usage per hectare is 0.63 kg in Turkey (Tanrıvermiş, 2000).

In a study of Küçük Menderes River in Turkey, OCPs and metals in surface water were determined. The extraction of water sample was done with separatory funnel and analysis of prepared samples was determined with GC-ECD. The results showed that Küçük Menderes River was still polluted with organochlorine pesticide like DDT which is banned over a long time. The concentrations of pesticides depended on the sampling season and the tendency was not the same for all detected pesticides. The DDTs (DDT, DDD, DDE) were detected in most water samples. DDD showed a high concentration among DDTs. Heptachlor epoxide had the highest concentration among organochlorine pesticides with a value of 281 ng L⁻¹. Fortunately, the concentrations were lower than most polluted water from other sources in the world (Turgut, 2003).

Some water pollution studies include pesticides pollution. For example, in a study in Sarıyar Dam Lake, the OCPs pollution was determined. Besides water samples, sediments samples were also collected. The analysis was done with GC-ECD. The concentration of p,p'-DDT was the highest concentration. In the samples of different locations, the pesticides found in water samples were o,p'-DDD, p,p'-DDT, and α -BHC. Aldrin and dieldrin were not detected (Ozmen et al., 2008).

Concentrations of 17 organochlorine and 14 organophosphorus pesticides were measured in 27 ground and 11 surface water samples collected from a heavily agricultural area, Kumluca, in spring and fall seasons of 2005. The extraction process was performed by using solid phase extraction. GC-ECD and GC-NPD systems were used for determination of organochlorine and organophosphorus pesticides, respectively. The quality check/quality assurance tests were performed and the uncertainties of measurement were calculated. The percent recoveries were changing between 61% and 100%. The most commonly observed pesticide was endosulfan and chlorpyrifos for organophosphorus and organochlorine pesticides, respectively. The highest average concentration was observed for heptachlor and fenamiphos. Generally pesticides were detected more often in surface waters, where the concentrations were also higher. The concentrations of organophosphorus pesticides in spring, and organochlorine pesticides in fall season were higher. The legal limit for a single pesticide (100 ng/L) was exceeded by 32 % of surface, 24 % of ground water samples (Öztaş, 2008).

2.2. Literature Survey about the Soil

2.2.1. Literature Survey around the World

2.2.1.1. Literature Survey Related with Europe

In a study was done in Czech borders with Poland, Germany and Slovakia. Five soil samples were taken from industrial area and five soils were sampled from the background site Kosětice. All soil samples were air-dried, and the content of organic carbon was determined. The pesticides other than DDTs and HCHs were analysed. Since the amounts of these pesticides applied in the Central European countries were generally low, and some of them were never used in this region, the

sampling sites were selected with the goal of evaluating the role of the long-range transport in the pesticide residue distribution. Although there is no evidence for the application in the Czech Republic, a long-range transport from neighbour countries affected from the mountain soils. Aldrin were not determined but dieldrin, the transformed form of aldrin and used in Czech Republic, was seen in the all mountain soils. In addition, heptachlor epoxide, γ -chlordane, α -chlordane, endrin and methoxychlor were detected in soil samples (Shegunova et al., 2007).

In another study which was done in Swiss horticultural fields, OCPs were detected in 27 fields of totally 41 fields (65.9%). The farming practice didn't have any effect on the contamination or level of OCP in soil. The sum of OCP-loads per field ranged from <0.01 to 1.3 mg kg^{-1} dry soil. Dieldrin (0.4 mg kg^{-1}) were the most detected pesticides over all investigated soils. PCA, dieldrin, α -chlordane and heptachloroepoxide were detected in five cucumber samples out of 41 *Cucurbitaceae* samples. Moreover, soil organic carbon, texture, and pH were measured. Statistical analysis was done and any significant influence of measured soil properties on the OCP-load of soils and cucumbers was not found, although there is evidence that the bioavailability of OCP in soils to *Cucurbitaceae* plants was influenced by the sorption of the compounds to soil organic matter and by the polarity of the pesticide molecules (Hilber et al., 2008).

In Romania, some selected persistent organic pollutants like polychlorinated biphenyls, DDT and its metabolites and HCH isomers were determined in soil, animal fat taken from chicken, pork, sheep and turkey and human serum samples. The samples were collected from rural, urban, industrial and waste sites. Soil samples from Iassy district showed a lower contamination with OCPs than samples from other Romanian regions. The DDTs concentrations in soil were significantly

higher at rural sites (in an average value 226.9 ng g^{-1}). However only few samples from 47 samples exceeded the legal Romanian norms for DDTs. In addition, animal fat samples showed high concentration organochlorine pesticides in Iassy. HCHs concentrations reached to 12370 ng g^{-1} fat in animal fat samples in which two samples from 24 exceeded the EU norms (1000 ng/g fat) for HCHs and DDTs in animal fat. OCPs were found in higher concentrations in some samples of human serum from Timisoara due to a broader age range. However, samples of human serum from Iassy mothers also showed higher HCHs and DDTs concentrations than samples from a similar group from Antwerp, Belgium. Romanian samples showed a higher ratio DDT/ Σ DDTs (Covaci et al., 2001)

2.2.1.2. Literature Survey Related with America

In a study performed in Argentina, pesticides were analyzed in different horizons of natural and horticultural soils, developed in highlands and lowlands. Physical and chemical characteristics (organic matter content, pH, moisture, texture, etc.) were determined. For analysis, GC- ECD was used. Soil samples which include high content of clay material and organic matter contained higher concentrations of total OCPs. Lindane, heptachlor, aldrin, DDT and metabolites were found in soils. Different behaviours were found by using physical and chemical characteristics of pesticides and soils. Lindane could leach lower horizons which is rich in clays. However, hydrophobic pesticides remain in the upper horizons where pesticides are retained by organic matter (Miglioranza et al., 1999).

Detailed analyses of persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs), congeners of polychlorinated biphenyls (PCBs) in soil and surface water from the northeastern São Paulo, Brazil was done by Rissato et al. (2006). This evaluation helped to determine contamination status, distribution and

possible pollution sources. The pesticides and PCBs demonstrated markedly different distributions, reflecting different agricultural, domestic and industrial usage in each region studied. The ranges of HCH, DDT, and PCBs concentrations in the soil samples were 0.05–0.92, 0.12–11.01, 0.02–0.25 ng g⁻¹ dry wt, respectively. High values of DDT were found in a site which is very close to agricultural practice regions. High ratios of metabolites of DDT to DDT isomers revealed the recent use of DDT in this environment. The sources of contamination were closely related to human activities, such as domestic and industrial discharge, street run-off, agricultural pesticides and soil erosion, due to deforestation as well as atmospheric transport (Rissato et al., 2006).

2.2.1.3. Literature Survey Related with Asia

The OCP residues in the vegetable fields that have been converted from paddy fields were investigated in Yixing city, Jiangsu province, China. Significant residues of DDTs and HCHs were found in these field after the usage of the pesticides have been banned since 1983. The subsoil and top soil samples was collected. There was not a significant difference for the OCPs residues between soil levels. On the other hand, there was a influence between the soil organic carbon and OCPs which affecting the residues of OCPs (Hao et al., 2008).

Another study was done in South Korea. The soils collected from the agricultural and industrial sides and were monitored for the 18 types of OCPs. The main pesticides found were γ and δ -HCH, heptachlor epoxide and dieldrin. The highest values were found in soils collected from the rice fields (Kim and Smith, 2001).

The methods of simultaneous extraction of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) from soils using different extraction

methods were established by Wang et al. (2007) and the extraction efficiencies was compared by using three methods (Soxhlet extraction, microwave-assisted extraction (MAE) and accelerated solvent extraction (ASE)). Moreover, soils with different total organic carbon contents were used to test the extraction efficiencies of the three methods. The results showed that the values obtained in this study were comparable with the values reported by other studies. In some respects such as method recovery and reproducibility, there were no significant differences among the three methods for the extraction of PAHs and OCPs (Wang et al., 2007).

2.2.2. Literature Survey Related with Turkey

In Izmir, soil and atmospheric concentrations of OCPs were investigated at an industrial site. Totally seven soil samples collected in summer and winter season. In addition, 48 soil samples from different region was collected. These samples ultrasonically extracted. γ -HCH, α -CHL, γ -CHL, trans-nonachlor, endosulfan-I, endosulfan-II, endosulfan sulfate, p,p'-DDT, p,p'-DDD, and p,p'-DDE were the most frequently detected. Endrin aldehyde, endrin ketone, and methoxychlor were not detected in any of the soil samples (Bozlaker et al., 2009).

In a study, OCPs was conducted to determine various environments such as waters, sediments and soils and in organisms. The sampling point was Göksu Delta, Tasucu. According to results, 13 different OC pesticide and their residues was found various environments and organisms. Moreover, OCP concentrations in soils taken from the agricultural areas higher than water and sediments (ranging from 0.006 ppm β -BHC in water to 5.416 ppm pp' DDE in agricultural soil) (Ayas et al., 1997).

In a study performed in city center, Bolu, 29 soil samples were collected and ultrasonically extracted with GC-ECD. The analysis of samples was done The surface layer concentration of total OCPs in all soil samples ranged from under the

detection limit. Endosulfan sulfate, methoxychlor, endrin, and β -HCH were mostly existed in soil samples. Endosulfan sulfate had the highest arithmetic mean (1.49 ng g^{-1}). The lowest concentration belonged to endosulfan I (0.353 ng g^{-1}). The eleven OCPs (β -HCH, 4, 4' -DDD, 4,4 '-DDE, endosulfan II endosulfan sulfate, endosulfan I, endrin, endrin aldehyde, endrin ketone, heptachloroepoxide, methoxychlor) were determined in summer while eight OCPs (β -HCH, endrin, endosulfan II, 4,4 '-DDE, endrin aldehyde, endosulfan sulfate, endrin ketone, methoxychlor) were determined in winter. Endosulfan sulfate had the highest values among its parents in both seasons while endosulfan I had the lowest in summer and not detected in winter. The observation percentage of the endrin was high in winter with a very low concentration. However the percent observation of endrin was higher in summer.

CHAPTER 3

EXPERIMENTAL STUDY

3.1. General Information about Bolu

Bolu is a city in the western Black Sea Region surrounded by Zonguldak, Karabük, Çankırı, Ankara, Bilecik, Eskişehir, Düzce and Sakarya. It has 9 districts and 511 villages. It is between the 30° 32' and 32° 36' east longitudes; and 40° 06' and 41° 01' north latitudes. The city has an average 1000 m altitude while the city center has a 725 m altitude. The total area of that city is 845.800 hectare. 149.664 hectare of this area is used for agriculture. Approximately 55% of the total area is covered with forests and mountains. The area used for the agriculture is 17.7% of the total area. Despite the small agricultural area usage, this city is important in agriculture for Turkey (DPT, 2002).

Bolu is located between İstanbul and Ankara, two important industrilized areas. There are lots of plain and lakes between these mountains related with the latitudes. Considering the total population, this city is 62nd city in Turkey (DPT, 2002).

Center of this city is located on the biggest plain of the Bolu, Bolu Plain. Total size of the plain 12.175 hectare with the latitudes of 730 metres. The other plains in the Bolu are Gerede- Dörtdivan and Göynük- Himmetoğlu plains with the

latitudes of 1300 and 600 m, respectively. There are lots of rain, stream and slope in these areas. This is the reason why Bolu has lots of small and big lakes. Abant, Yeniçağa, Çubuk, Karagöl, Karamurat, Sünnet, Gölcük, Aladağ Lakes and Gölköy Dam Lake are the important water sources. Climate of the city is similar to Black Sea region and generally is warm in summer, cold in winter and rainy in all seasons. In this study, water samples were collected from five distincts (the city center, Göynük, Kıbrısık, Mudurnu, Seben) of Bolu (Figure 3.1).

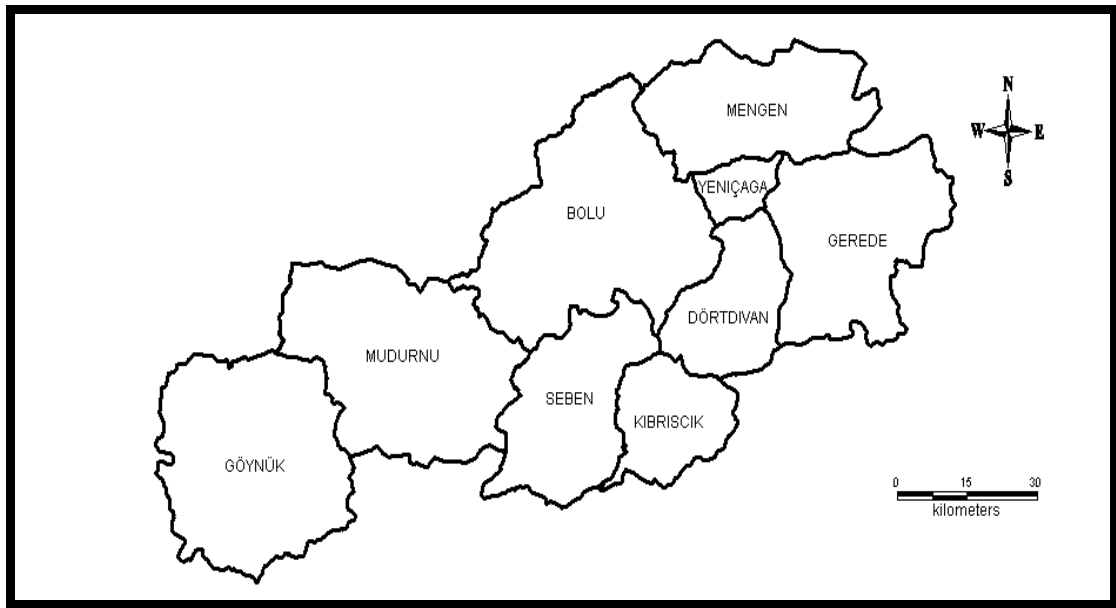


Figure 3.1. The map of Bolu

The most important agricultural products are wheat, barley, corn, oat, rice as cereals, potato, sugar beet and sugar beet seed as industrial plants. The sunflower plants can also be produced in some part of the city. There is little fruit and vegetable production. The common fruit is an apple which is grown in Seben district. Vegetables are the secondary products for the people's own needs. Related with this products endosulfan and chlorpyrifos are the most used pesticides in the study area. Endosulfan is applied into water and soil by mixing before planting and chlorpyrifos is applied to plant root after or before watering. Therefore it may contaminate with

soil and groundwater. The pesticides applied in two seasons. These are spring and autumn seasons.

3.2 Sampling Strategy

The map of Bolu was divided into 10x10 grids (Figure 3.2). If it was possible the water samples were collected from each grids in the five district of Bolu (the city center, Mudurnu, Seben, Göynük and Kıbrısık). It was planned to take 1-3 samples from every grids.

Two sampling periods were chosen to collect the samples for pesticide analysis, namely summer (June) and autumn (October). In the spring period, there is an increase in production and it causes the increased pesticides application. In autumn, applications of pesticides are not heavy. For this reason, the collection of the samples was performed in two seasons. Soil samples were also taken from the places where the water samples were taken if it was possible. In the summer period, the samples were collected on 18th of June 2009 from the city center, on 19th of June 2009 from the Mudurnu, on 20th of June from Göynük, on 22nd of June 2009 from Kıbrısık and Seben. In the autumn period, the samples were collected on 10th of October 2009 from the city center.

3.3. Sample Collection

3.3.1. Preparation for Sampling

Before the sampling, the cleaning of the sampling apparatus is important for the determination of pesticides. 1 L amber glass bottles that used to take water samples are washed with commercial detergent in hot water and rinsed with tap water, deionized water, acetone and several times with hexane. Then they were dried in oven at 100 °C and stored until usage. Aluminium foil for soil sample is washed

with several times with acetone and hexane and then it was dried in an oven. It is also stored in a clean aluminium foil pocket which was man-made. The 2.5% solution of NaN_3 is prepared for water samples to protect the water samples from microbial growing.

3.3.2. Water Sampling

Water samples were collected into clean 1 L amber glass bottle. 1-2 mL of 2.5% NaN_3 is added and closed with stopper. The pH, salinity and conductivity of water samples were also measured at sampling site. 75 water samples were collected from the center of Bolu, Göynük, Mudurnu, Kırisciık and Seben district in summer season. Ground water samples were collected generally around 16-100 m depth wells. In autumn season, 17 water samples were collected from the city center. Coordanites of the sampling points were determined by Geographical Positioning System (GPS). General information about the sampling points were shown in Appendix 2. Maps which show ground and surface water sampling points were shown in Figure 3.2.

3.3.3. Soil Sampling

In this study, surface soil samples were collected around the water sampling points. Surface soil samples (0.5 cm below surface) were collected by a steel spoon. The composition of soil in the selected regions is similar (Appendix III). These samples were collected in summer and autumn seasons to observe the deposition of pesticides on soil. All soil samples were closed in an aluminum foil, dried in an oven at 40°C for one day and kept at 4°C until the analysis time. Soil sampling points are shown in Figure 3.2.

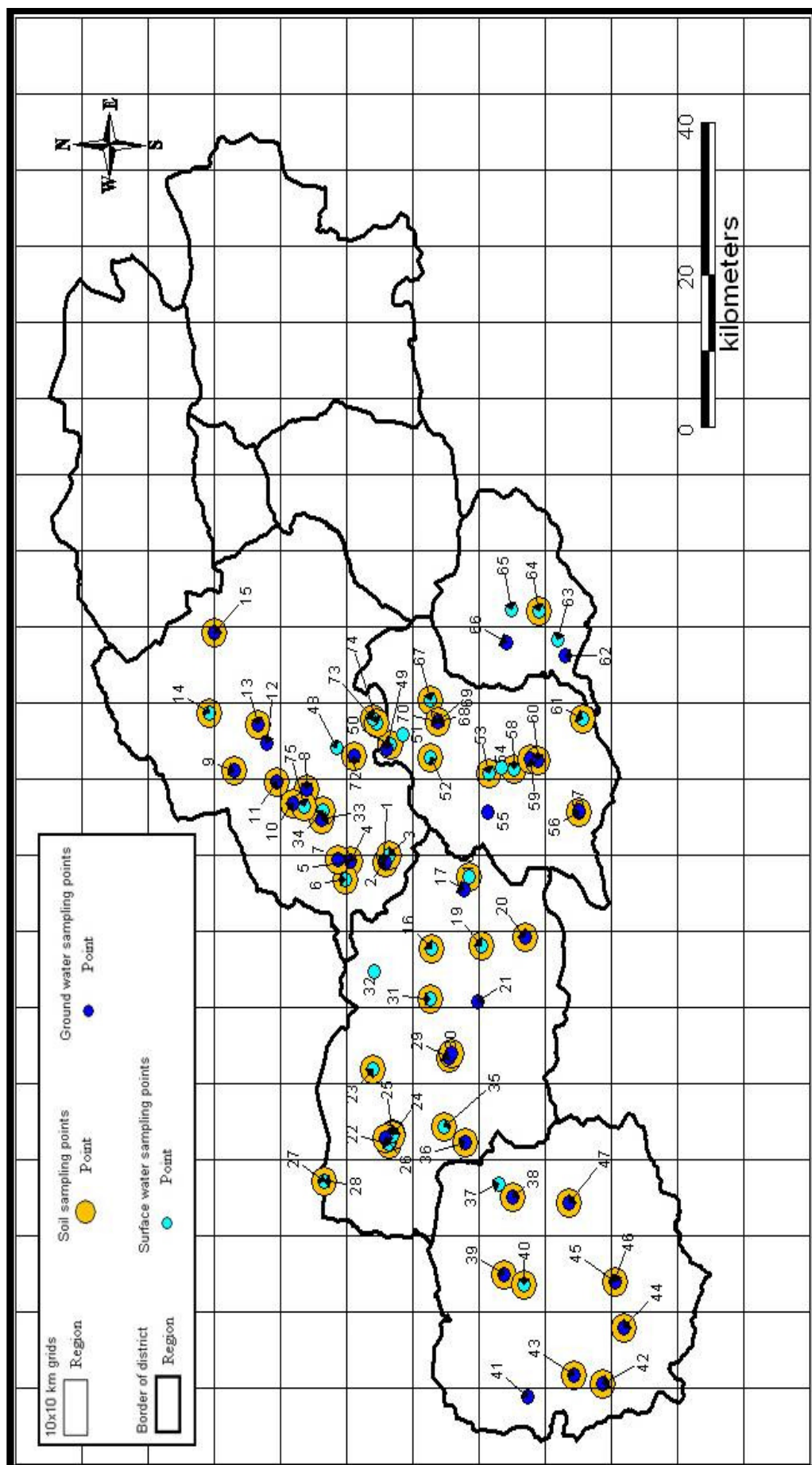


Figure 3.2. Ground water, surface water and soil sampling points

3.4. Preparation of Glasswares for Analysis

The glassware, used in the extraction, and clean-up steps were washed with commercial detergent in hot water and rinsed with tap water, deionized water, acetone and several times with hexane, respectively. Then, they were dried in an oven and were stored in closed and dark cupboards until usage. To decrease the level of contamination with organic matter, the glasswares were also conditioned at 400°C in muffle furnace except sensitive glasswares like volumetric flasks. The mouth of glasswares were closed with washed clean aluminum foil. Since the amounts of compounds were very low in samples, extreme precautions were necessary to eliminate the contamination.

3.4.1. Reagents, Materials and Apparatus

Acetone, acetonitrile, dichloromethane, ethyl acetate, and n-hexane were GC grade (99.99% purity) and were purchased from Merck Company (Germany) as well as Petroleum benzene (40-60°C) with 90% purity. The SPE cartridges were purchased from Biotech Company (USA). Sodium sulfate, florisil (0.150- 0.250 mm) and neutral aluminum oxide (0.063-0.2 mm) were purchased from Merck Company (USA). The granulated sodium sulfate was anhydrous and has 99 % purity for drying of solvents and gases. Glass microfiber filters (47 mm) were from Whatman Company (USA). N₂ gas was pure grade (99.999%) and purchased from Habas Company (Turkey). Calibration standard solutions (Mix-163 and Mix-102) were purchased from Dr. Ehrenstorfer (Germany). Intermediate stock solutions were prepared from the main stock standards with appropriate dilutions with n-hexane.

All of the stock, intermediate and standard solutions were stored in a refrigerator. 1000, 500, 100, 50, 25, and 10 µL gas tight glass syringes (Hamilton,

USA) were used in the preparation of the standards in 2 mL amber vials from Agilent company (USA). Whereas SPE system was purchased from Agilent (USA), filtering system was purchased from Jiteng company (Japan). Ultrasonic extractions were performed by using an ultrasonic bath (Bandelin, Germany). A rotary evaporator (Heidolph, Germany) was used to reduce the volumes of extracts. Automatic pipettes with different volumes were used (Brand transferpette, UK) (5000-500 μ L, 1000-100 μ L, 100-10 μ L). An oven (Binder, Turkey), (0-250°C), was used to dry glasswares. A muffle furnace (Boyut, Turkey) was used to baking organics on the glasswares and conditioning of the analytes as well as GFFs. A sieve (Retsch, Netherlands) (mesh number 30) was used to separate the sizes of soil samples. The analytical balance (0.1 mg) (And, Japan) was used for all weighing processes.

3.5. Solid Phase Extraction

To extract the water samples, solid phase extraction technique is used. 1.00 L of water sample was filtered from the 47 mm glass fiber filters. Then 500 mL water samples were measured with volumetric flask. Conditioning of the cartridge was done with 10 mL of 1:1 acetonitrile (ACN) and dicloromethane (DCM) mixture, 5 mL methanol, and 5 mL of deionized water, respectively. After the conditioning, the sample was passed through a cartridge with chemically bonded C₁₈ organic phase. The analytes were trapped on the cartridge. To remove the water from the cartridge, the cartridge was dried for half an hour. These organic compounds which was trapped on the cartridge, were eluted with 9 mL of ACN:DCM mixture and 3 mL n-hexane. This solvent mixture was evaporated by gentle stream of nitrogen near to dryness and the volume was completed to 0.5 mL with n-hexane.

3.6. Ultrasonic Extraction

Collected soil samples around the water sampling station were sieved from mesh number 30, which has pore width 0.595 mm to remove bigger part-stones and organic fossils. Then two 30 g subsamples were weighed and all prepared soil samples were waited in a 30 mL mixture of dichloromethane (DCM) and petroleum ether (PE) (1:4) for 24 hours. Then 30 minutes ultrasonic extraction was done. Finally, sodium sulfate was added into the filter paper so as to remove traces of water. The samples were concentrated under the nitrogen flow and transferred to the 10 mL vials. The samples were stored at 4°C in the refrigerator until clean-up procedure. For clean-up, a column was prepared by using one gram of aluminum oxide, florisil, sodium sulfate, respectively. This column was activated with hexane following the sample addition. Analytes were eluted with 1:1 ethyl acetate:hexane mixture and collected in a beaker. The analyte mixture was preconcentrated by rotary evaporator until 1 mL and the rest analyte mixture was evaporated by gentle stream of nitrogen near to dryness and the volume was completed to 0.5 mL with n-hexane.

3.7. Analysis of Samples

For halogenated organic compounds, sensitive and comprehensive instrumental studies are required. Therefore, we select an instrument, Hewlett Packard (HP) 6890N series gas chromatography equipped with electron capture dedector (Agilent, USA). A 30 m, 0.25 mm id., 0.25 mm film thickness, cross linked 5 % phenyl methyl siloxane, HP-5MS, capillary column was selected. For injections, Agilent 7683B series automatic injector (Agilent, USA) was used in the instrument. The operating parameters of GC- ECD instrument are given in Table 3.1. Sampling, extraction and evaluation scheme was shown in Figure 3.3.

Table 3.1. Operating Parameter of GC-ECD

Operation Parameters	
GC Column	30 m x 250 μm x 0.25 μm nominal film thickness, 5% phenyl Methyl siloxane, HP-5MS capillary column
Liner	Splitless glass liner, deactivated
Mobile Phase	Ultra purified Helium 99.999%, 1 mL min^{-1}
Type of injection	Splitless
Temperature of the injection port	250°C
Temperature of oven (Temperature programs)	50 (1 min), 25°C min^{-1} to 170°C, 5°C min^{-1} to 300 (2.00 min)
Volume of Injection	1 μL
Dedector Temperature	350°C

3.8. Method and Validation

3.8.1. Linearity

Pesticide working solutions were prepared between the range of 0.05 ppb- 50 ppb. The total chromatogram was completed in 33.8 minute. A chromatogram of 25 ppb solution is given in Figure 3.4.

Calibration curves were obtained from the eight calibration solutions. Linearity was evaluated by using r^2 values. The r^2 values were higher than 0.9909. The results are summarized in Table 3.2.

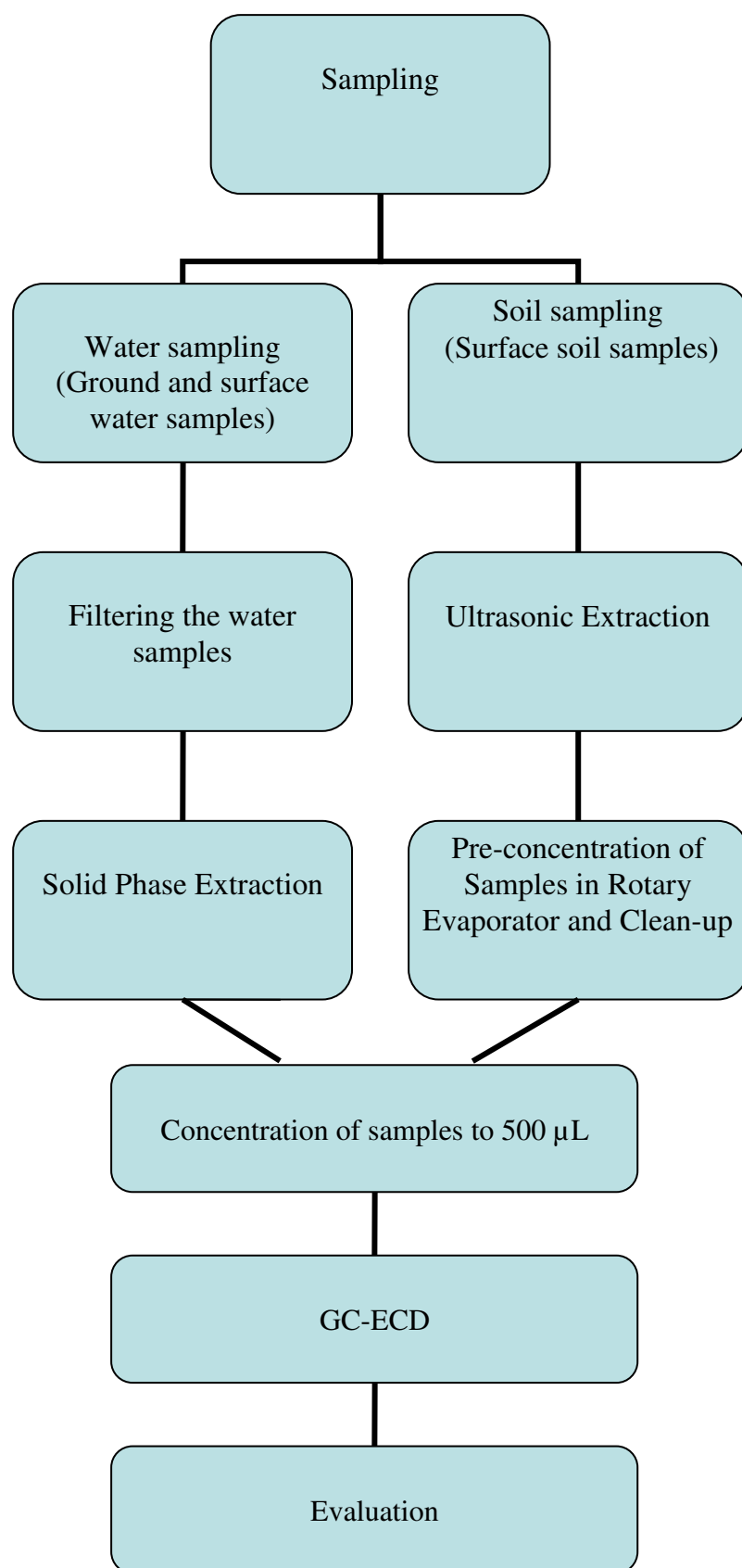


Figure 3.3. Sampling, extraction and analysis scheme

Table 3.2. Regression Coefficient of OCPs and LOD and LOQ values

Pesticides	Retention times (in minutes)	R ²	LOD (ng mL ⁻¹) for water samples	LOQ (ng mL ⁻¹) for water samples	LOD (ng g ⁻¹) for soil samples	LOQ (ng g ⁻¹) for soil samples
α -HCH	10.838	0.9997	0.044	0.15	7.33x10 ⁻⁴	2.5x10 ⁻³
β -HCH	11.470	0.9999	0.22	0.74	3.67x10 ⁻³	1.23x10 ⁻²
γ -HCH	11.649	0.9995	0.099	0.33	1.65x10 ⁻³	5.50x10 ⁻³
δ -HCH	12.248	0.9968	0.047	0.16	7.83x10 ⁻⁴	2.67x10 ⁻³
Heptachlor	13.269	0.9909	0.19	0.65	3.17x10 ⁻³	1.08x10 ⁻²
Aldrin	14.659	0.9998	0.14	0.48	2.33x10 ⁻³	8.00x10 ⁻³
Heptachlor epoxide	16.009	0.9999	0.068	0.22	1.13x10 ⁻³	3.67x10 ⁻³
Endosulfan I	17.021	0.9999	0.30	1.00	5.00x10 ⁻³	1.67x10 ⁻²
4,4'-DDE	17.789	0.9998	0.11	0.37	1.83x10 ⁻³	6.17x10 ⁻³
Dieldrin	17.855	0.9999	0.11	0.35	1.83x10 ⁻³	5.83x10 ⁻³
Endrin	18.559	0.9987	0.19	0.64	3.17x10 ⁻³	1.07x10 ⁻³
Endosulfan II	18.862	0.9999	0.060	0.20	1x10 ⁻³	3.33x10 ⁻³
4,4' DDD	19.158	0.9986	0.055	0.18	9.17x10 ⁻⁴	3x10 ⁻³
Endosulfan sulfate	20.271	0.9932	0.22	0.75	3.67x10 ⁻³	1.25x10 ⁻²
4,4' DDT	20.402	0.9994	0.13	0.44	2.17x10 ⁻³	7.33x10 ⁻³
Methoxychlor	22.354	0.9970	0.24	0.79	4x10 ⁻³	1.32x10 ⁻²

Some chromatograms have signals which were not qualified. These peaks may be related with the presence of other substances in the samples containing chlorine.

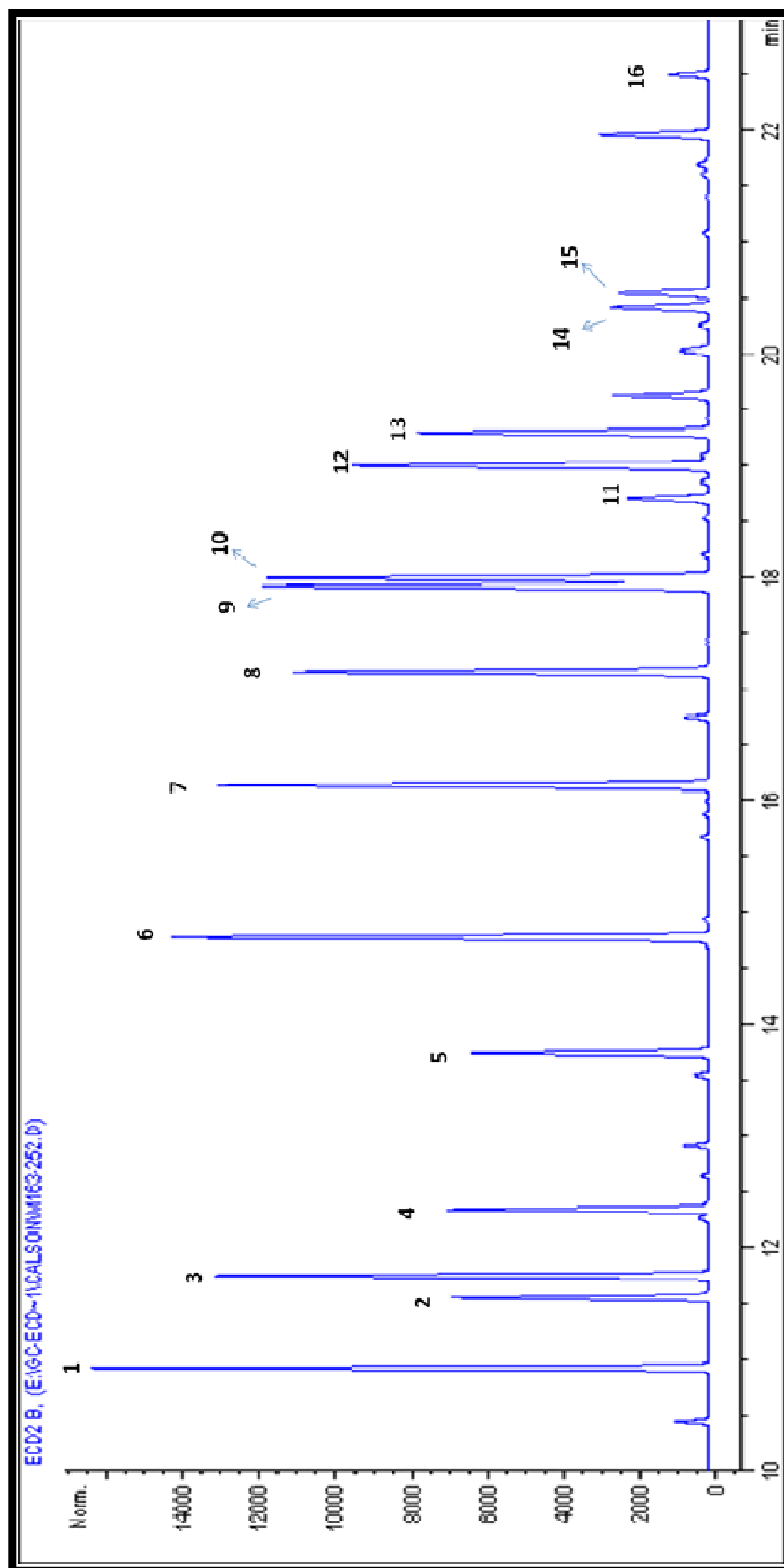


Figure 3.4. A sample chromatogram of 25 ppb mixture of OCP. 1. α -HCH, 2. β -HCH, 3. γ -HCH, 4. δ -HCH, 5. Heptachlor, 6. Aldrin, 7. Heptachlor-endo-epoxide, 8. Endosulfan I, 9. 4,4' DDE, 10. Dieldrin, 11. Endrin, 12. Endosulfan, 13. 4,4'-DDE, 14. Endosulfan sulfate, 15. 4,4'-DDT, 16. Methoxychlor.

3.8.2. Limit of Detection (LOD) and Limit of Quantification (LOQ)

To examine the capability of the systems for low concentrations, the detection limits were calculated for GC-ECD. Detection limits were calculated by using ten 2.5 ng mL⁻¹ standards. Ten replicate of 2.5 ng mL⁻¹ standart solutions were analyzed. LOD values are the 3 times standard deviation of ten replicates, LOQ values are the ten times standard deviation of ten replicates. The results were summarized in Table 3.2.

3.8.3. Recovery and Repeatability of SPE Method

The SPE procedure used in this work was evaluated from Ms Thesis of Binici (2007). However, in that work, rain water samples were extracted. Because of using ground and surface water samples, those procedures were checked to obtain higher recoveries.

Standard solution which was used for spiking was in hexane and hexane is insoluble in water. For that reason, hexane in 500 µL 10 ppm standard solution was evaporated by gentle stream of nitrogen and 500 µL acetone was added. From that solution, 15 ppb mix was prepared. For that purpose, 250 mL deionized water poured into a 500 mL volumetrik flask. Then 500 µL of 15 ppb pesticides mix solution was added and diluted to 500 mL to obtain a homogeneous mixture. Prepared six deionized water samples were extracted at the same day according to determined extraction procedure and these procedure were repeated for five days. The spiking was performed at the middle part of linear range (15 ng mL⁻¹). Firstly, 250 mL surface the surface and ground water poured into a 500 mL volumetrik flask. Then 500 µL of 15 ppb pesticides mix solution was added and diluted to 500 mL with deionized water to obtain a homogeneous mixture. Prepared six samples were extracted at the same day according to determined extraction procedure and these

procedures were repeated for five days for surface and ground water samples. The recoveries of each pesticide at each water samples were evaluated. The results were shown in the Table 3.3, Table 3.4 and Table 3.5. The recoveries in deionized water were changing between 56 and 118 with RSD% values ranging between 2 and 20.

Table 3.3. Mean recoveries values of each pesticide in deionized water (N=6)

Days	1		2		3		4		5	
Pesticides	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%
α -HCH	80	22	95	11	97	9	97	8	98	12
β -HCH	63	21	114	10	113	11	113	20	118	6
γ -HCH	66	11	90	14	105	5	105	7	112	14
δ -HCH	72	15	99	6	96	9	96	14	113	8
Heptachlor	87	13	87	20	101	5	101	8	106	2
Aldrin	67	20	72	18	77	19	81	3	77	12
Heptachlor Epoxide	73	18	101	8	114	6	114	10	112	6
Endosulfan I	73	12	101	6	112	5	112	12	108	5
4, 4' DDE	56	13	70	19	80	12	91	16	69	16
Dieldrin	73	17	103	7	114	3	114	8	110	6
Endrin	87	6	99	6	91	6	91	7	105	6
Endosulfan II	83	23	115	9	114	8	114	7	112	4
4, 4' DDD	72	18	93	15	95	10	95	14	98	11
Endosulfan sulfate	75	20	109	11	97	8	97	9	93	9
4, 4' DDT	82	20	65	17	72	11	72	20	68	15
Methoxychlor	85	21	82	15	84	18	84	8	76	15

Table 3.4. Mean recoveries values of each pesticide in ground water matrix (N=6)

Days	1		2		3		4		5	
Pesticides	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%
α -HCH	90	11	95	7	88	11	109	24	92	13
β -HCH	103	17	128	25	104	17	110	13	105	15
γ -HCH	96	14	114	15	93	13	114	14	96	16
δ -HCH	71	7	82	17	73	9	105	23	73	9
Heptachlor	97	20	93	15	84	16	102	14	103	17
Aldrin	72	12	61	16	73	12	62	18	75	12
Heptachlor Epoxide	87	9	94	21	87	10	80	20	88	8
Endosulfan I	81	8	78	18	82	8	75	18	81	8
4, 4' DDE	60	17	42	17	62	13	42	22	63	18
Dieldrin	83	9	83	19	85	10	81	22	87	11
Endrin	79	7	96	19	78	6	95	23	79	6
Endosulfan II	87	12	86	9	89	12	84	9	83	11
4, 4' DDD	74	15	70	7	76	13	80	24	76	14
Endosulfan sulfate	66	13	77	7	66	12	86	26	65	14
4, 4' DDT	93	19	85	14	86	12	101	20	91	18
Methoxychlor	65	20	96	20	59	12	102	21	67	20

Table 3.5. Mean recoveries values of each pesticide in surface water matrix (N=6)

Days	1		2		3		4		5	
Pesticides	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%	Average Recovery	RSD%
α -HCH	106	6	98	11	103	12	107	6	101	16
β -HCH	83	15	87	12	83	5	71	15	94	18
γ -HCH	96	7	91	11	92	8	89	7	94	12
δ -HCH	97	3	95	19	89	11	104	5	90	15
Heptachlor	112	12	84	11	88	8	103	6	94	18
Aldrin	71	5	75	13	78	10	68	5	74	13
Heptachlor Epoxide	91	14	91	16	83	13	91	8	92	21
Endosulfan I	91	15	96	16	85	11	97	8	103	18
4, 4' DDE	62	11	66	19	59	20	58	10	56	14
Dieldrin	86	17	91	17	90	17	97	9	105	12
Endrin	93	13	94	20	90	19	88	13	84	11
Endosulfan II	92	12	101	22	87	17	88	9	97	19
4, 4' DDD	103	12	80	19	79	20	102	12	90	4
Endosulfan sulfate	74	10	88	22	76	18	87	8	92	20
4, 4' DDT	99	28	72	19	86	19	157	0.4	105	7
Methoxychlor	90	19	63	24	87	20	104	14	81	14

3.8.4. Recovery and Repeatability of Ultrasonic Extraction Method

The ultrasonic extraction procedure used in this work was based on the previous study (Öz, 2008).

According to calibration curves range, the spiking was performed at middle fortification level. The soil samples were put in six different beakers and known concentration of pesticide mix was added on these soils. Then, all prepared soil samples were waited in a 30 mL mixture of dichloromethane (DCM) and petroleum ether (PE) (1:4) for 24 hours. The same procedure selected before were applied to all prepared matrix. The recoveries of each pesticide in each soil sample were evaluated. The results were shown in the Table 3.6. The recoveries of heptachlor epoxide, aldrin, dieldrin, endosulfan II was lower. For that reason, the correction was applied for the samples.

Table 3.6. Mean recovery values of each pesticide in soil (N=6)

Pesticides	Average Recovery	RSD%	Pesticides	Average Recovery	RSD%
α -HCH	62	8.3	4, 4' DDE	74	5.3
β -HCH	77	9.2	Dieldrin	40	7.8
γ -HCH	90	9.9	Endrin	70	7.4
δ -HCH	105	6.7	Endosulfan II	47	6.3
Heptachlor	102	15.4	4, 4' DDD	116	4.3
Aldrin	50	7.0	Endosulfan Sulfate	131	17.5
Heptachlor Epoxide	46	9.5	4, 4' DDT	83	21.3
Endosulfan I	67	7.4	methoxychlor	106	7.2

CHAPTER 4

RESULT AND DISCUSSION

The produced data will be evaluated by using different statistical methods in this chapter. In addition, both water and soil samples were collected to determine the concentration of OCP compounds in water and soil samples and evaluate the seasonal and spatial variations. These evaluations help us to determine the levels and sources of pesticides and the effects of pesticides to water quality in 5 districts of Bolu city.

4.1. OCPs in Water

Because of the persistent and mobile character, the OCP compounds property of OCP compounds, they can be found in various types (ground and surface water) of water bodies. Totally 92 water samples were collected. 75 water samples were collected from the city center, Mudurnu, Göynük, Seben and Kıbrısık district of Bolu in the summer. In addition, 17 water samples were collected just in the city center in the autumn to see the seasonal changes in OCP concentrations. Autumn samples include 7 surface water, 10 ground water samples while summer samples include 37 surface water and 38 ground water samples. Although the method for 19

OCP compounds (α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor, aldrin, heptachlor epoxide, endosulfan I and II, endosulfan sulfate, 4,4' DDD, 4,4' DDE, 4,4' DDT, endrin, dieldrin, methoxychlor, metolachlor, alachlor, chlorpyrifos) were validated and used in optimization process, it was possible to determine 13 OCP compounds (α -HCH, β -HCH, γ -HCH, δ -HCH, aldrin, endosulfan I and II, endosulfan sulfate, 4,4' DDD, 4,4' DDE, 4,4' DDT, endrin, dieldrin) in water samples.

4.1.1. Statistical Interpretion of the Data

The statistical evaluations of total (ground and surface water) OCP concentrations are given in Table 4.1. In this table, number of observed sample, percent observation, arithmetic mean, median, geometric mean, standard deviation, minimum and maximum values were calculated for one OCP compound. According to this table, endosulfan sulfate has the highest maximum concentration (11.2 ng L^{-1}) in a ground water samples in summer. The percent observations were changing between 1% and 85%. The highest arithmetic mean also belonged to the endosulfan sulfate. Aldrin observed only in one ground water sample in the summer season. The order of the highest arithmetic mean concentrations for OCPs in water samples as follows: Endosulfan sulfate > 4, 4', DDT > endrin > α -HCH > δ -HCH > endosulfan I > γ -HCH > endosulfan II > β -HCH > 4, 4', DDD > 4, 4', DDE, dieldrin.

Table 4.2 summarizes the surface water results taken in the summer. In surface water samples, endosulfan sulfate had the highest average concentration (1.40 ng L^{-1}). The highest percent observation was observed for α -HCH. Endosulfan I observed only in one sampling point. Aldrin was not observed in any of the surface water samples.

Table 4.3 also summarizes the results of ground water samples taken in summer. In these water samples, endosulfan sulfate had the highest average

concentration (1.76 ng L⁻¹) and maximum concentration (11.2 ng L⁻¹). The most observed OCPs in ground water samples were endosulfan sulfate and DDT in autumn season (Table 4.4).

Table 4.1. Statistical evaluation of ground and surface water samples taken from sampling points in both seasons (ng L⁻¹) (Total number of samples=92)

Pesticide	N	PO(%)	Art. Mean	Median	Geo. Mean	SD	Min	Max
α -HCH	60	64	0.75	0.46	0.60	0.81	0.36	5.77
β -HCH	10	11	0.35	0.52	0.33	0.17	0.23	0.80
γ -HCH	31	33	0.57	0.64	0.56	0.099	0.50	1.02
δ -HCH	43	46	0.71	0.69	0.70	0.11	0.54	1.27
Aldrin	1	1.1	0.20	0.042	0.20		0.20	0.20
Endosulfan I	2	2.1	0.61	0.23	0.58	0.28	0.42	0.81
4, 4' DDE	9	9.6	0.19	0.20	0.18	0.058	0.12	0.27
Dieldrin	8	8.5	0.19	0.29	0.18	0.074	0.11	0.29
Endrin	26	28	0.84	0.25	0.40	1.80	0.047	9.10
Endosulfan II	10	11	0.43	0.17	0.18	0.89	0.067	2.94
4, 4' DDD	14	15	0.20	1.15	0.14	0.20	0.051	0.77
Endosulfan Sulfate	80	85	1.81	1.13	1.55	1.38	0.84	11.2
4, 4' DDT	80	85	1.03	0.99	0.91	0.501	0.30	2.52

PO: Percent Observation, **Art M:** Arithmetic Mean, **Geo M:** Geometric Mean, **SD:** Standard Deviation, **Min:** Minimum, **Max:** Maximum, **N:** Number of Observed Samples

Table 4.2. Statistical evaluation of surface water sample taken in the summer (ng L⁻¹) (Total number of samples=37)

Pesticide	N	PO(%)	Art. Mean	Median	Geo. Mean	SD	Min	Max
α -HCH	32	87	0.96	0.62	0.73	1.05	0.36	5.77
β -HCH	5	14	0.39	0.33	0.35	0.23	0.25	0.80
γ -HCH	16	43	0.54	0.53	0.53	0.032	0.50	0.61
δ -HCH	21	57	0.69	0.68	0.69	0.053	0.62	0.83
Endosulfan I	1	2.7	0.81	0.81	0.81		0.81	0.81
4, 4' DDE	3	8.1	0.16	0.16	0.16	0.039	0.12	0.20
Dieldrin	4	11	0.15	0.14	0.15	0.043	0.11	0.21
Endrin	14	38	0.66	0.33	0.44	0.81	0.20	3.03
Endosulfan II	5	14	0.66	0.069	0.17	1.27	0.065	2.94
4, 4' DDD	6	16	0.10	0.084	0.090	0.039	0.058	0.17
Endosulfan Sulfate	29	78	1.40	1.11	1.30	0.62	0.89	3.29
4, 4' DDT	29	78	1.08	1.06	0.98	0.49	0.45	2.52

PO: Percent Observation, **Art M:** Arithmetic Mean, **Geo M:** Geometric Mean, **SD:** Standard Deviation, **Min:** Minimum, **Max:** Maximum, **N:** Number of Observed Samples

Table 4.3. Statistical evaluation of ground water sample taken in the summer (ng L⁻¹)

(Total number of samples=38)

Pesticide	N	PO(%)	Art. Mean	Median	Geo. Mean	SD	Min	Max
α -HCH	19	51	0.47	0.39	0.44	0.19	0.36	1.09
β -HCH	5	14	0.32	0.27	0.30	0.10	0.23	0.47
γ -HCH	12	32	0.59	0.53	0.58	0.14	0.52	1.02
δ -HCH	22	60	0.73	0.69	0.72	0.15	0.54	1.27
Aldrin	1	2.7	0.20	0.20	0.20		0.20	0.20
Endosulfan I	1	2.7	0.42	0.42	0.42		0.42	0.42
4, 4' DDE	6	16	0.21	0.24	0.20	0.063	0.12	0.27
Dieldrin	4	11	0.24	0.27	0.22	0.077	0.13	0.29
Endrin	11	30	0.39	0.39	0.51	2.63	0.21	9.10
Endosulfan II	5	14	0.19	0.19	0.18	0.049	0.10	0.24
4, 4' DDD	7	19	0.31	0.22	0.23	0.24	0.056	0.77
Endosulfan Sulfate	33	89	1.76	1.22	1.42	1.87	0.84	11.2
4, 4' DDT	33	89	0.88	0.68	0.74	0.55	0.30	2.34

PO: Percent Observation, **Art M:** Arithmetic Mean, **Geo M:** Geometric Mean, **SD:** Standard Deviation, **Min:** Minimum, **Max:** Maximum, **N:** Number of Observed Samples

Table 4.4. Statistical evaluation of all kinds of water samples in the autumn (ng L⁻¹)

(Total number of samples=17)

Pesticide	N	PO(%)	Art. Mean	Median	Geo. Mean	SD	Min	Max
α -HCH	8	47	0.54	0.47	0.54	0.14	0.39	0.80
γ -HCH	3	18	0.63	0.62	0.63	0.098	0.55	0.74
Endosulfan Sulfate	17	100	2.65	2.88	2.52	0.78	1.11	3.76
DDT	17	100	2.87	1.15	0.15	0.43	0.57	2.17

PO: Percent Observation, **Art M:** Arithmetic Mean, **Geo M:** Geometric Mean, **SD:** Standard Deviation, **Min:** Minimum, **Max:** Maximum, **N:** Number of Observed Samples

Table 4.1 shows the average concentrations of OCPs in surface and ground water samples in the summer. Endosulfan sulfate had the highest average concentration in both types of samples. Average concentration of it was higher in ground water than in surface water. Endosulfan is widely used in the region and has very low water solubility. It is applied the soil before or after watering the plants.

This explained why endosulfan and its derivatives had higher concentrations in ground water samples than in surface water samples.

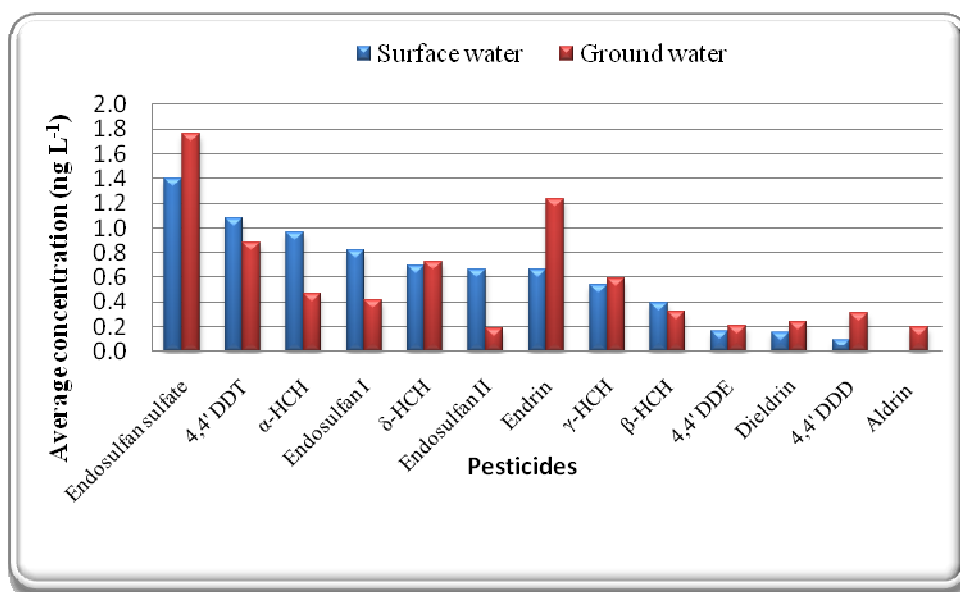


Figure 4.1. Average concentrations of OCPs in surface and ground water in summer season (ng L^{-1})

The percent observations in water samples help us to evaluate the data. In Figure 4.2, the percent observations of surface and ground water samples are shown.

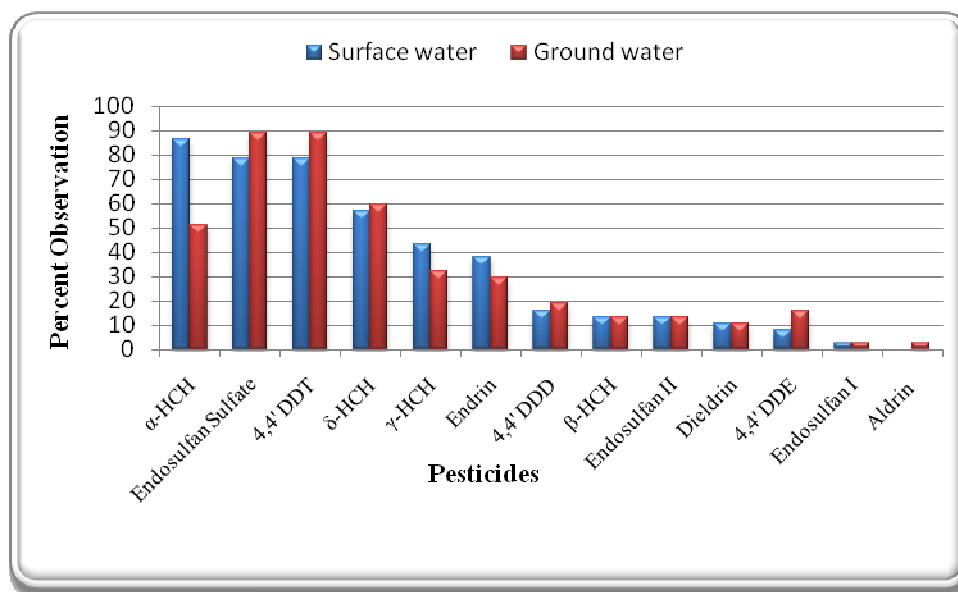


Figure 4.2. Percent occurrence for each observed pesticides in surface and ground water in summer season

According to this Figure, aldrin has the lowest percent observation in both kinds of samples. Because of its persistent property and past usage, it can be seen in water samples. Endosulfan sulfate and DDT had the highest percent observations. Moreover, the percent observation of α -HCH in surface water was higher than in ground water.

4.1.2. Seasonal Changes of the OCPs in Water Samples

To observe the seasonal changes, the second water sampling was carried out in the city center in autumn season. The seasonal evaluations were done by using concentration of water samples taken from city center in the summer and autumn season.

If the autumn and summer samples were individually discussed, seasonal variations can be seen. The Figure 4.3 shows the seasonal difference for each observed pesticides. In summer sampling, 13 pesticides were observed in surface and ground water samples. Percent observations in summer samples in the city center were between 16.7% to 94.4%. The highest arithmetic mean belonged to endosulfan sulfate and endosulfan II had the lowest arithmetic mean. Heptachlor, epoxy-heptachlor, chlorpyrifos, metolachlor, alachlor and methoxychlor were not observed in water samples in summer season. In autumn sampling, 4 pesticides were observed in surface and ground water samples. The percent observations were between 5.9% and 100%. Endosulfan sulfate and 4,4' DDT were observed in all of the samples. Endosulfan sulfate had the highest arithmetic mean. β -HCH, δ -HCH, aldrin, endosulfan I and II, endrin, dieldrin, 4,4'DDE, 4,4' DDD, methoxychlor, metolachlor, alachlor, chlorpyrifos were not observed in autumn samples.

When a comparison was done with the average concentrations of each observed pesticides (Figure 4.3), it was found that average concentrations in summer

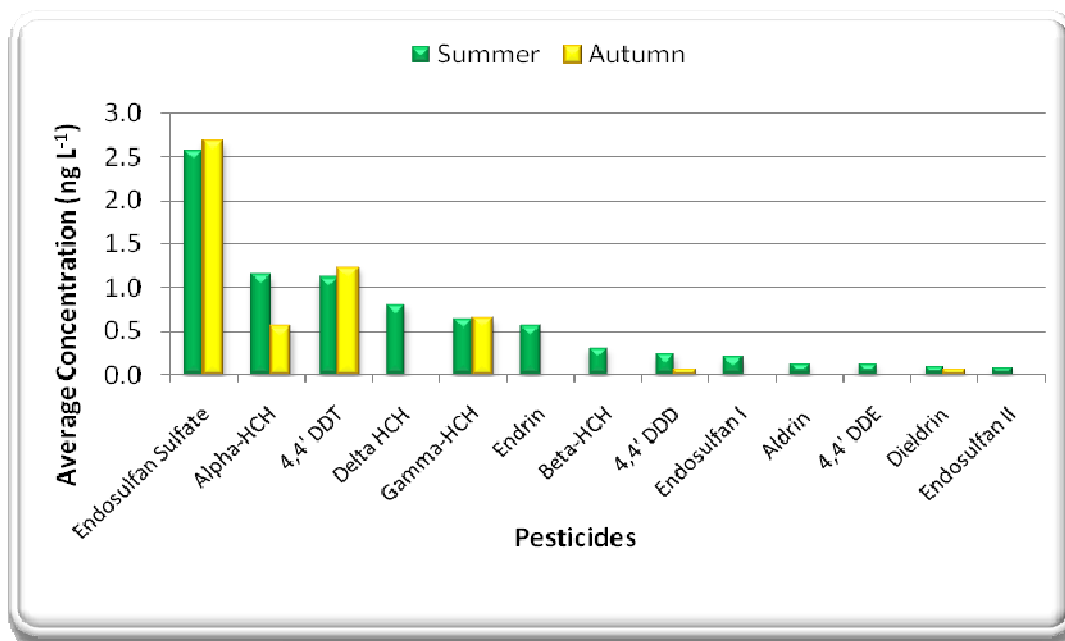


Figure 4.3. The seasonal difference in average concentrations for each observed pesticides

samples were higher than average concentrations in autumn except for endosulfan sulfate and 4,4' DDT. Total OCP concentrations in each sampling site were calculated and shown in Figure 4.4. In some of the ground water samples near to agricultural areas like 2, 8, 9, 10 had higher concentrations.

4.2. OCPs in Soil

Because of the persistent character of OCP compounds, they can be found in soil as well as in water samples. 45 soil samples were collected from the city centre, Mudurnu, Göynük, Seben and Kırbriscık district of Bolu in summer. In addition, 17 soil samples were collected in autumn from the city center to see the seasonal changes in OCP concentration in the city center.

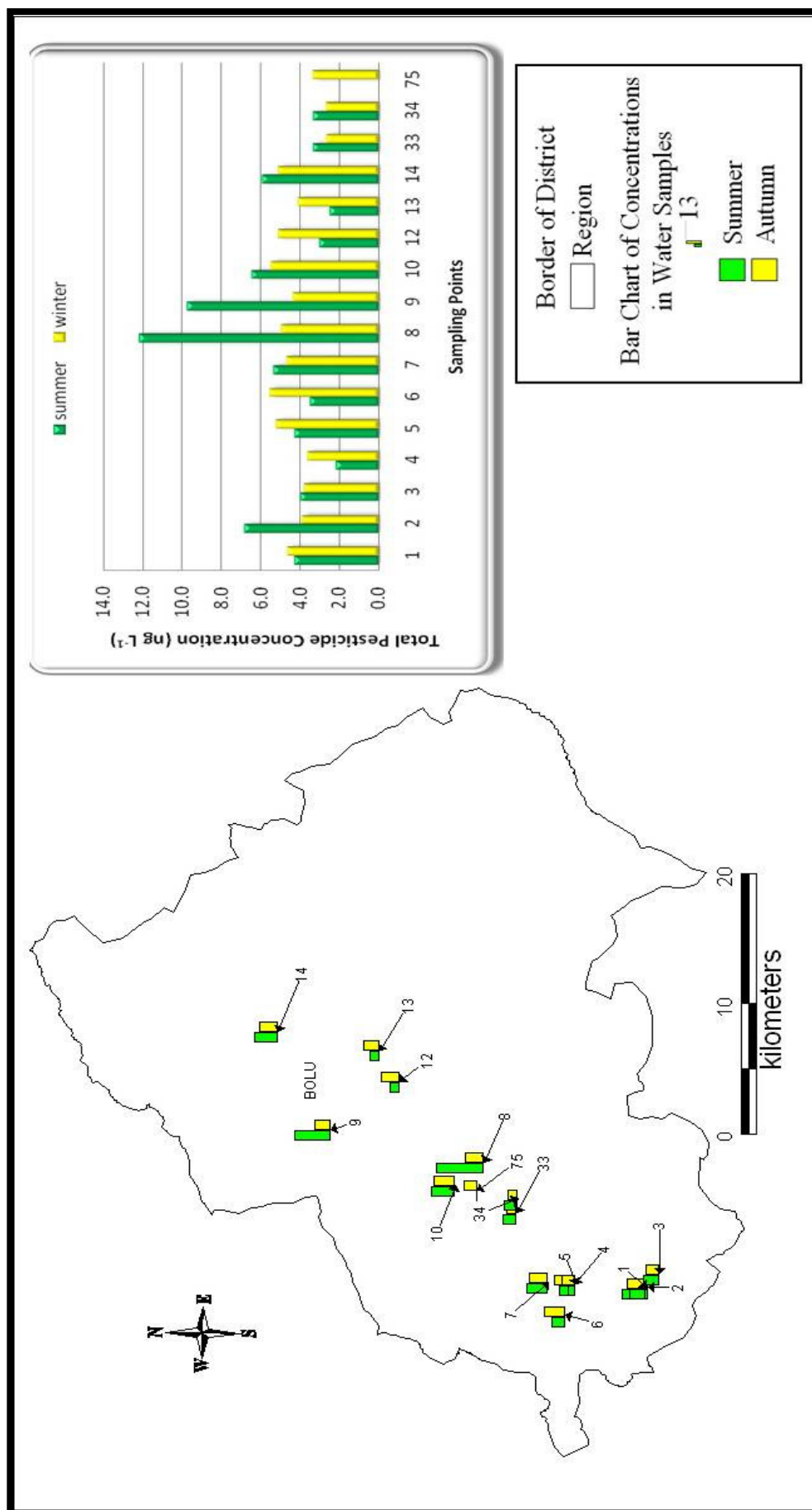


Figure 4.4. Total concentrations of OCPs in surface and ground water samples taken from city center in summer and autumn seasons

4.2.1. Statistical Interpretation of the Data

The statistical evaluations of OCPs concentrations in soil samples are given in Table 4.5. In this table, number of observed sample, percent observation, arithmetic mean, median, geometric mean, standard deviation, minimum and maximum values were calculated for one OCP compound. According to this table, endosulfan sulfate had the highest concentration (0.98 ng g^{-1}) in soil samples. The percent observations were changing between 2% and 55%. Endosulfan sulfate was the most observed OCPs in soil samples. The order of the highest arithmetic mean concentrations for OCPs in soil samples in both seasons as follows: Endosulfan sulfate > 4, 4', DDE > endosulfan II > 4,4' DDT > endosulfan I > 4, 4', DDD > δ -HCH > α -HCH > γ -HCH > β -HCH > aldrin.

Table 4.5. Statistical evaluation of soil samples taken from sampling points in both seasons (ng g^{-1}) (Total number of samples= 54)

Pesticide	N	PO(%)	Art. Mean	Median	Geo. Mean	SD	Min	Max
α -HCH	3	7.9	0.041	0.029	0.033	0.032	0.016	0.078
β -HCH	3	7.9	0.019	0.018	0.017	0.011	0.0089	0.030
γ -HCH	9	23	0.025	0.023	0.024	0.0054	0.020	0.037
δ -HCH	4	10	0.057	0.060	0.34	0.0074	0.049	0.6324
Aldrin	1	2	0.0055	0.0055	0.0055		0.006	0.0055
Endosulfan I	1	2	0.24	0.24	0.24		0.24	0.24
4,4' DDE	18	47	0.62	0.19	0.12	1.31	0.0044	5.54
Endosulfan II	17	44	0.34	0.10	0.093	0.95	0.015	4.00
4,4' DDD	16	42	0.21	0.062	0.070	0.39	0.0022	1.59
Endosulfan sulfate	21	55	0.98	0.070	0.11	3.90	0.025	18.0
4,4' DDT	18	47	0.29	0.051	0.074	0.78	0.015	3.21

PO: Percent Observation, **Art M:** Arithmetic Mean, **Geo M:** Geometric Mean, **SD:** Standard Deviation, **Min:** Minimum, **Max:** Maximum, **N:** Number of Observed Samples

4.2.2. Seasonal Changes of the OCPs in Soil Samples

To observe the seasonal changes, the second soil sampling was carried out in the city center in autumn season. The seasonal evaluations were performed by using

concentration of pesticides in soil samples taken from city center in the summer and in the autumn season.

If the autumn and summer samples were individually discussed, seasonal variations can be seen. The Figure 4.5 shows the seasonal difference for each observed pesticides. In summer sampling, 8 pesticides were observed in soil samples. The percent observation in summer samples in the city center were between 4.4% to 40%. The highest arithmetic mean belonged to 4,4' DDE . In autumn sampling, 7 pesticides were observed in soil samples. The percent observations were between 5.9% and 41.2%. Endosulfan sulfate had the highest percent observation. Dieldrin had the lowest arithmetic mean and 4,4' DDT had the highest arithmetic mean.

When a comparison was done with the arithmetic mean of each observed pesticides (Figure 4.5), it was found that the average concentrations in the summer samples were higher than the average concentrations in autumn except for 4,4' DDT. However, the total OCP concentrations in sampling points 10 (Karaköy), 11 (Kılıçarslan) and 13 (Yakabayat) were higher in the summer (Figure 4.6). For these

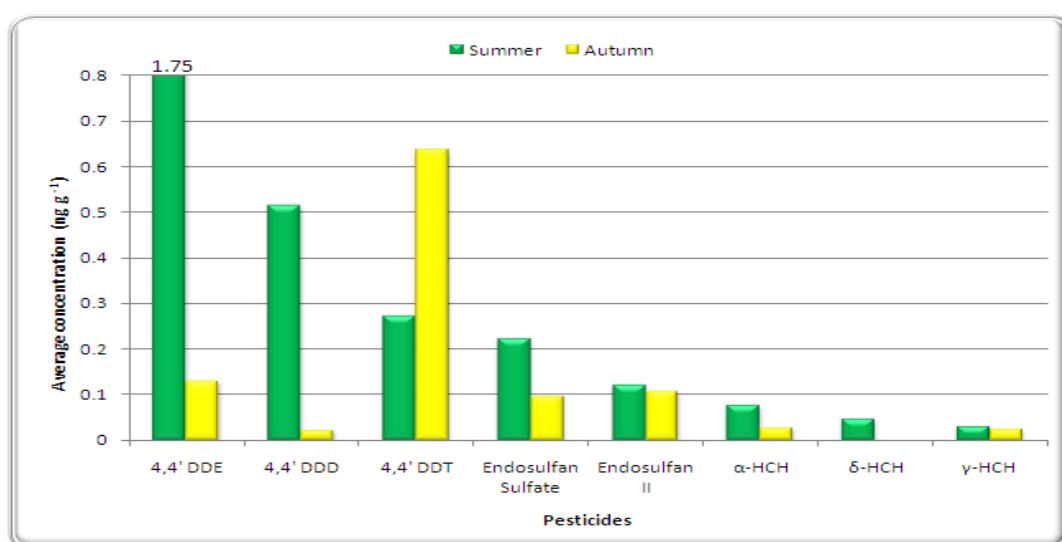


Figure 4.5. The seasonal difference in average concentrations for each observed pesticides in soil samples taken from city center

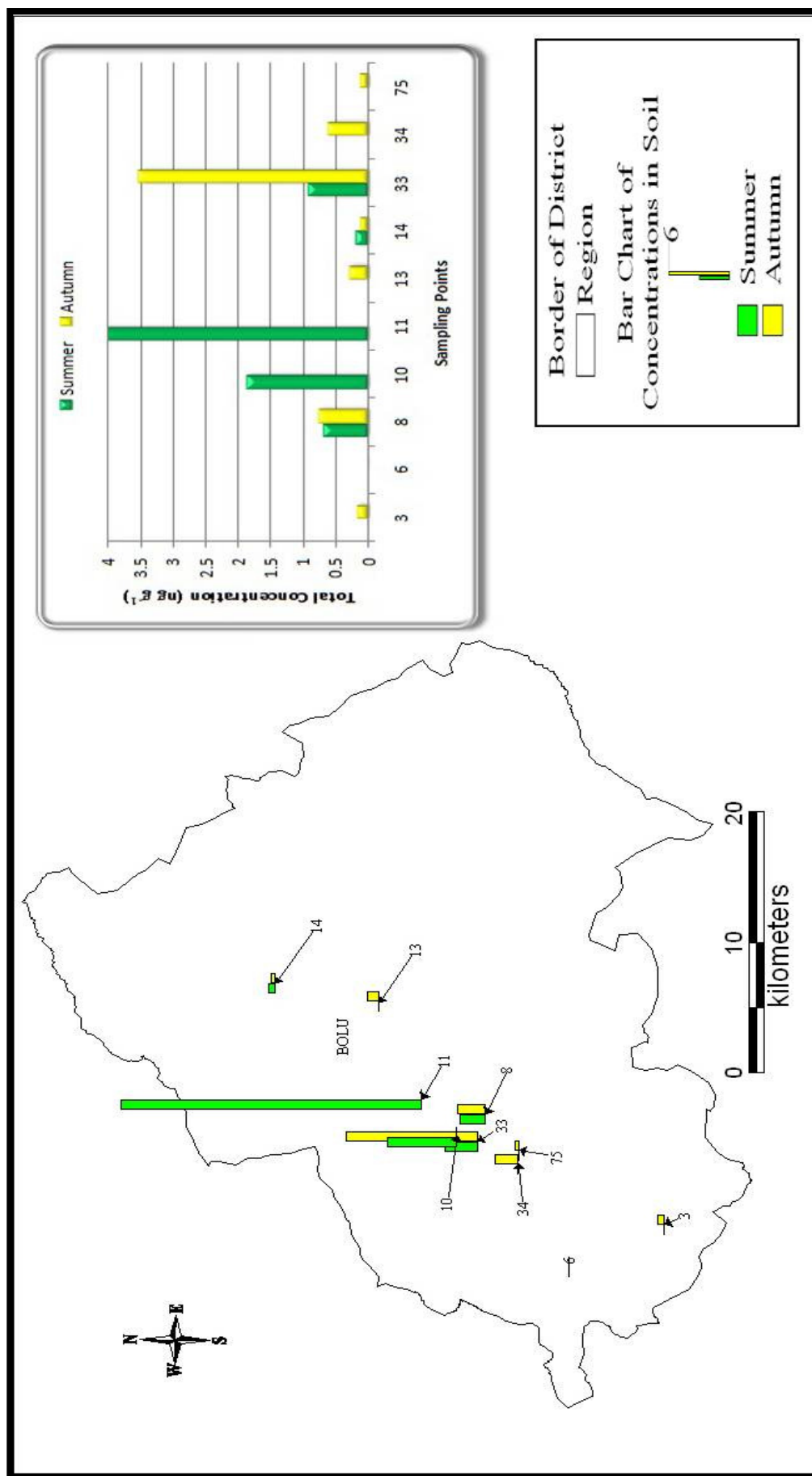


Figure 4.6. Total concentrations of OCPs in soil samples taken from city center in summer and autumn season

sampling points 10 and 13 are near to agricultural areas in which fruits and wheat production are performed. In addition, the soil sample couldn't be taken from sampling point 11 in the autumn. Wheat production is highly performed in the sampling point 33 (Çepni). The soil sample in Çepni was taken from near a lake which is used for plant production.

4.3. A Comparision of OCP Concentrations with Literature Values

The concentrations of OCPs in surface water, ground water and soil were compared with literature values in order to evaluate pollution levels in Bolu. The data for similar studies in the literature were given in Table 4.6. The properties of sampling sites and samples were given in the first column of the Table 4.6 to compare the average concentrations of OCPs in water samples.

The concentration ranges of surface water samples except for endrin in this study were considerably less than concentration ranges in other studies. The highest average concentration in surface and ground water samples were belonged to the endosulfan sulfate in our study. The range of concentration of endosulfan isomers and their derivatives in surface water was lower than that in ground water. The concentrations of 4,4' DDT and its derivatives had lower range of concentrations than the studies performed in Greece, India and Turkey. This pesticides and its derivaties was not detected in Spain (Claver et al., 2006). Endrin can be detected in Greece and Brazil. However, the concentration ranges in Greece were higher than the range of concentrations in this study whereas other study had similar ranges. Endrin can not be detected in polluted area in Antalya (Öztaş, 2009).

Table 4.6. A comparison of mean OCP concentrations in surface and ground water samples with literature values (ng L⁻¹)

Reference	α -HCH	β -HCH	γ -HCH	δ -HCH	Aldrin	Endosulfan I	Endosulfan II	Endosulfan sulfate	4, 4' DDE	4, 4' DDD	4,4' DDT	Endrin	Dieldrin
This study (Bolu, Turkey), (Suburban), ground water	0.044-1.09	0.22-0.47	0.099-1.02	0.047-1.27	0.14-0.20	0.30-0.42	0.060-0.24	0.22- 11.2	0.055-0.77	0.11-0.27	0.13-2.34	0.19-9.10	0.11-0.29
This study (Bolu, Turkey), (Suburban), surface water	0.044-5.77	0.22- 0.80	0.099-0.61	0.047-0.83	<0.14	0.30-0.81	0.060-2.94	0.22-3.29	0.055-0.17	0.11-0.20	0.13-2.52	0.19-3.03	0.11-0.21
Öztaş, N., 2009 (Antalya, Turkey)(Agricultural), ground water	60.6	88.1	82.0	160.2	166.1	125.8	176.7	209.3	85.5	74.5	107.9	<LOD	74.3
Öztaş, N. , 2009 (Antalya, Turkey) (Agricultural), surface water	129.9	128.7	<LOD	67.5	198.7	125.3	146.2	164.5	33.4	69.2	213.4	<LOD	218.4
Claver et al., 2006 (Gallur, Spain) (Agricultural), Surface water	<LOD	<LOD	27	<LOD	<LOD	<LOD		<LOD	<LOD		<LOD	<LOD	<LOD
Golfinopoulos et al., 2003 (Greece) (Agricultural), lake water	8-49	20- 401	8-30		8-104	8-39	LOD	8-50	8-13	8-112	12-18	8-21	8-31
Golfinopoulos et al., 2003 (Greece) (Agricultural), river water	8-131	20-96	8-81		8-101	8-20	8-22	8-58	8-64	Nd	12-35	LOD	8- 39
Sankaramakrishnan et al., 2005 (Kanpur, India) (Agricultural), Surface water	190± 20	260±30											1671±36
Júnior and Ré- Poppi, 2007 (Brazil) (Rural), ground water	0.01-32.5	0.06-6.8	0.0013-12.8	0.015-198	0.03-1.6	0.025-3.0	0.1-0.9	0.1-1.4	0.45-14.9	0.3-4.9	0.45-2.3	0.15-3.7	0.03-3.6
Shukla et al., 2006 (India) (Rural), ground water			65-139			149-1098				219-878	150.8-195		
Sankaramakrishnan et al. 2005 (India) (Agricultural), ground water	189±30	Nd	303±20	Nd	Nd				Nd		Nd		Nd

LOD: Limit of Detection Nd: Not detected

Literature values related with soil were given in Table 4.7. The comparison was also performed for soil samples. The concentrations of pesticides in soil samples in another study conducted in Bolu by Öz, (2009) were higher than that of this study except for endosulfan sulfate in summer season. The reason can be the usage of high amounts of endosulfan isomers for agricultural practices in Bolu. However in winter season the concentration of endosulfan sulfate were lower than the previous study (Öz, 2009). The values in the study performed in İzmir (Bozlaker et al., 2009) were close to values obtained in this study except for 4,4' DDD and 4,4' DDT. Σ HCH and Σ DDT values in our study were also lower than that in the study performed in Romania (Covaci et al., 2001). In Korea, the concentration of dieldrin was lower than that of this study whereas other pesticide concentrations were higher than the concentrations obtained in this study. Aldrin was used for the wheat production in Bolu and dieldrin is the conversion product of aldrin.

In this study, the concentrations of OCPs were also lower than the maximum permitted limit of 100 ng L⁻¹ for each pesticide in water samples and which is determined in European Union directive 98/83/EC by European Union. There is no limit for soil contamination.

Table 4.7. A comparison of mean OCP concentrations in soil samples with literature values (ng g⁻¹)

Reference	α -HCH	β -HCH	γ -HCH	δ -HCH	Aldrin	Endosulfan I	Endosulfan II	Endosulfan sulfate	4, 4' -DDD	4,4' DDT	4, 4' -DDE
This study (Bolu, Turkey) (Suburban area) Summer	0.047±0.043	0.019±0.010	0.025±0.0057	0.060±0.0075	0.0055	0.24	0.44±1.13	1.42±4.77	0.24±0.41	0.29±0.21	0.73±1.43
This study (Bolu, Turkey) (Suburban area) Autumn	0.029	<3.67x10 ⁻³	0.024	<7.83x10 ⁻⁴	<2.33x10 ⁻³	<5.00x10 ⁻³	0.11±0.051	0.098±0.057	0.022±0.028	0.64±1.32	0.130±0.22
Bozlaker et al., 2009 (Izmir, Turkey) (Industrial) Summer	0.034±0.075	0.11±0.047	0.035±0.0074	0.0099±0.0035		0.119±0.075	0.072±0.040	0.080±0.037	10.1±0.82	1.1±0.94	
Bozlaker et al., 2009 (Izmir, Turkey) (Industrial) Winter	0.068±0.023	0.20±0.056	0.069±0.015	0.033±0.006		0.077±0.036	0.034±0.016	0.17±0.065	9.58±0.832	0.802±0.042	
Öz, 2009 (Bolu, Turkey) (Suburban) Summer		0.321- 2.06				0.248-0.458	0.092-1.96	0.919- 1.74	0.408- 1.19		
Öz, 2009 (Bolu, Turkey) (Suburban) Winter		0.153-2.02					0.048- 0.429	1.25-1.64			
Covacı et al., 2001(Romania) (Agricultural)	0.7-7.3 *									3.5- 119.5**	
Kim and Smith, 2001, (Korea) (Agricultural)		0.25- 0.80	0.17- 0.94	0.76- 2.97	0.34- 0.79	0.1- 0.64	0.1- 0.89		0.1- 0.48		0- 0.34
LOD: Limit of detection * Σ HCHs concentration ** Σ DDTs concentration											

4.4. Spatial Distributions

4.4.1. Spatial Distributions by Graphs

The total pesticide concentration in water and soil samples taken from five districts were shown in Figure 4.7, 4.8, 4.9, 4.10. Although the highest total concentration in soil samples and surface water samples were detected in Mudurnu, the highest total concentration in ground water was detected in Seben.

In the city center, the ground water sample taken from point 8 (Doğancı) which is near to agricultural region had the highest total concentration. The highest total pesticide concentration in soil is belonged to the sampling point 11 (Kılıçarslan). These soil sample was taken from a agricultural field used for fruit production. Surface water sample (14) which is taken from nonagricultural region is high in the city center. In Mudurnu and Göynük surface and ground water concentration values were not very much different from each other. In Seben, ground water sample taken from the sampling point 59 in agricultural region had the highest concentrations. In Kıbrısık, one ground water, one surface water and one soil sample can be taken. The concentration of surface water sample taken from (Şaduman Stream) was higher in Kıbrısık.

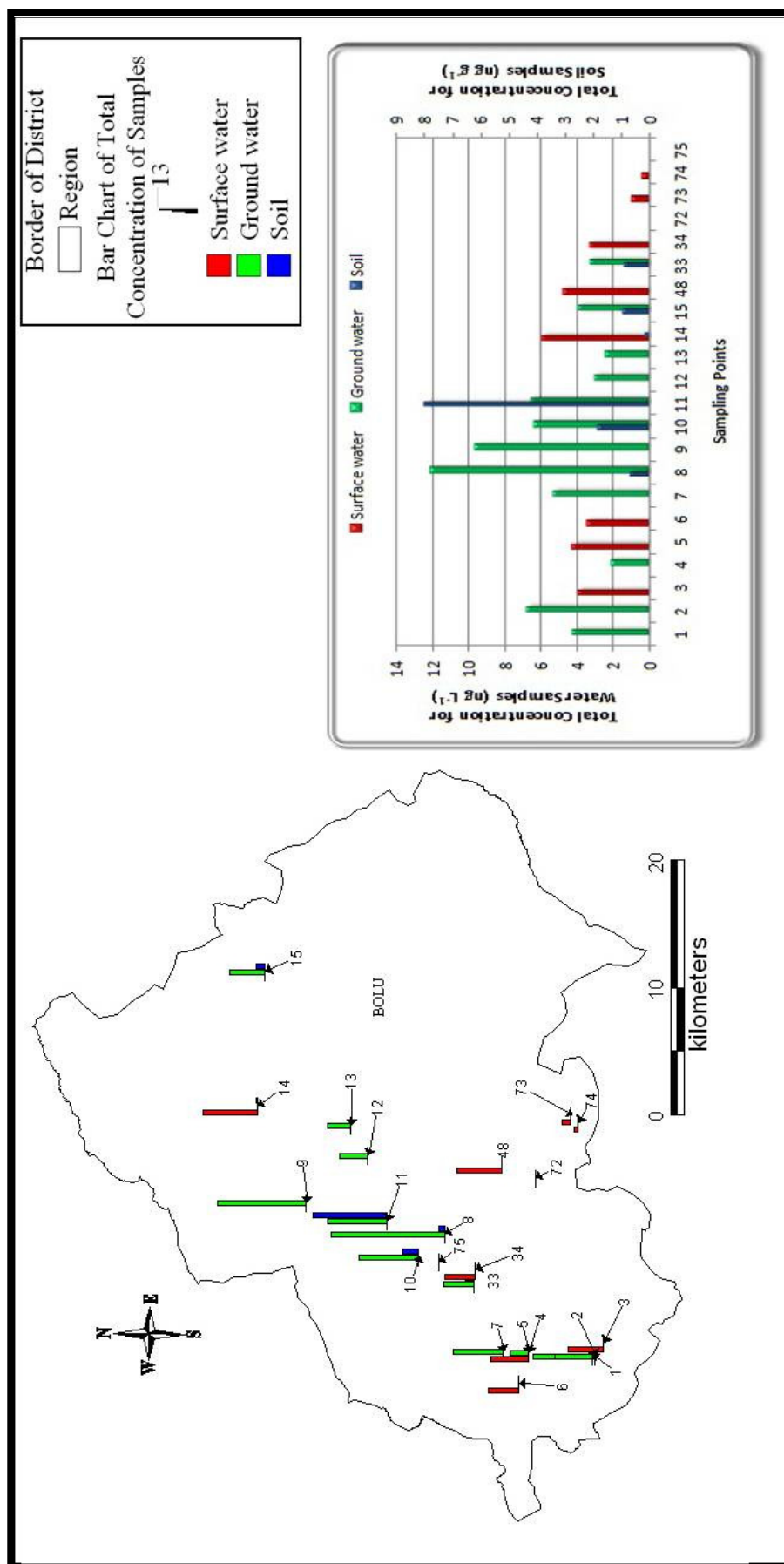


Figure 4.7. The total pesticide concentration in the city center in each sampling point

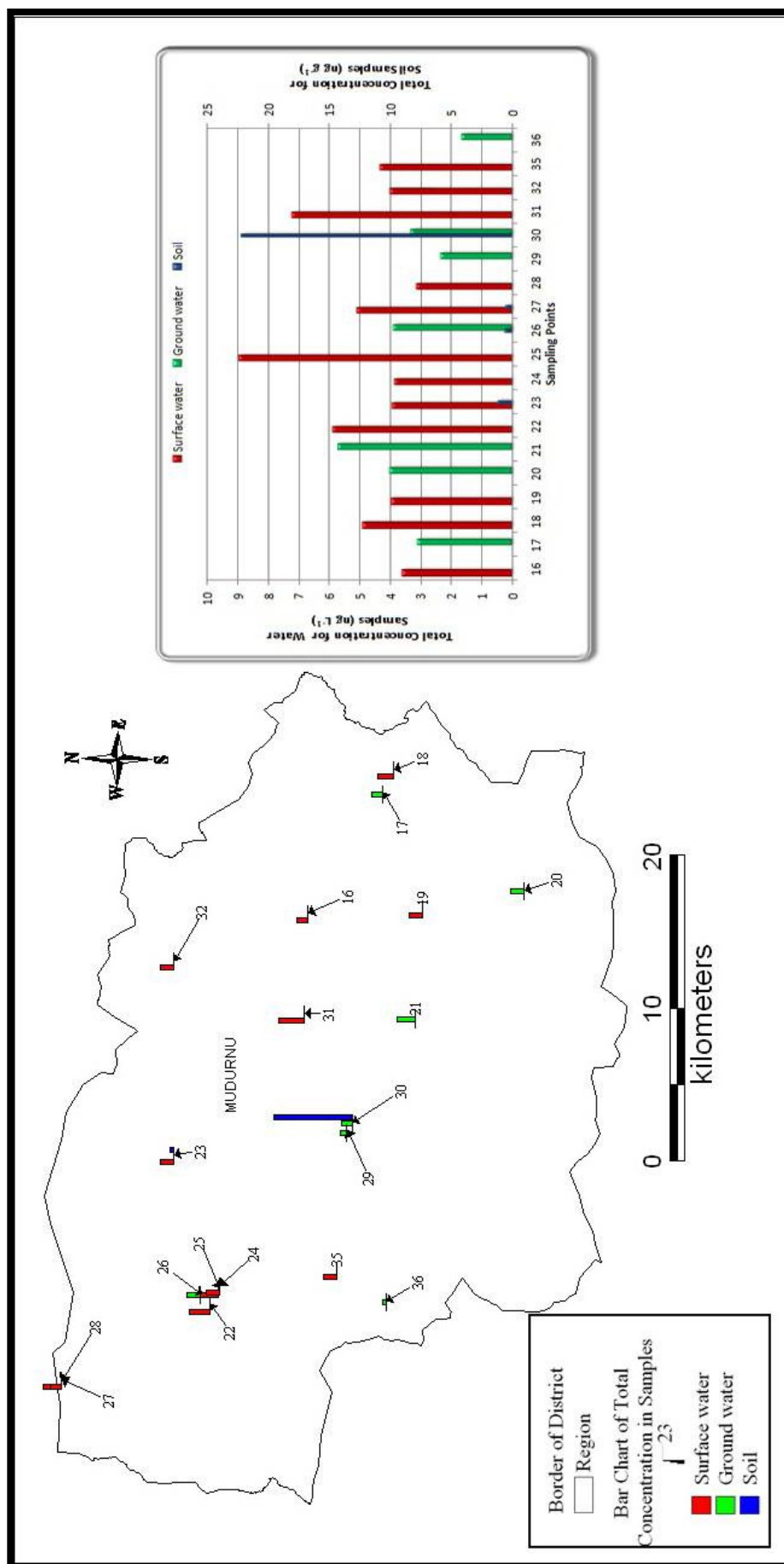


Figure 4.8. The total pesticide concentration in Mudurnu in each sampling point

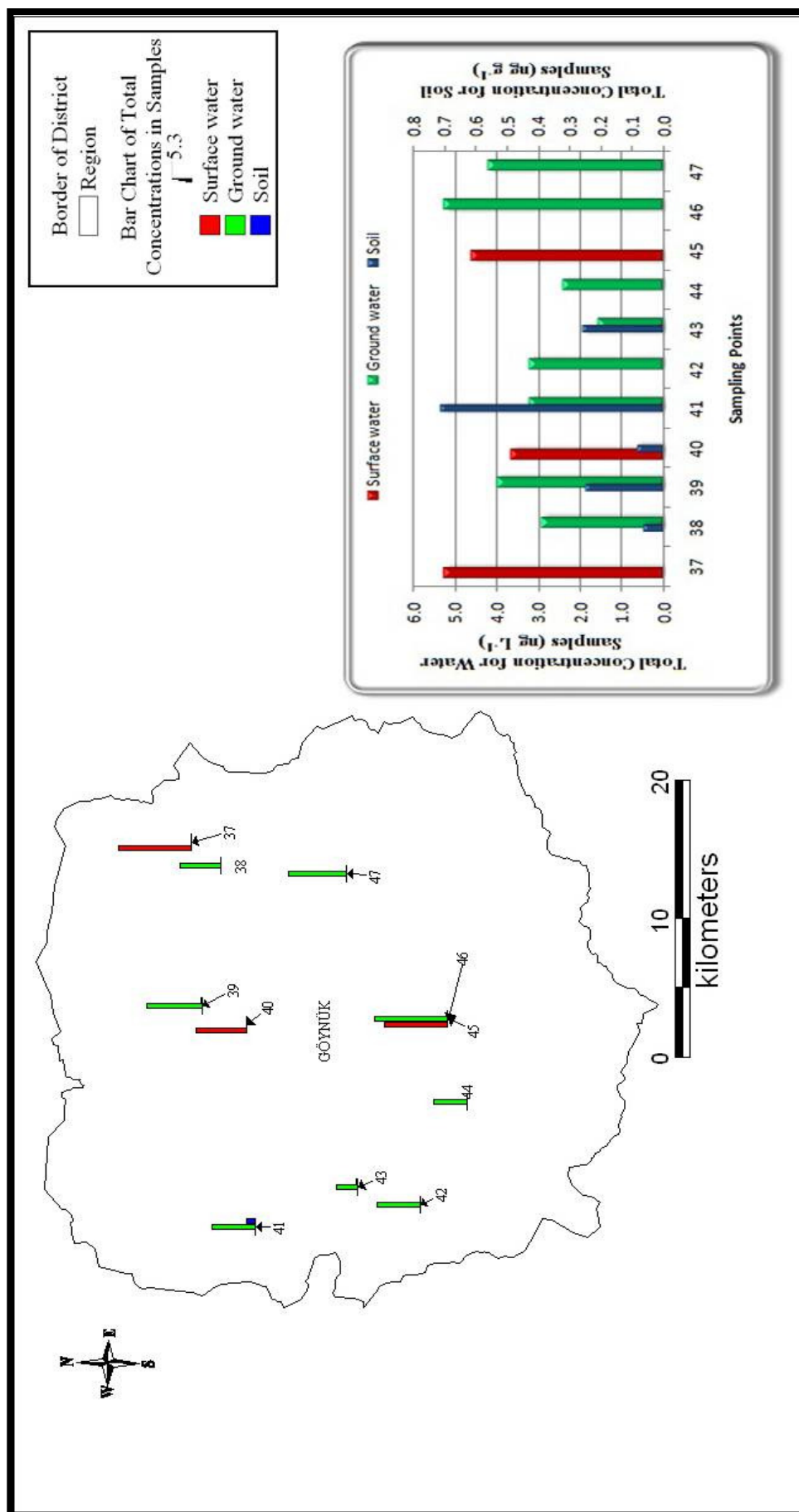


Figure 4.9. The total pesticide concentration in Göynük in each sampling point

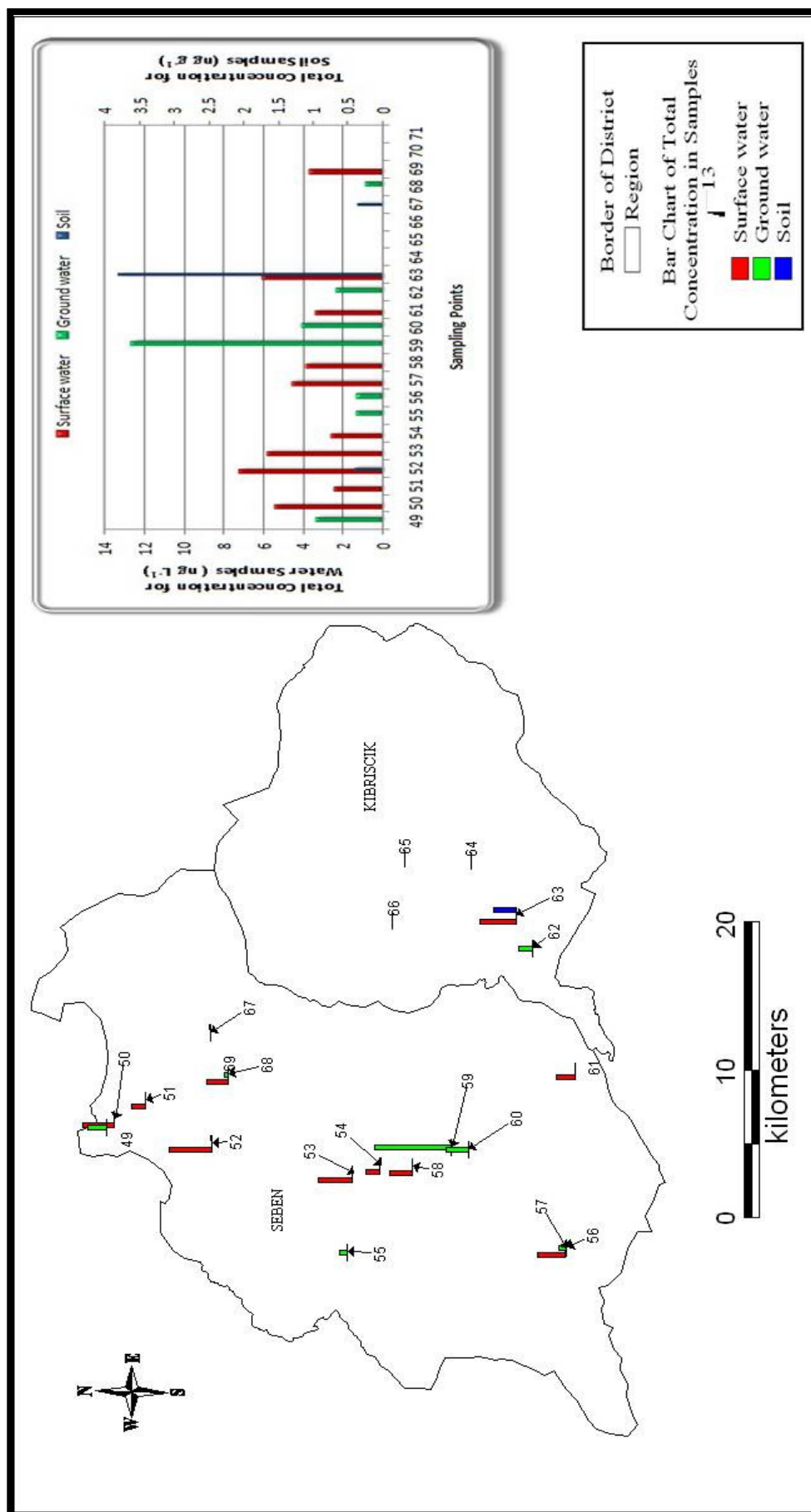


Figure 4.10. The total pesticide concentration in Seben and Kibriscik

4.4.2. Spatial Distributions by Contour Maps

In order to evaluate the pesticide pollution in five districts of Bolu, the spatial distribution of the each target analytes was presented by contour maps. By the help of these maps, the relationship between the observed concentration and the characteristics of sampling points will be seen in this section.

Endosulfan Isomers and Their Derivative

Commercial endosulfan contains endosulfan I and endosulfan II isomer in ratios from 2:1 to 7:3 depending on the technical mixture. These two isomers can be converted to endosulfan sulfate by oxidation in biotic and abiotic degradation. Although the usage of endosulfan is in discussion from 2007 in Turkey (Anonymous 14, 2010), endosulfan has still been used in agricultural activities. The aqueous solubility of endosulfan II is higher than endosulfan I and therefore, its partition to aqueous phases is easier to happen. Moreover, both endosulfan II and endosulfan sulfate are scavenged from the atmosphere easily by precipitation due to their higher solubilities than endosulfan I and so they can be carried to the surface water by long range transport (Chan et al., 1994, 2003). Technical endosulfan has been currently used in Bolu. In Figure 4.11, the percent occurrences of endosulfan isomers and their derivative in our samples were shown. The higher solubility of endosulfan II in water affected the percent observations (Figure 4.11), not mean concentrations (Figure 4.12) because of the low ratios in technical endosulfan. Endosulfan sulfate has also been identified as the main degradation product of endosulfan isomers in soil (Antonious and Byers, 1997; Ghadiri and Rose, 2001; Wan et al., 2005).

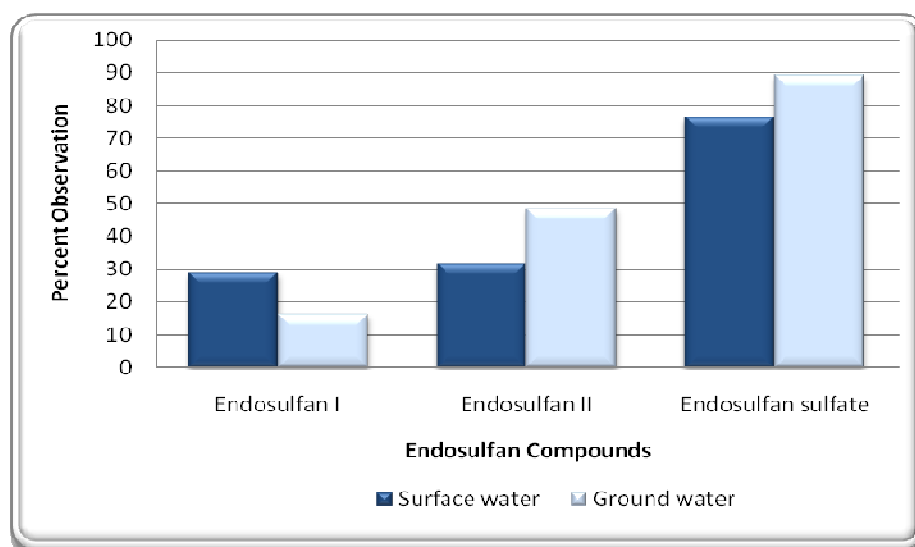


Figure 4.11. Percent occurrence of endosulfan isomers and its derivative in different water samples

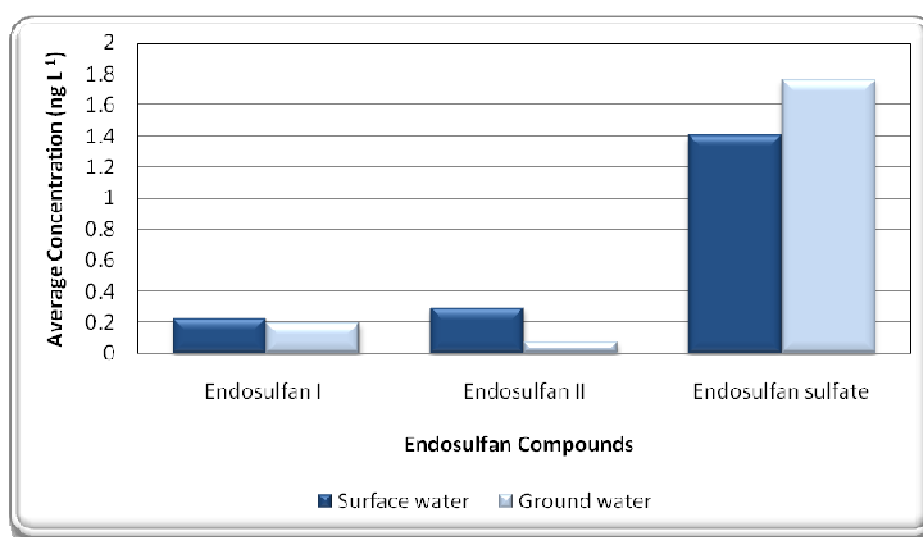


Figure 4.12. Average concentration of endosulfan isomers and its derivative in different water samples.

The spatial distributions of endosulfan II and endosulfan sulfate in surface water, ground water and soil samples are shown in Figure 4.13, 4.14, 4.15, 4.16, 4.17, 4.18. Generally, technical endosulfan is used for the production of apple, rice and vegetables which are mostly produced in Bolu. For that reason, the degradation

product endosulfan sulfate was seen mostly in ground water samples in all districts. However, endosulfan II concentrations in surface water samples in Seben (57,69) and endosulfan II concentrations in ground water samples in Mudurnu and agricultural areas in the city center (9, 10, 11, 21) show us the current usage of this pesticide in agriculture (Figure 4.13, 4.14). The data was filled with the detection limit values in non-detectable samples to draw the maps. The concentrations of endosulfan II in soil samples were higher in Mudurnu (Figure 4.15). Because of the low solubility in water, endosulfan I was not seen in many of the water samples. Endosulfan sulfate which is the degradation product of endosulfan isomer was mostly detected in surface (especially in Seben and Kırisciık) and ground water samples (in the city center) because of the past usage of endosulfan isomers (Figure 4.15, Figure 4.16).

Soil properties like higher water content can affect the endosulfan degradation (Weber et al., 2009). In Mudurnu the endosulfan sulfate and endosulfan II concentration in soil was higher than that in the other districts. Because the soil has higher water content in Mudurnu (Figure 4.18).

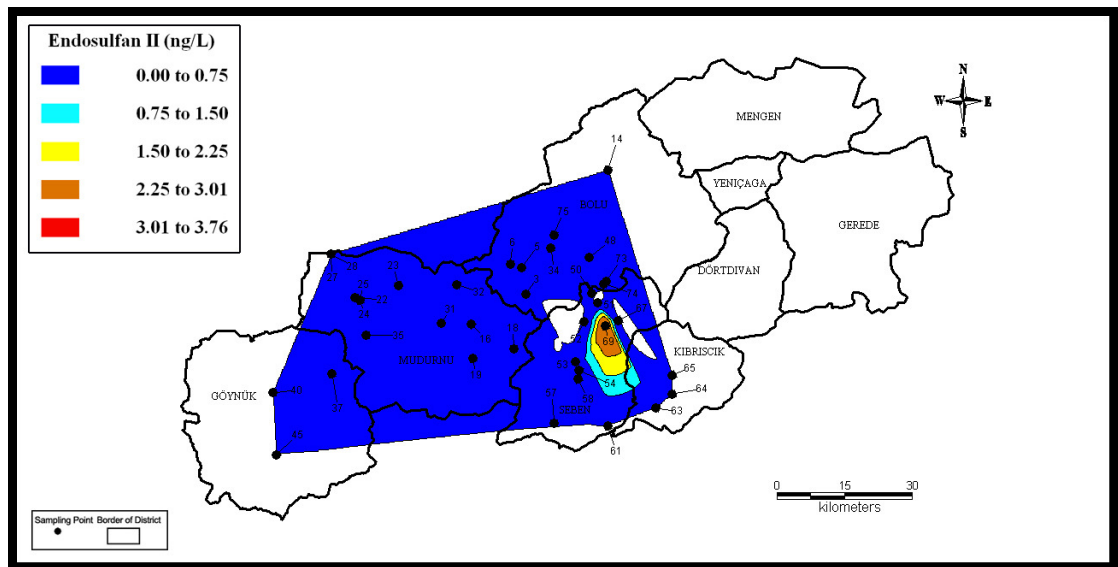


Figure 4.13. The spatial distribution of endosulfan II in surface water samples

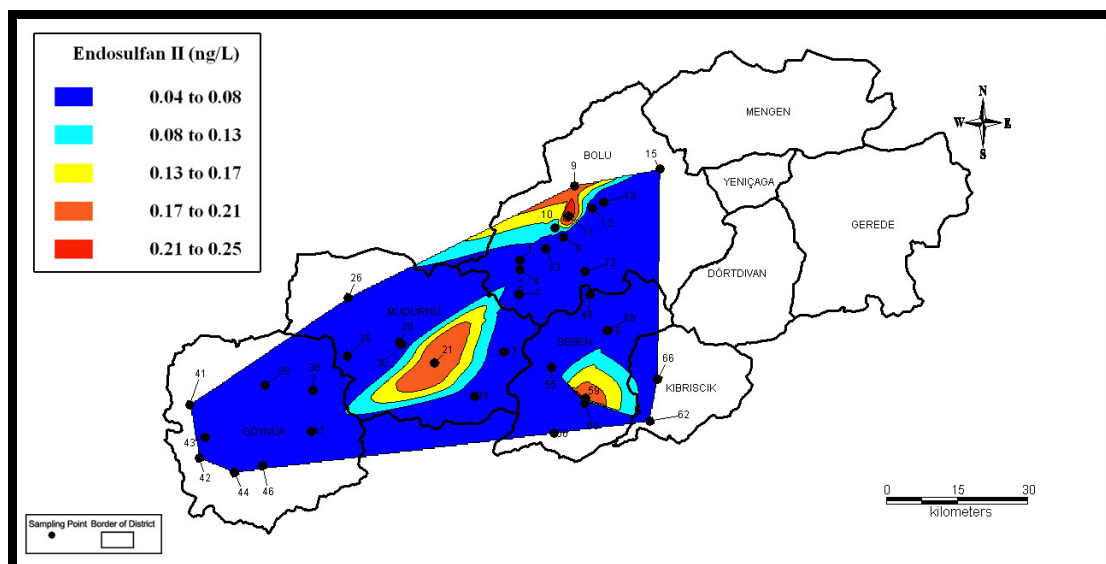


Figure 4.14. The spatial distribution of endosulfan II in ground water samples

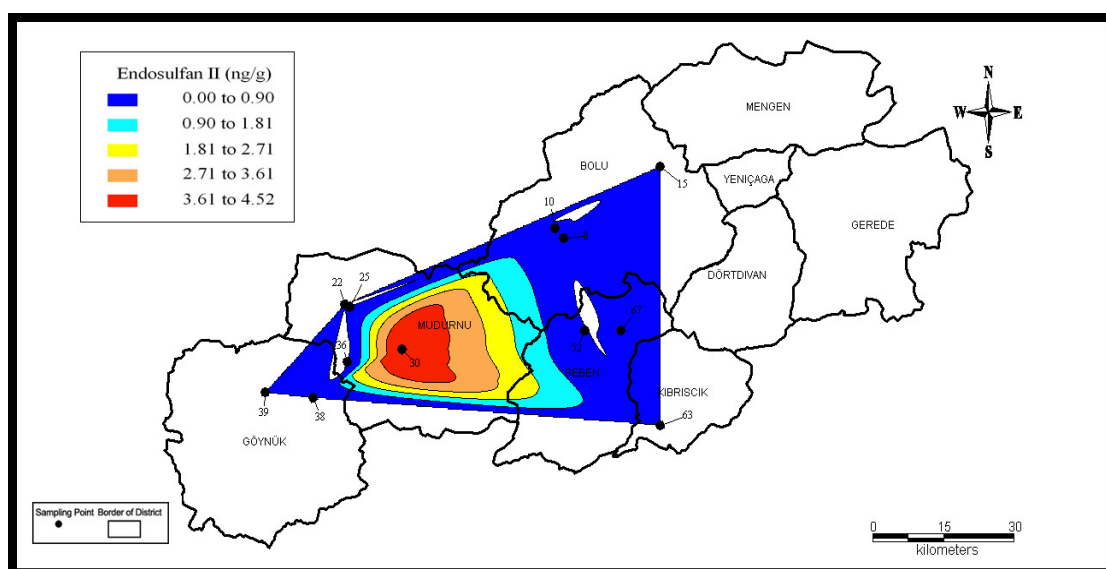


Figure 4.15. The spatial distribution of endosulfan II in soil samples

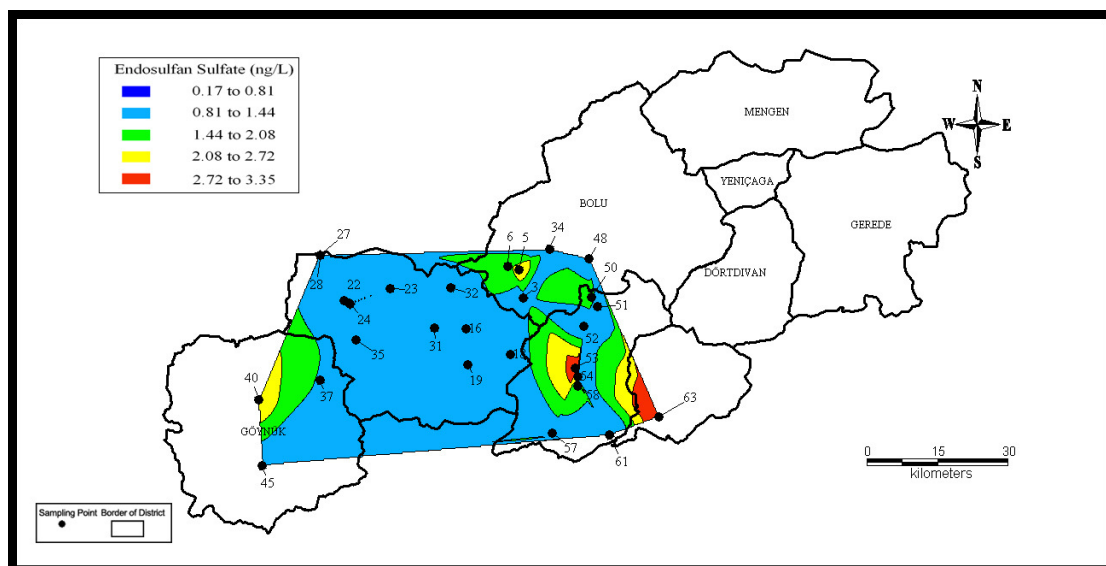


Figure 4.16. The spatial distribution of endosulfan sulfate in surface water samples

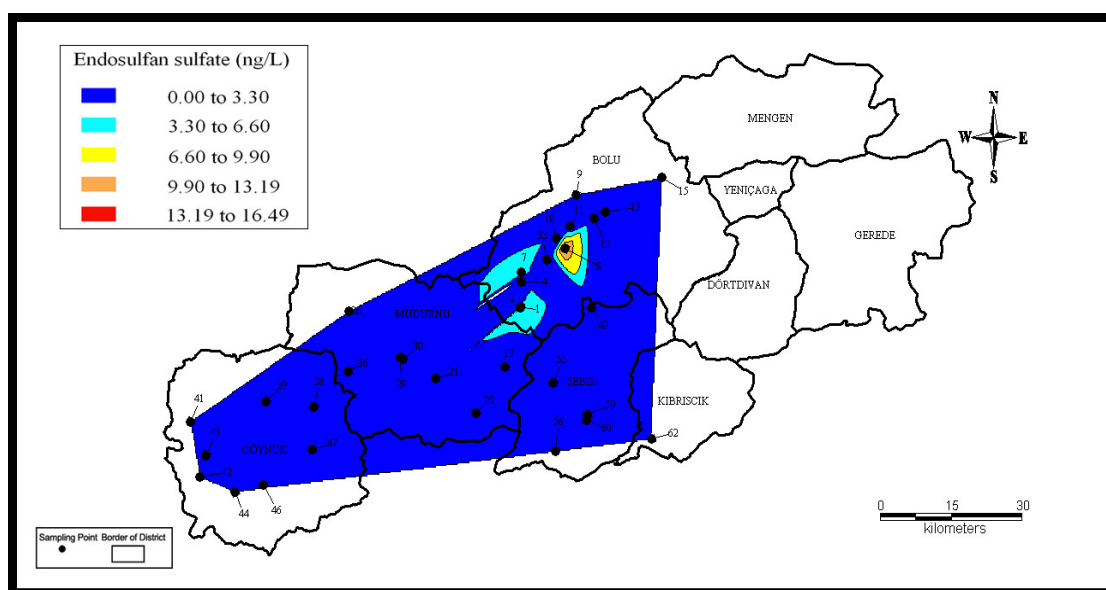


Figure 4.17. The spatial distribution of endosulfan sulfate in ground water samples

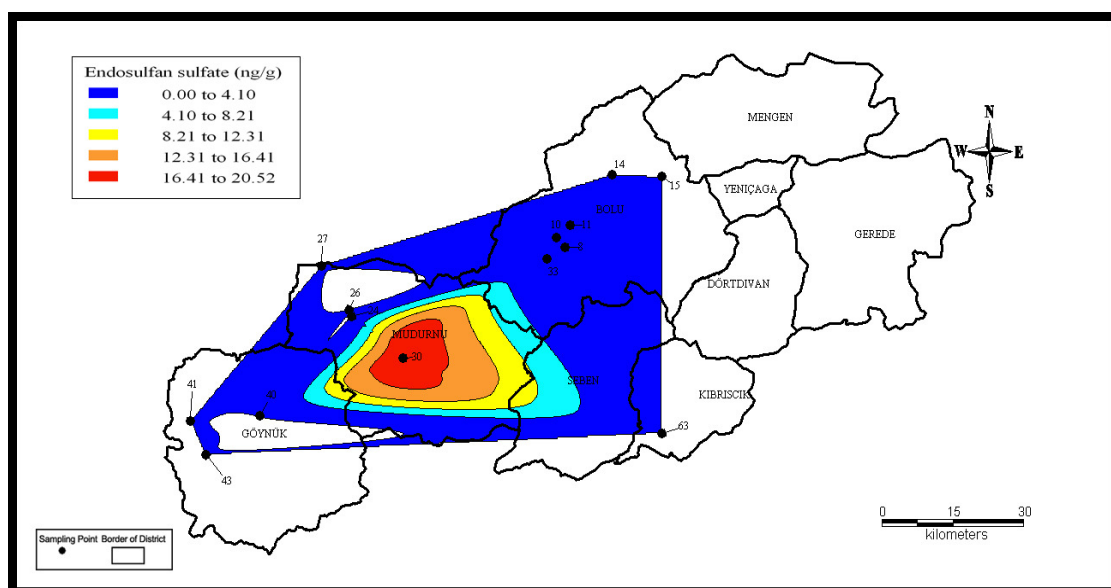


Figure 4.18. The spatial distribution of endosulfan sulfate in soil samples

Aldrin and Dieldrin

Under the most environmental conditions, aldrin is largely converted to dieldrin and dieldrin is significantly more persistent. Most environmental releases of aldrin and dieldrin are directly to soil. They have low water solubility and tendency to bind strongly to soils. Therefore, both compounds migrate downward very slowly through soils or into surface or ground water. Most surface water aldrin/dieldrin has been attributed to particulate by surface run-off. For this reason, it is possible that significant volatilization of aldrin/dieldrin might occur, with subsequent atmospheric photodegradation or rainfall (USEPA, 2003).

Aldrin was determined only in 1 samples. According to the local authorities aldrin has not been in use after the ban in 1980s. Therefore, the observed presence of aldrin can be explained by its past usage. In Figure 4.19, a comparison of observed concentration of aldrin and dieldrin was presented. This figure also supports the old usage of aldrin and its conversion to dieldrin. Figure 4.20 shows the spatial distribution of dieldrin in ground water samples. The data was filled with half of the

detection limit values in non-detectable samples to draw the maps. Because of the low observation of aldrin, the concentrations can not be interpolated in drawing maps. From the map, it can be understood that the concentrations of dieldrin were high in agricultural areas due to its past usage. Dieldrin can be detected in 4 sampling points. In the sampling point 9 (Köprücüler), dieldrin concentrations were higher than the other ground water samples. In surface water samples and soil, dieldrin can not be detected in 5 districts of Bolu.

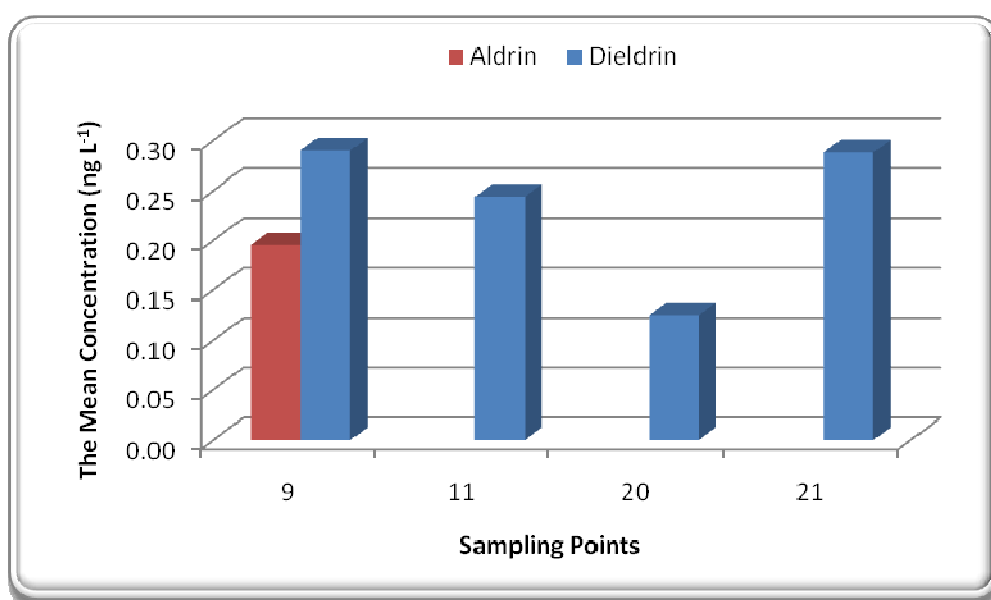


Figure 4.19. The mean concentrations of aldrin and dieldrin in all water samples

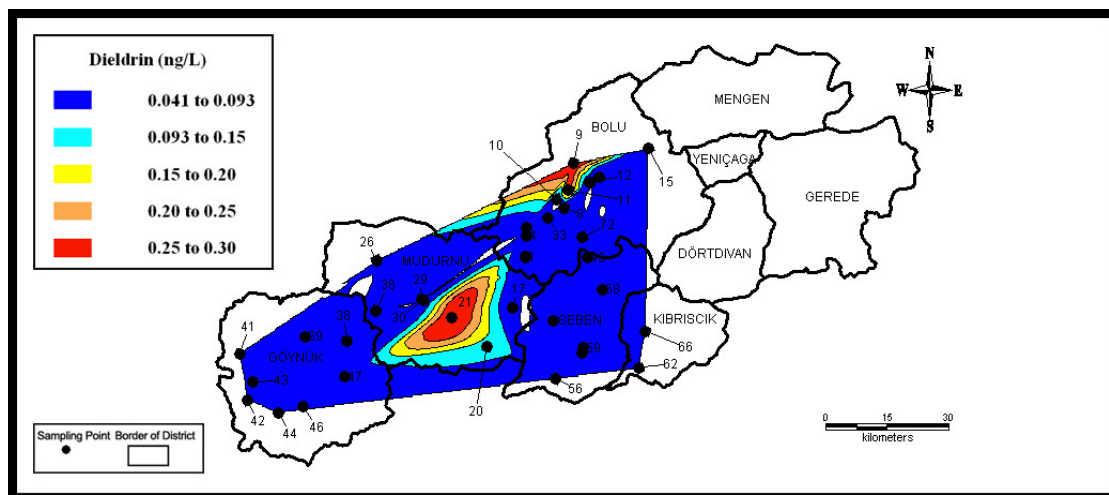


Figure 4.20. The spatial distribution of dieldrin in ground water samples

Hexachlorobenzene isomers (HCHs)

Because of the toxicological and environmental effect of the HCHs, the environmental chemists and toxicologists study about them. It was used as an insecticide in wheat production. HCHs were one of the most widely used organochlorine pesticides and they have relatively high volatility, they can be found in any environmental samples and also in pristine locations like Arctics (Willett et al., 1998). In technical grade HCH, α to γ -isomer ratio is between the 3 and 7. Global sources of HCH and the transfer of HCHs away from the source can be evaluated by using the α to γ -isomer ratios. For example, a current usage of lindane (γ -HCH) shows this ratio near or less than unity (Hargrave et al., 1988). Therefore, higher α to γ ratios in water samples can be explained by differential gas exchange across air-water interfaces, washout by precipitation or volatilization- adsorption variations between the isomers (Iwata et al., 1993). For that reason, by using the water samples in which α and γ -isomer were determined, a graph was drawn for two sample types (Figure 4.21 and 4.22). α to γ isomer ratios in Bolu were between 0.65 and 5.45 in

surface water samples. Besides the high wheat production areas in the sampling point like 31, 34, 35 and 63, high α to γ - isomer ratios can also be seen in nonagricultural region like Abant Lake (32), Seben Lake (52). Especially, Seben Lake is a new artificial lake and this lake is filled with snow water. Long range transport can be effective in this lake. For ground water samples, α to γ - isomer ratios were between 0.44 and 0.77. In some sampling points, all isomers were seen. The percent contributions of samples are presented in Figure 4.23. The major constituent of surface water was α -HCH. The higher existence of α -HCH in surface water indicated the photo degradation of lindane (Willett et al., 1998; Rissato et al., 2006). In ground water samples, major constituent is δ -HCH. γ -HCH can be transformed into α -HCH or δ -HCH by nonenantioselective isomerization during incubation, though the rate of conversion was extremely slow (Buser and Muller, 1995). High constituent of δ -HCH in ground waters in this study indicated that the transformation of lindane was dominant.

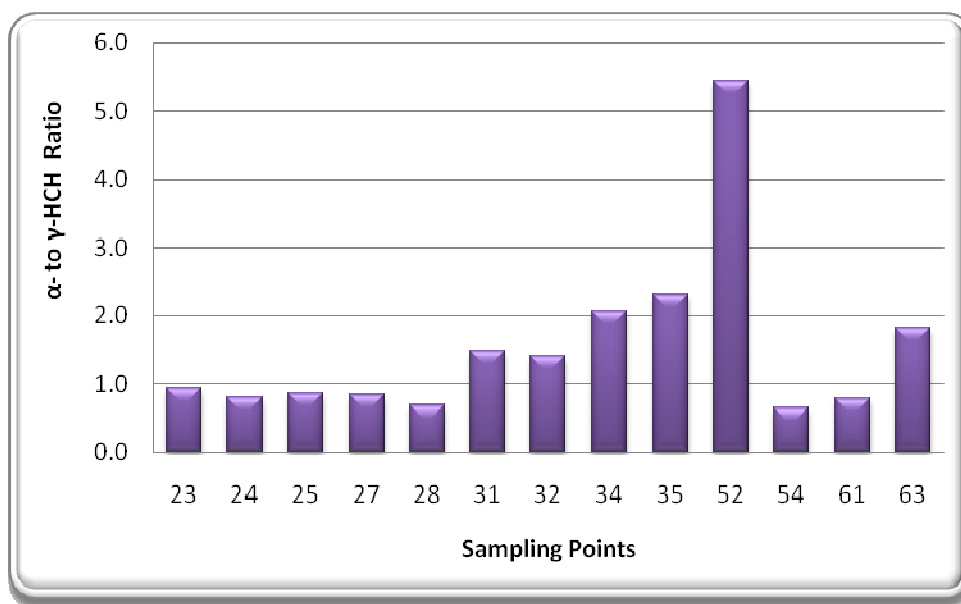


Figure 4.21. α to γ ratios of HCHs in surface water samples

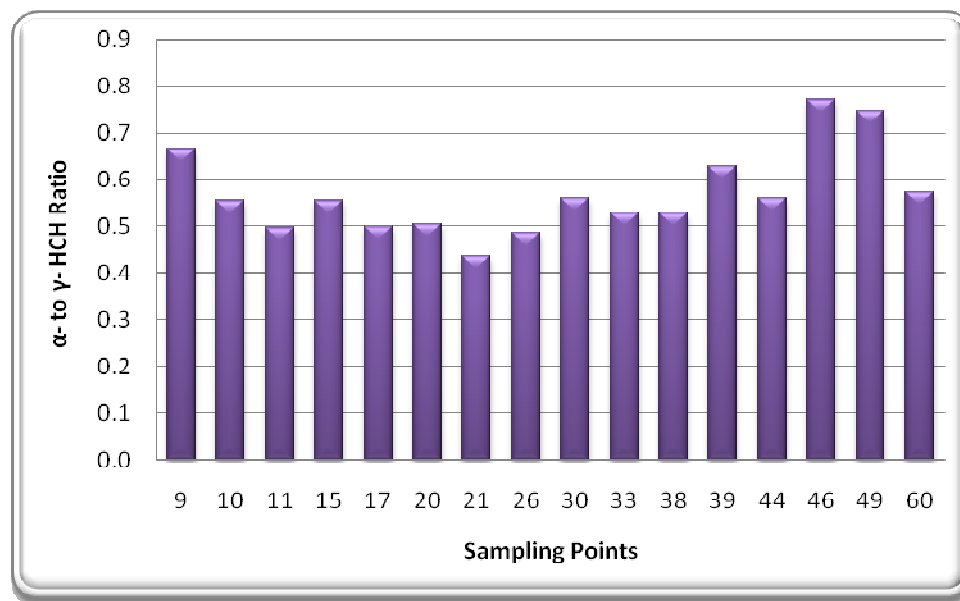


Figure 4.22. α to γ - ratios of HCHs in ground water samples

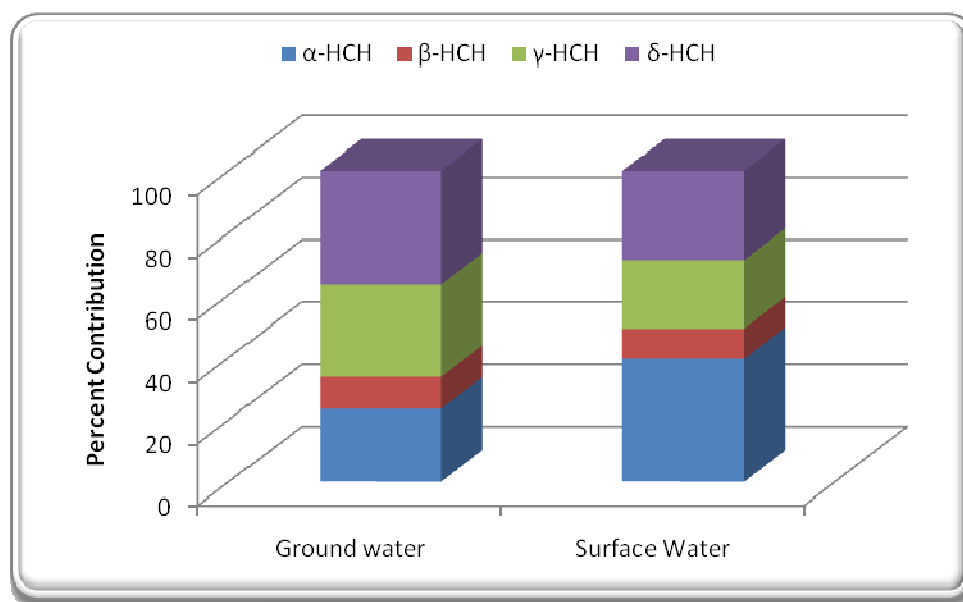


Figure 4.23. The distribution of isomers in samples taken from Bolu

The Figures 4.24 and 4.25 show us the spatial distribution of α - isomer in surface and ground water samples. α -HCH concentrations in surface and ground water samples can be determined in even nonagricultural areas. Especially nonagricultural areas between the Seben and city center (like the sampling point 14,

and 52) (Figure 4.24) were more affected. In ground water samples, the samples taken from the sampling point 49 (nonagricultural area in Seben) and the sampling point 9 (agricultural area in the city center) contained the highest concentrations of α -HCH (Figure 4.25). β -HCH concentrations were higher in the city center in surface and ground water samples (Figure 4.26 and 4.27). The data was filled with half of the detection limit values in non-detectable samples to draw the maps. γ -HCH was high in surface water samples (nonagricultural sampling point 50, 52 in Seben, agricultural sampling point 31 in Mudurnu), ground water sample (sampling point 9 in the city center) and soil sample (sampling point 10 in the city center) (Figures 4.30, 4.31 and 4.32). The maps in Figure 4.28 and 4.29 filled by half of detection limit in non-detectable samples. The map in Figure 4.30 filled by detection limit in non-detectable samples. δ -HCH was detected in 5 district of Bolu in surface and ground water samples. The highest concentration of δ -HCH was seen in Mudurnu for surface water sample (Figure 4.31) and in the city center in ground water sample (Figure 4.32).

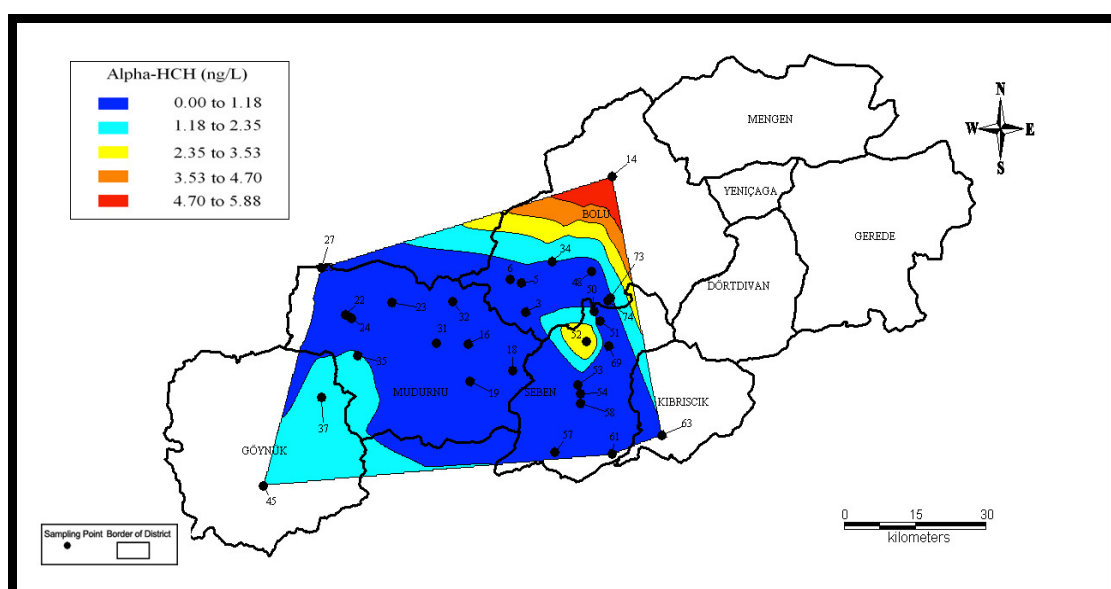


Figure 4.24. The spatial distribution of α -HCH in surface water samples

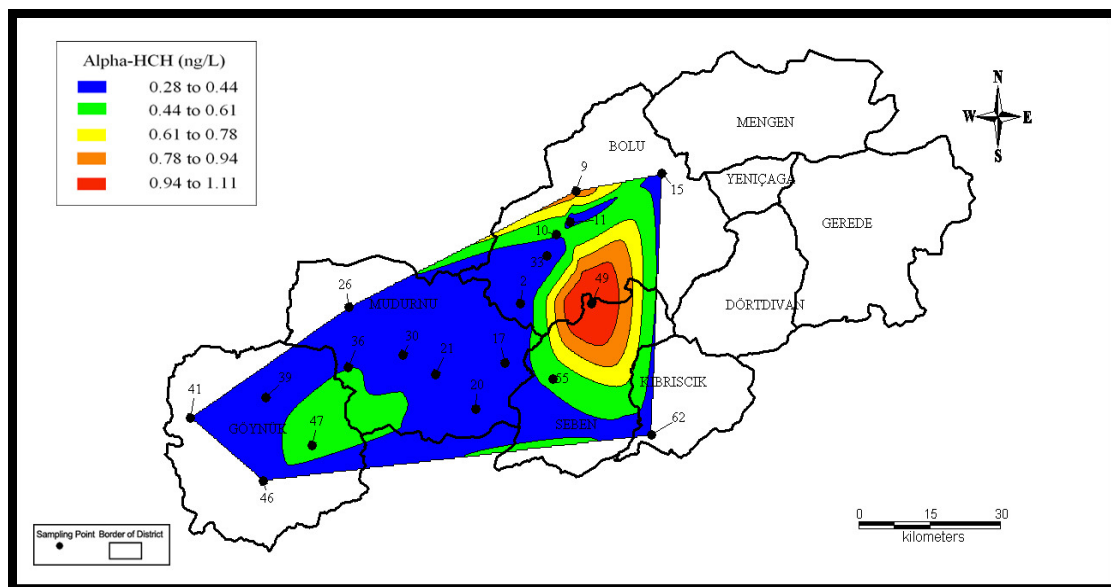


Figure 4.25. The spatial distribution of α -HCH in ground water samples

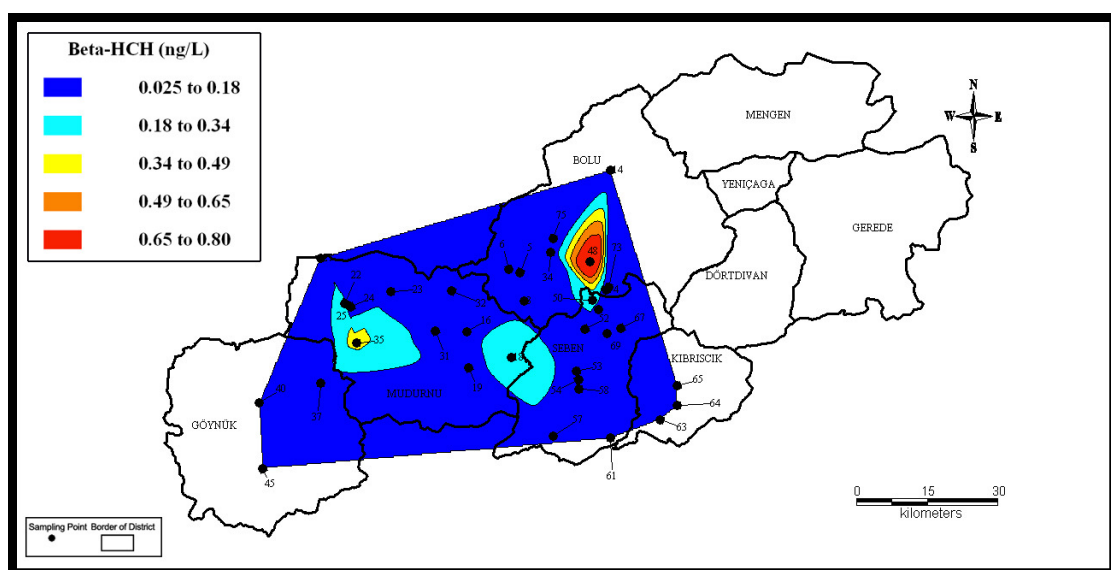


Figure 4.26. The spatial distribution of β -HCH in surface water samples

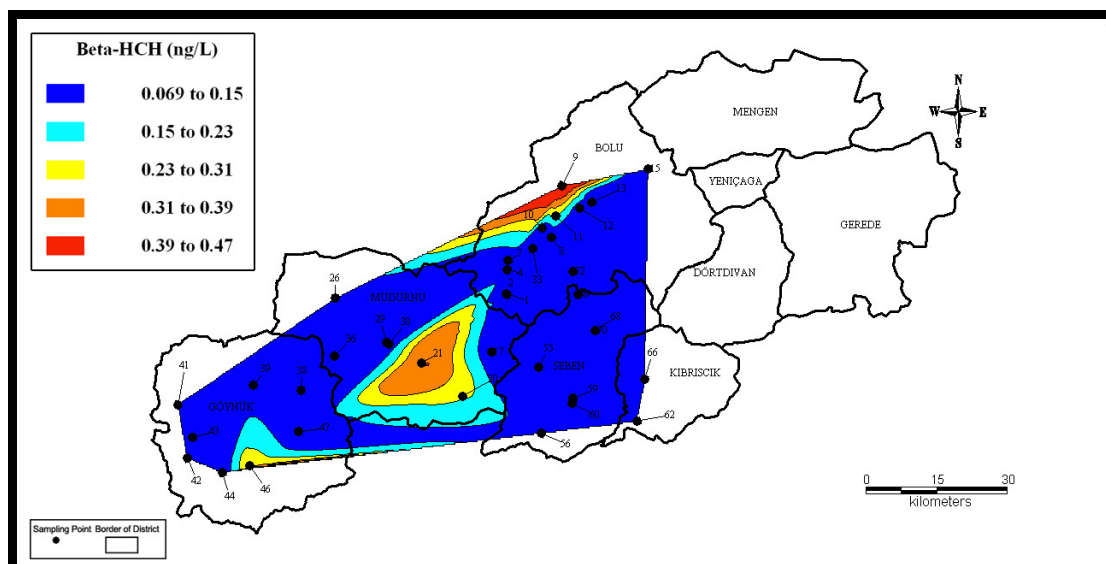


Figure 4.27. The spatial distribution of β -HCH in ground water samples

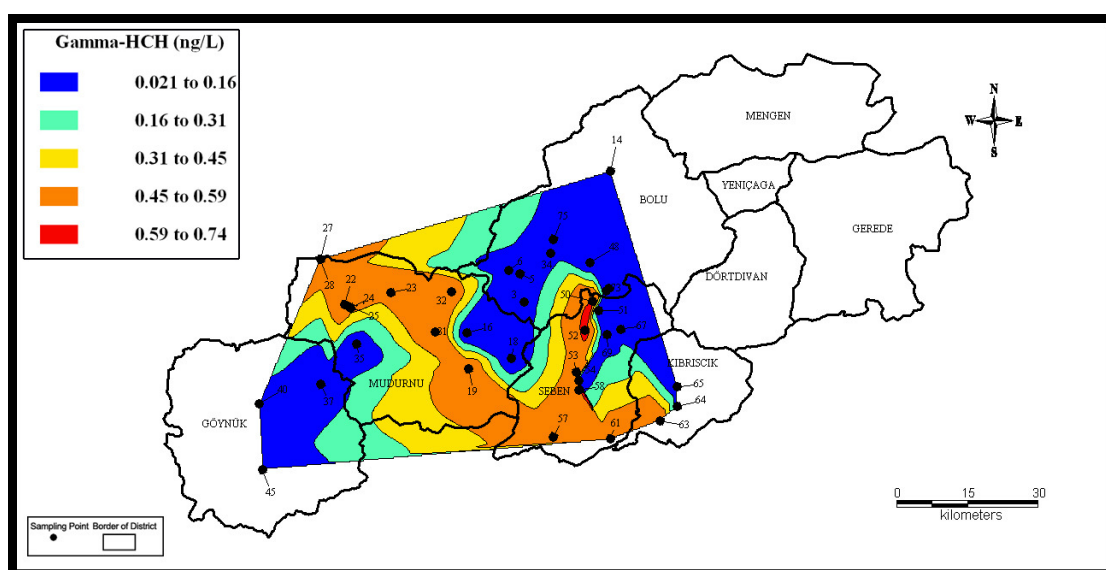


Figure 4.28. The spatial distribution of γ -HCH in surface water samples

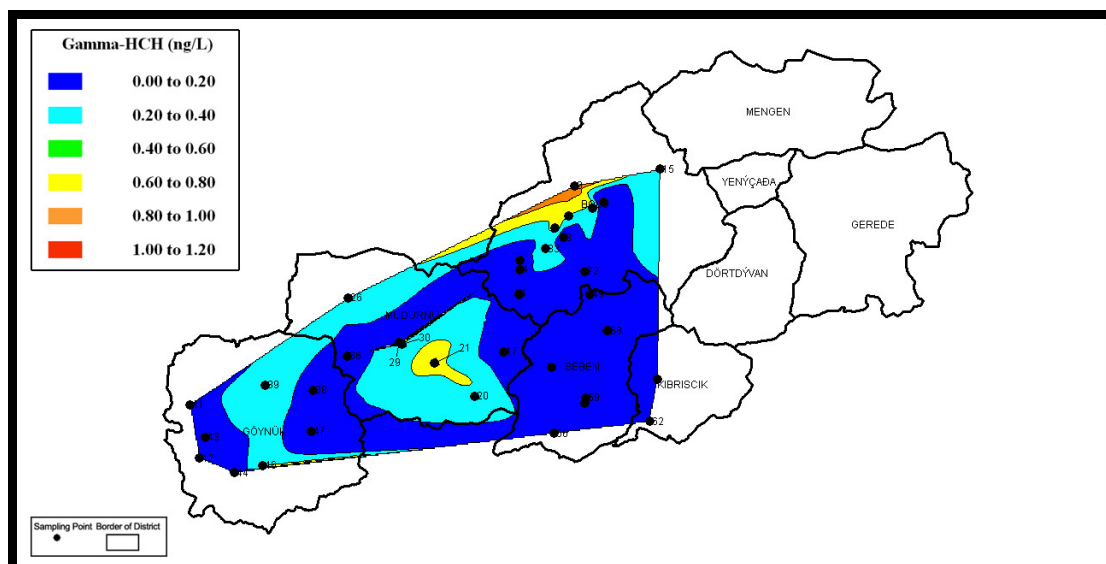


Figure 4.29. The spatial distribution of γ -HCH in ground water samples

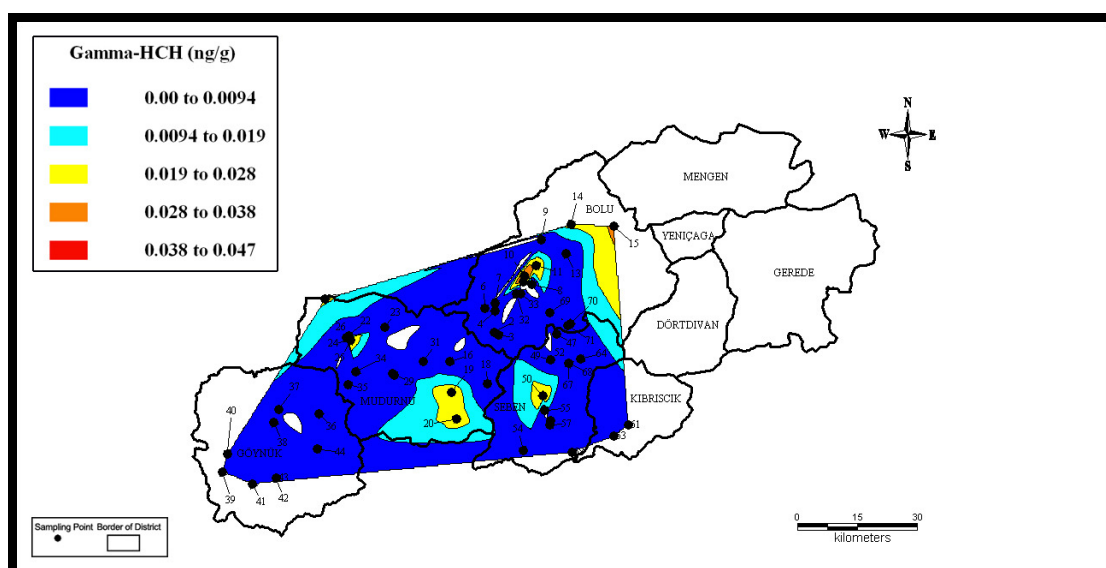


Figure 4.30. The spatial distribution of γ -HCH in soil water samples

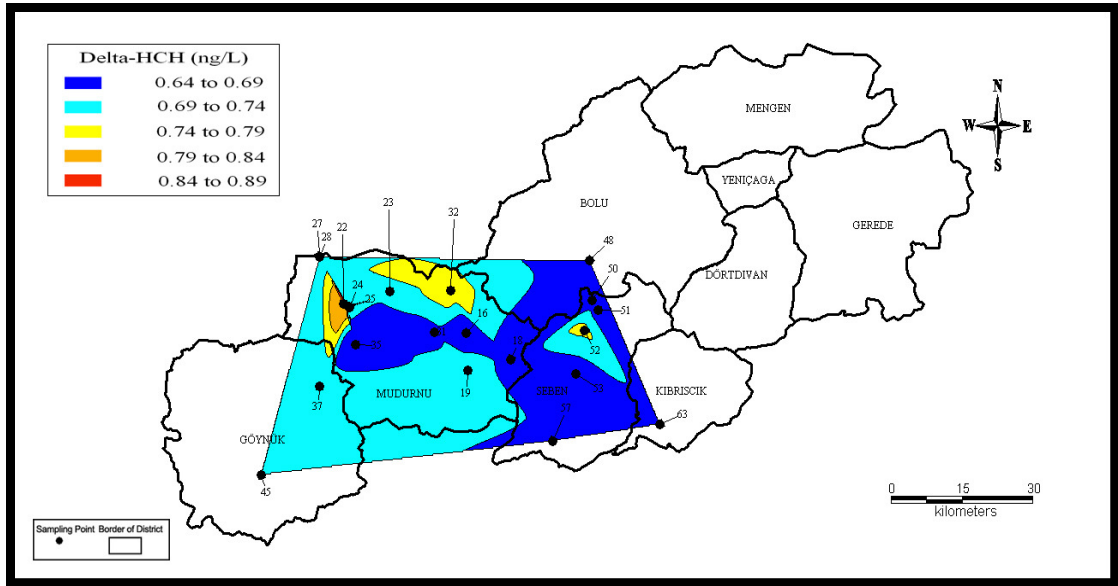


Figure 4.31. The spatial distribution of δ -HCH in surface water samples

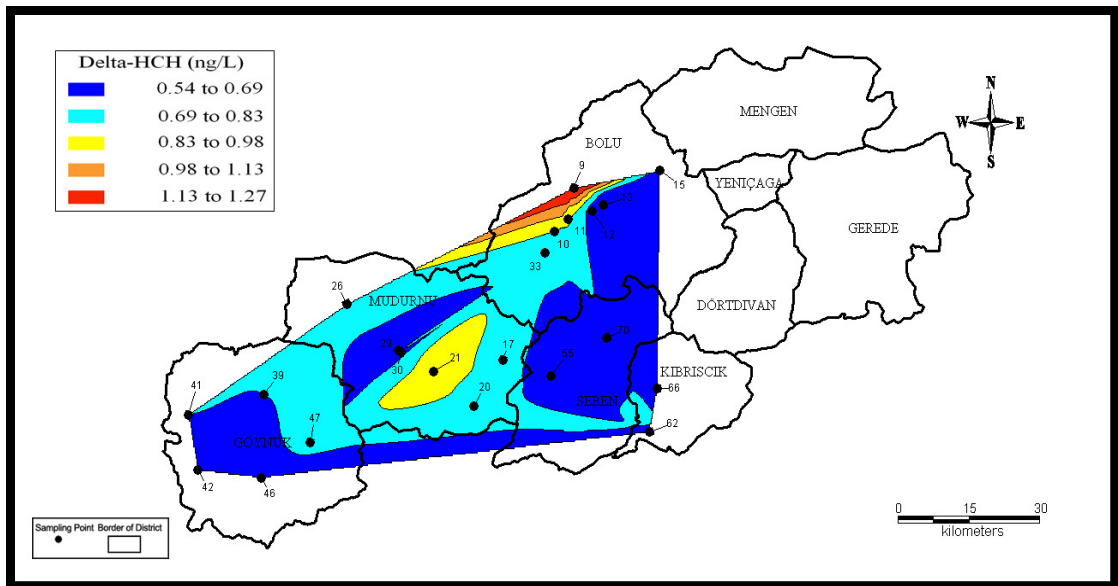


Figure 4.32. The spatial distribution of δ -HCH in ground water samples

Endrin

Endrin is very insoluble in water. Detection of endrin in ground and surface water are rare. Although endrin has low volatility, it was found at higher concentration in the air during its manufacture. It was never found in urban areas

where it was rarely used (ATSDR, 1996). Endrin was used in the production of sugar cone, gran crops, sugar beet and rice as an insecticide. These plants are produced in the sampling region of this study (DPT, 2002).

Endrin was found in some of the water samples in Bolu. The old usage of endrin can be the reason of presence in water samples. Figure 4.35 and Figure 4.36 show the spatial distribution of endrin concentration in surface and ground water samples. The data was filled with half of the detection limit values in non-detectable samples to draw the maps. According to these figures, the endrin concentrations in surface water were high in agricultural region in Mudurnu (sampling points 22, 24, 25). It was also seen in nonagricultural region like 53. Endrin can also be seen in ground water samples. In Seben, the grain production is performed. The ground water sample taken from the sampling point 59 in an agricultural area. Seben had the highest endrin concentration in this study. Endrin degradation in soil does not appear significantly. About 41% of applied endrin can remain in a field until 14 years (Nash and Woolson, 1967). Endrin can not be detected in any soil samples. It was thought that it was carried from atmosphere to water bodies.

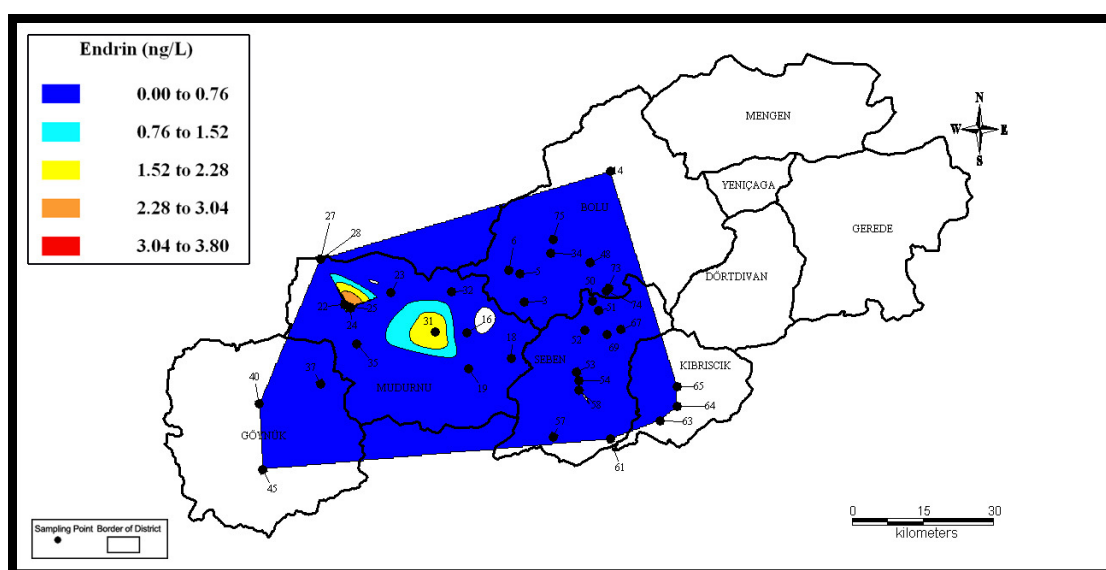


Figure 4.33. The spatial distribution of endrin in surface water samples

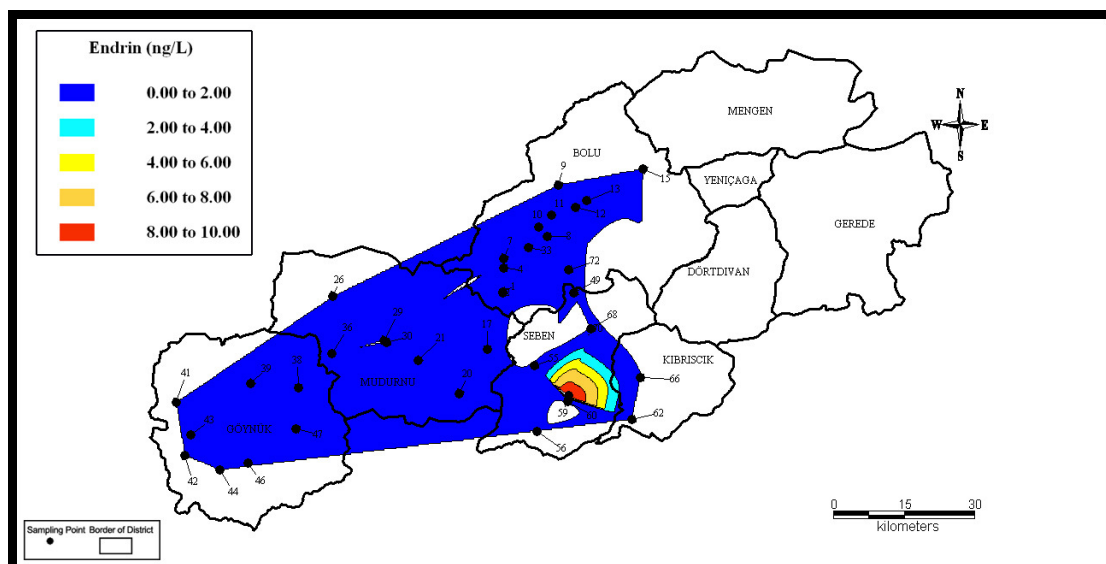


Figure 4.34. The spatial distribution of endrin in ground water samples

4,4' DDT, 4,4' DDE, 4,4' DDD

DDT can contaminate to surface waters primarily by run-off, atmospheric transport, drift or by direct application. DDT is persistent in soil and does not move easily to groundwater (EPA, 1993). The ratios of DDT/ (DDD+DDE) and DDE/DDD have been used to indicate the degree of DDT composition and to find a sign for fresh input of DDTs. If the ratio is higher than unity, the fresh usage of this pesticides can be possible (Lee et al., 2001). The DDT/ (DDD+DDE) ratios were changing from 3.9 to 61.1 in surface water samples and from 0.9 to 40.6 in ground water samples in summer season. Besides the persistency of DDT, it was used in very huge amounts in this area, illegal usage of DDT is also possible in our country (Anonymous 15, 2010) and the results of this study can show us some possible fresh inputs of DDTs in this region. The Figure 4.35, 4.36, 4.37, 4.38, 4.39, 4.40., 4.41, 4.42, 4.43 show the spatial distribution of 4,4' DDT, 4,4' DDE and 4,4' DDD concentrations. The data was filled with the detection limit values in non-detectable samples to draw the maps. As shown in Figures 4.35 and 4.36, 4,4' DDT can be seen

almost in all samples. It can be seen in agricultural areas like 9, 59 or nonagricultural area like Abant Lake (32). 4,4' DDE and 4,4' DDD can also be seen in an abandoned agricultural areas because of the huge amount past usage of DDT.

DDT is persistent in soil and does not leach or move easily to groundwater. Routes of loss and degradation include runoff, volatilization, photolysis and biodegradation (under aerobic condition to DDE and under anaerobic condition to DDD) (Hong et al., 1999; Doong et al., 2002; Zhou et al., 2006). These processes generally occur very slowly. DDE and DDD are the initial breakdown products of DDT in the soil environment. In our study, 4,4' DDE, 4,4' DDT and 4,4' DDD were also seen in some of soil samples like the samples taken from the sampling point 8, 9, 10, 11, 21, 26, 27. 4,4' DDT concentrations in ground water samples was in sampling point 9, 7, 41, 42, 59, 60. In surface water samples in the sampling point 25, 24 and 22 had highest concentration. This pesticides can seen in soil samples taken from the sampling point in 11. DDD in surface and ground water samples were higher in the city center (Figure 4.38 and 4.39). The highest concentration in DDD was seen in the sampling point 11 in the city center (Figure 4.40) and DDE can be observe in the city center and Mudurnu (Figure 4.41, 4.42, 4.43). The data was filled with half of the detection limit values in non-detectable samples to draw the maps.

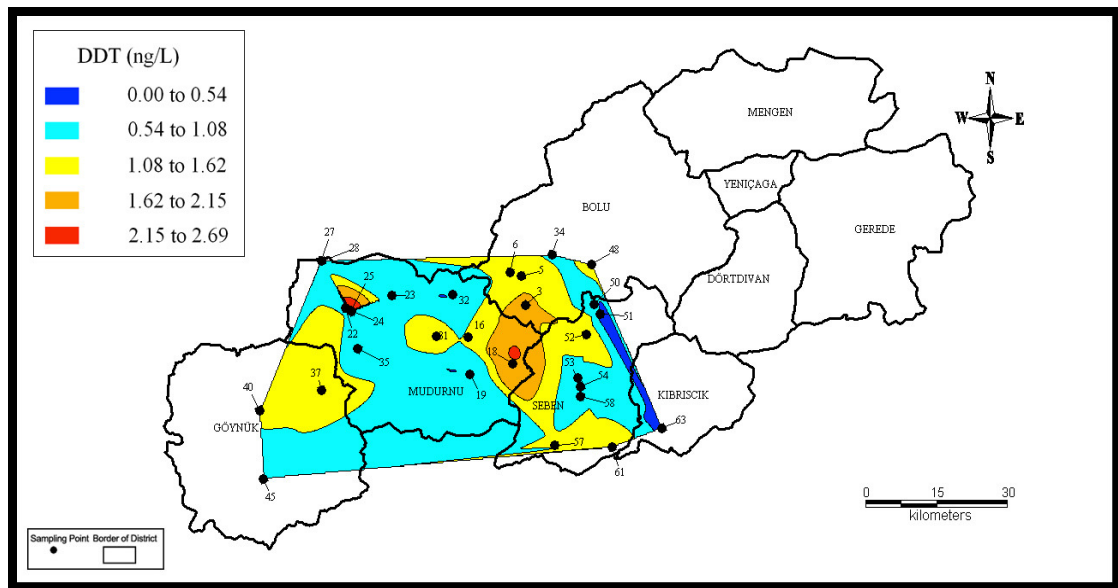


Figure 4.35 . The spatial distribution of 4,4' DDT in surface water samples

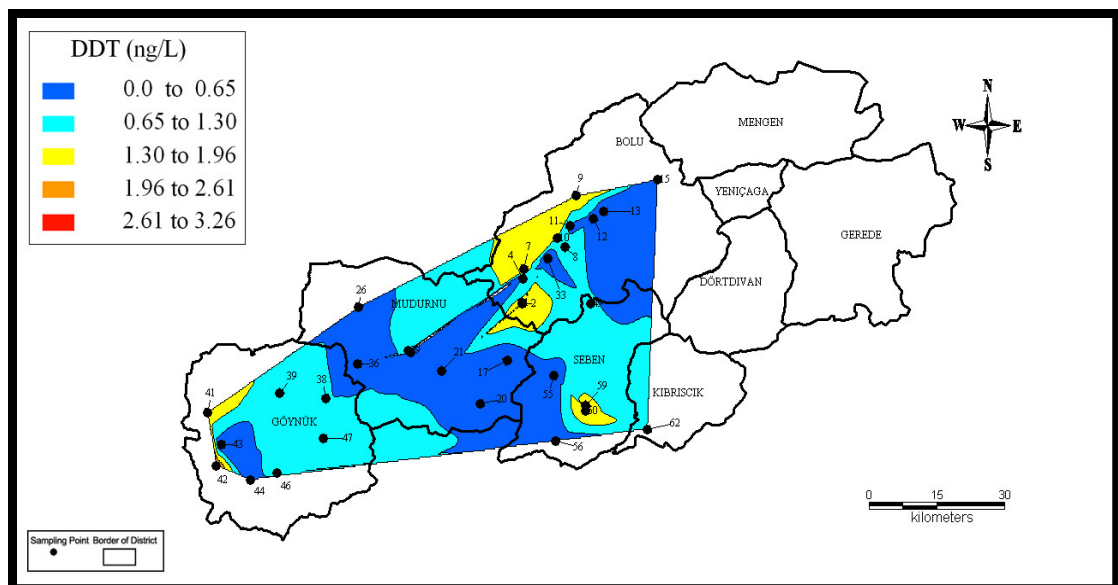


Figure 4.36. The spatial distribution of 4,4' DDT in ground water samples

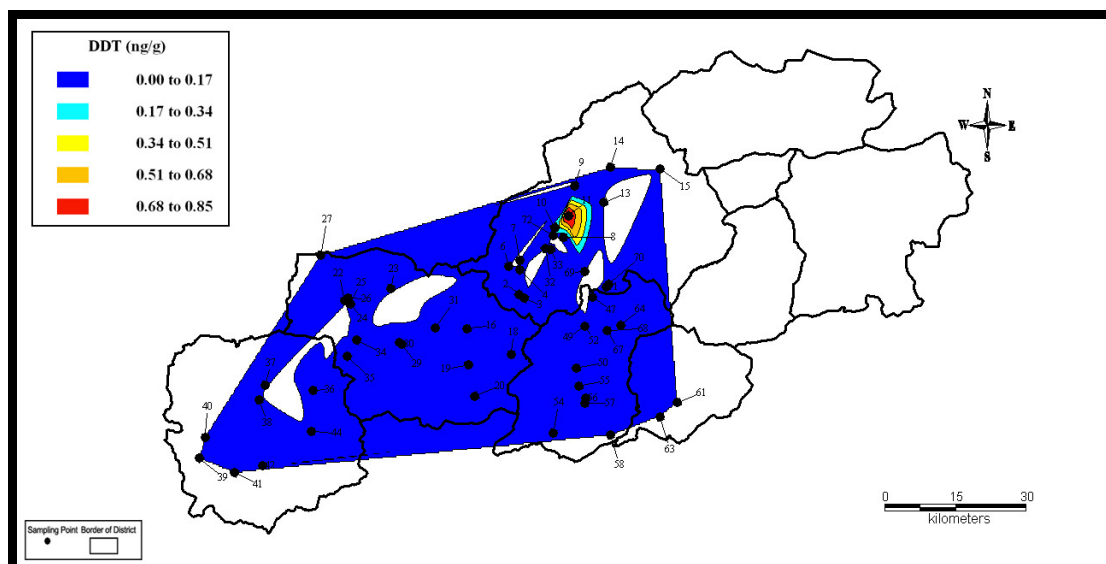


Figure 4.37. The spatial distribution of 4,4' DDT in soil samples

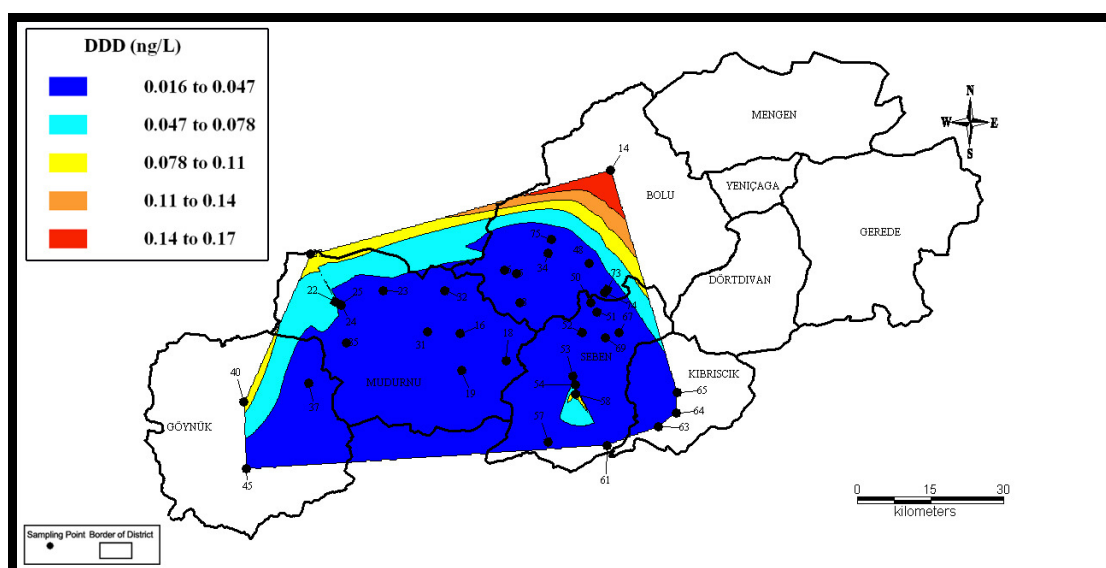


Figure 4.38. The spatial distribution of 4,4' DDD in surface water samples

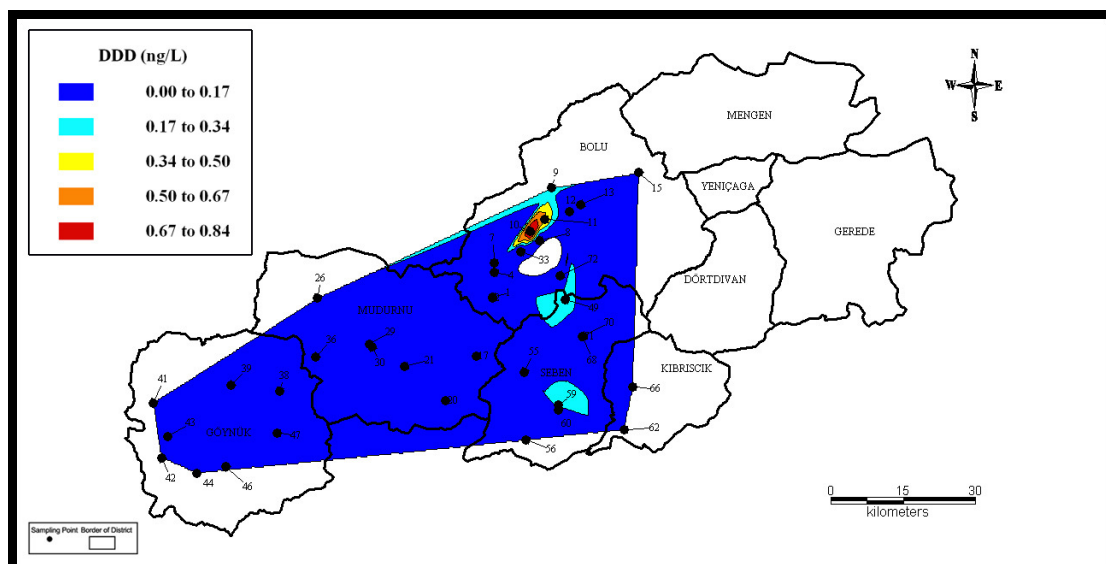


Figure 4.39. The spatial distribution of 4,4' DDD in ground water samples

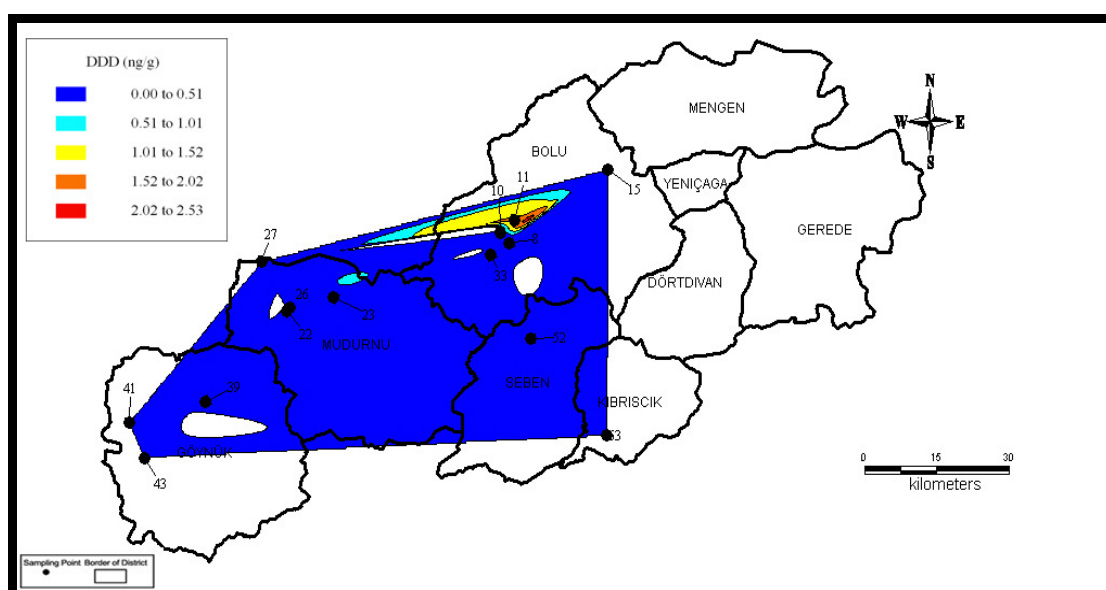


Figure 4.40. The spatial distribution of 4,4' DDD in soil samples

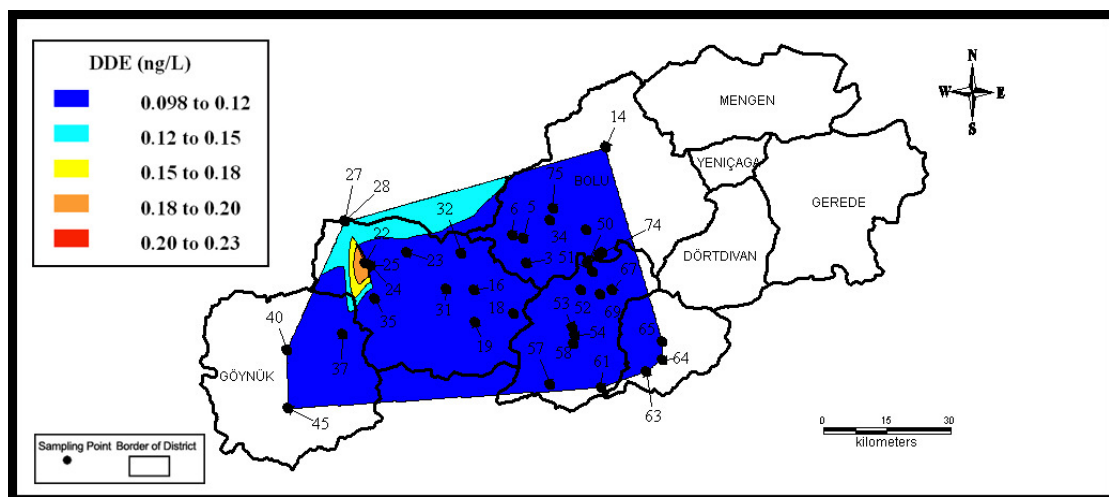


Figure 4.41. The spatial distribution of 4,4' DDE in surface water samples

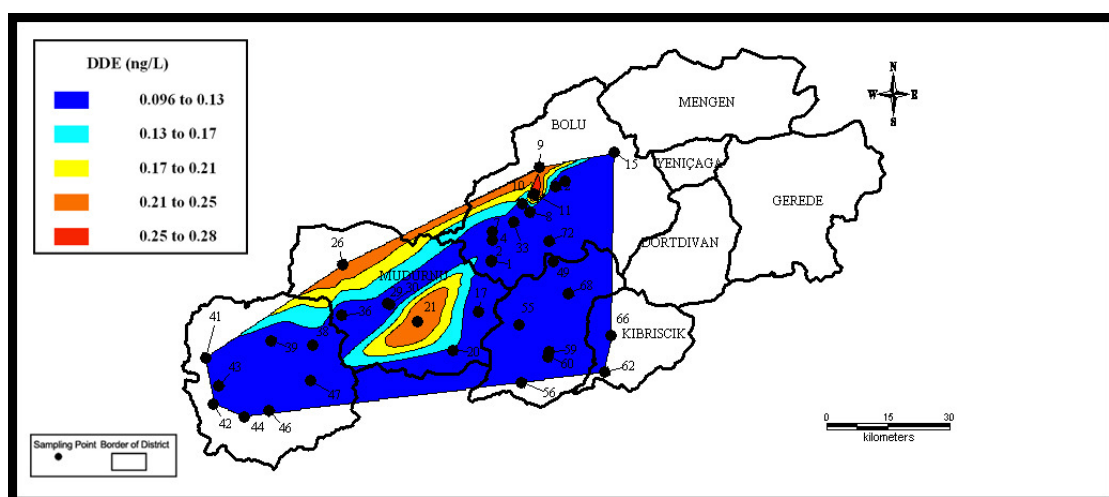


Figure 4.42. The spatial distribution of 4,4' DDE in ground water samples

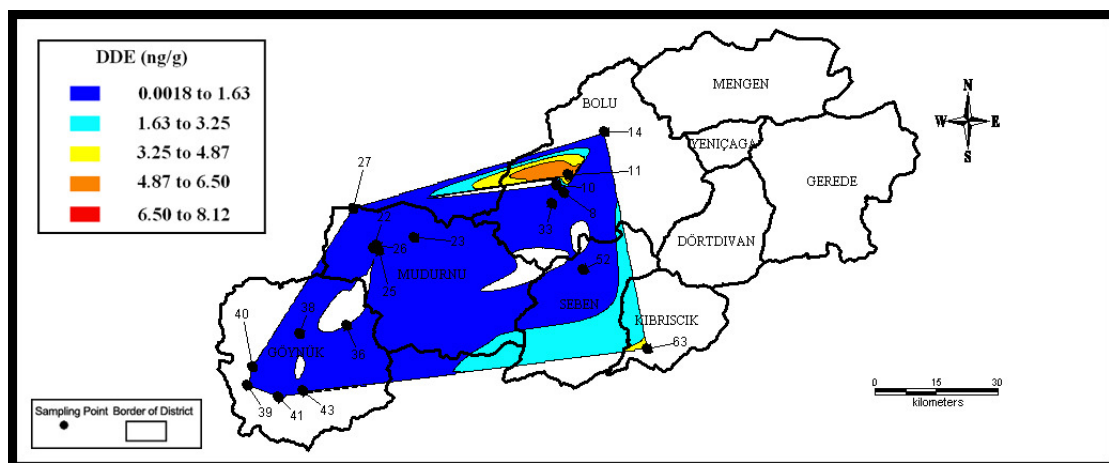


Figure 4.43. The spatial distribution of 4,4' DDE in soil samples

CHAPTER 5

CONCLUSION

In this study, the determination of concentrations of OCPs in surface water, ground water and soil samples was performed. The sampling was performed in the city center, Seben, Kıbrısık, Göynük, Mudurnu in Bolu. To observe the seasonal changes, the sampling was repeated just in the city center of Bolu. SPE and UE techniques were used for the extraction of compounds from water and soil samples, respectively. The samples were analyzed by GC-ECD. It was possible to determine the concentrations of 13 OCPs in water samples, 11 OCPs in soil samples.

The spiked samples were used for recovery tests. The recoveries were ranging from 72 to 108% for water sample and from 40 to 131% in soil samples. They were generally in the limit of acceptance (70- 130%) according to EPA except for aldrin, heptachlor epoxide, dieldrin in soil samples.

The usage of the OCP compounds except for endosulfan was banned in Turkey. However, some of them are still in use or illegally used. Although these compounds were not water soluble, they can be detected in surface and ground water samples and soil samples in the world. In surface water samples, endosulfan sulfate had the highest average concentration. The percent observations were changing between 2.7-86.5%.

The highest percent observation belonged to α -HCH. Endosulfan I had the lowest percent observation. In ground water samples, the percent observation was between 2.7-85%. Endosulfan sulfate and 4,4' DDT had the highest percent observations. The most observed OCPs in ground water samples were endosulfan sulfate and 4,4' DDT in the autumn season.

Seasonal variations can be seen in city center water and soil samples. According to the median values of the summer and autumn seasons, the concentrations of endosulfan sulfate and 4, 4' DDT were higher in the autumn than summer. δ -HCH, aldrin, endosulfan I and II and dieldrin were not observed in autumn samples. In soil samples, the concentrations of 4,4' DDT were higher in autumn season.

The spatial distributions were evaluated by using contour maps and graphs. Endosulfan is currently used in Bolu and for this reason it was mostly determined in 5 districts. Although the usage of 4, 4' DDT was banned, it was also observed generally in Bolu. It showed us the possibility of current usage of this pesticide. Generally, districts of Bolu were affected by the pesticides which is used agricultural usage.

The concentrations were less than the 100 ng L^{-1} which is the limit of European Union for each pesticides in water sources. Soil and water samples had lower concentration than the literature values.

APPENDICES

Appendix I: Information about the sampling points

Number	District	Height	N Coordinates	E Coordinates
1	City center	1390	40.59005	31.45163
2	City center	1392	40.58825	31.45172
3	City center	1548	40.58192	31.46443
4	City center	883	40.63532	31.45368
5	City center	883	40.63532	31.45368
6	City center	1258	40.64135	31.42483
7	City center	1018	40.65305	31.45460
8	City center	710	40.69593	31.56285
9	City center	711	40.79445	31.59038
10	City center	748	40.71388	31.54132
11	City center	791	40.73645	31.57485
12	City center	757	40.75085	31.63508
13	City center	774	40.76368	31.66315
14	City center	1159	40.82933	31.67915
15	City center	653	40.82543	31.80410
16	Mudurnu	888	40.52305	31.32038
17	Mudurnu	992	40.47983	31.41363
18	Mudurnu	965	40.47417	31.43220
19	Mudurnu	1112	40.45518	31.32572
20	Mudurnu	1217	40.39557	31.34140
21	Mudurnu	1105	40.45867	31.24025
22	Mudurnu	508	40.57600	31.01642
23	Mudurnu	756	40.59927	31.13132
24	Mudurnu	535	40.57062	31.03080
25	Mudurnu	531	40.57128	31.02972
26	Mudurnu	520	40.58160	31.02452
27	Mudurnu	701	40.66267	30.95527
28	Mudurnu	701	40.66267	30.95527
29	Mudurnu	765	40.49730	31.15240
30	Mudurnu	740	40.49387	31.15928
31	Mudurnu	796	40.52413	31.24262
32	Mudurnu	1333	40.60127	31.28190
33	City center	814	40.67472	31.51728
34	City center	860	40.67390	31.52990
35	Göynük	642	40.50148	31.04530
36	Göynük	684	40.47173	31.02212
37	Göynük	1063	40.42505	30.95695

Number	District	Height	N Coordinates	E Coordinates
38	Göynük	1068	40.40675	30.93772
39	Göynük	800	40.41610	30.81787
40	Göynük	915	40.38790	30.80270
41	Göynük	534	40.37928	30.63070
42	Göynük	940	40.27785	30.65362
43	Göynük	938	40.31735	30.66708
44	Göynük	618	40.25058	30.74147
45	Göynük	604	40.26428	30.81125
46	Göynük	604	40.26428	30.81125
47	Göynük	867	40.32912	30.93267
48	Seben	1203	40.65588	31.62945
49	Seben	1346	40.58793	31.62905
50	Seben	1324	40.58377	31.63600
51	Seben	1372	40.56585	31.65095
52	Seben	1439	40.52807	31.61683
53	Seben	899	40.44802	31.59452
54	Seben	849	40.43190	31.60175
55	Seben	1139	40.45012	31.53235
56	Seben	816	40.32473	31.53827
57	Seben	800	40.32592	31.53723
58	Seben	816	40.41392	31.60108
59	Seben	694	40.39197	31.61688
60	Seben	688	40.38173	31.61548
61	Seben	606	40.32143	31.67962
62	Kıbrıscık	1074	40.34730	31.77698
63	Kıbrıscık	976	40.35682	31.80292
64	Kıbrıscık	881	40.38313	31.84597
65	Kıbrıscık	1083	40.42067	31.84718
66	Kıbrıscık	1210	40.42697	31.79723
67	Seben	1439	40.52950	31.70573
68	Seben	1463	40.51915	31.67287
69	Seben	1457	40.51930	31.67203
70	Seben	1457	40.51930	31.67203
71	Seben	1457	40.51930	31.67203
72	City center	1633	40.63223	31.61613
73	City center	1341	40.60797	31.67458
74	City center	1331	40.60300	31.66847
75	City center	776	40.69982	31.53747

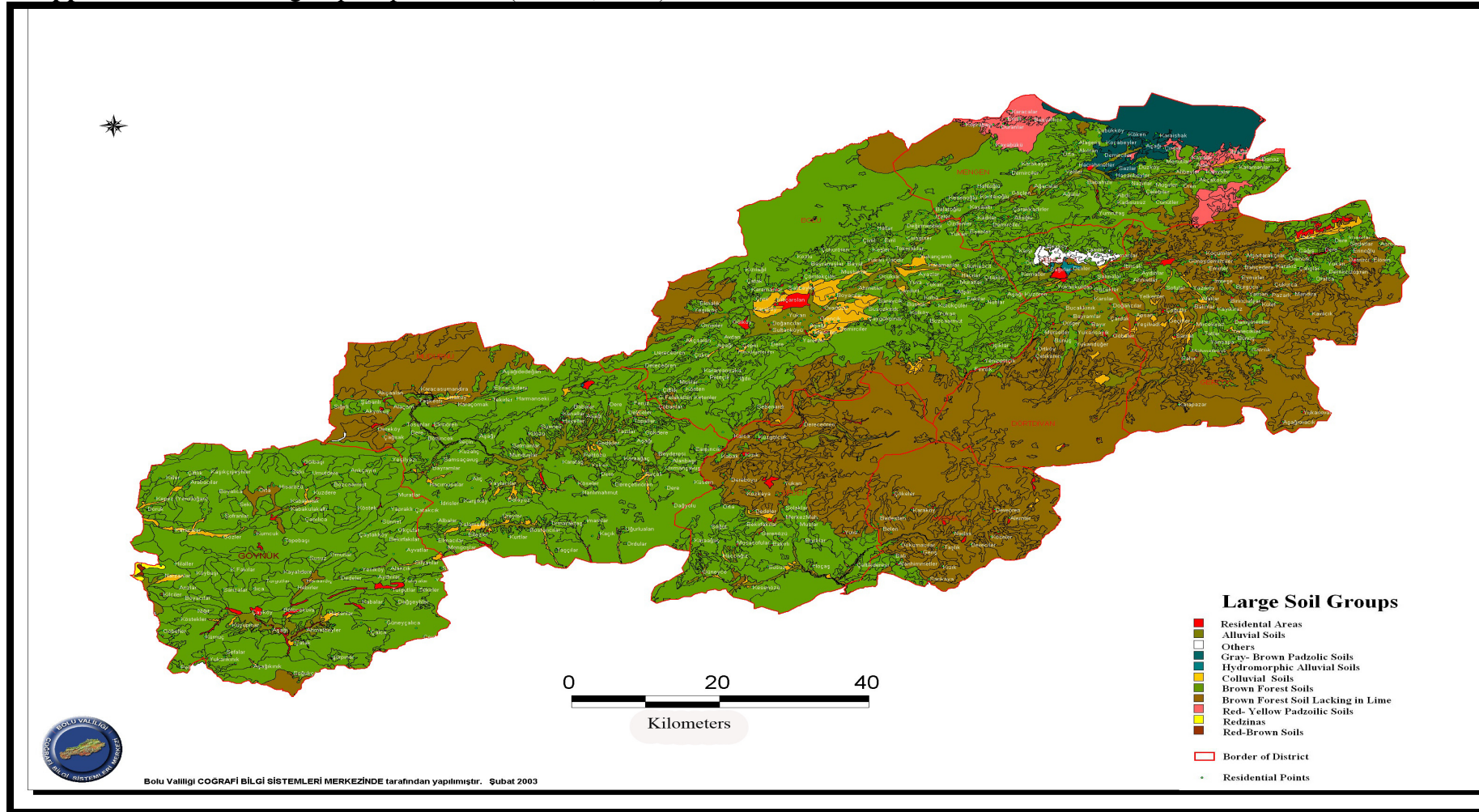
Appendix II. Chemical and Physical Properties of OCPs (Anonymous 16, 2011)

Common Name	CAS Number	Formula	Molecular Weight	Color	Melting Point °C	Boiling Point °C	Vapor Pressure	Solubility 25°C in water mg/L	Log K _{ow}	Log K _{oc}
α -HCH	319-84-6	C ₆ H ₆ Cl ₆	290.83	white	159–160	288	4.5x10 ⁻⁵ mmHg at 25°C	10	3.8	3.57
β -HCH	319-85-7	C ₆ H ₆ Cl ₆	290.83	white	314–315	60 at 0.5 mmHg	3.6x10 ⁻⁷ mmHg at 20 °C	5	3.78	3.57
γ -HCH (lindane)	58-89-9	C ₆ H ₆ Cl ₆	290.83	NI	112.5	323.4	4.2x10 ⁻⁵ mmHg at 25°C	17	3.72	3.57
δ -HCH	319-86-8	C ₆ H ₆ Cl ₆	290.83	NI	141–142	60 at 0.36 mmHg	3.5x10 ⁻⁵ mmHg at 25 °C	10	4.14	3.8
Heptachlor	76-44-8	C ₁₀ H ₅ Cl ₇	373.32	white	95-96	145	3x10 ⁻⁴ mmHg at 20 °C	0.05	6.1	4.34
Aldrin	309-00-2	C ₁₂ H ₈ Cl ₆	364.91	white	104–105.5	Decomposes	7.5x10 ⁻⁵ mmHg at 20 °C	0.011	6.5	7.67
Heptachlor-endo-epoxide	1024-57-3	C ₁₀ H ₅ Cl ₇ O	389.40	white	160-161.5	ND	1.95x10 ⁻⁵ mmHg at 30°C	0.275	5.4	4.37
Dieldrin	60-57-1	C ₁₂ H ₈ Cl ₆ O	380.91	white	176–177	Decomposes	3.1x10 ⁻⁶ mmHg at 20 °C	0.11	6.2	6.67
Endosulfan sulfate	1031-07-8	C ₉ H ₆ Cl ₆ O ₄ S	422.9	Brown	181	No data	1x10 ⁻⁵ mmHg at 25 °C	0.117	3.66	No data
Endosulfan I	959-98-8	C ₉ H ₆ Cl ₆ O ₃ S	406.93	Colorless	108–110	ND	1x10 ⁻⁵ mmHg at 25 °C	0.53	3.83	3.55

Appendix II. Chemical and Physical Properties of OCPs (Anonymous 16, 2011) (continued)

Common Name	CAS Number	Formula	Molecular Weight	Color	Melting Point °C	Boiling Point °C	Vapor Pressure	Solubility 25°C in water mg/L	Log K _{ow}	Log K _{oc}
Endosulfan II	33213-65-9	C ₉ H ₆ Cl ₆ O ₃ S	406.93	Cream	208–210	No data	1x10 ⁻⁵ mmHg at 25 °C	0.28	3.52	No data
Endrin	72-20-8	C ₁₂ H ₈ Cl ₆ O	380.9	White	235	decomposes	2.0x10 ⁻⁷ mmHg at 25 °C	0.25-0.26	5.34	4.53
Chloropyrifos	2921-88-2	C ₉ H ₁₁ C ₁₃ NO ₃ P S	350.59	Colorless crystals	42	No data	2.5x10 ⁻⁵ mmHg at 25 °C	1.18	5.50	3.8
Alachlor	15972-60-8	C ₁₄ H ₂₀ ClNO ₂	269.77	White or cream	40	No data	2.9x10 ⁻⁵ mmHg at 25 °C	242	3.5	2.08-2.28
Methoxychlor	72-43-5	C ₁₆ H ₁₅ Cl ₃ O ₂	345.65	Pale yellow	89	No data	1.4x10 ⁻⁶ mmHg at 25 °C	0.045	4.68–5.08	4.9
4,4'-DDT	50-29-3	C ₁₄ H ₉ Cl ₅	354.49	Colorless crystals	109	decomposes	1.60x10 ⁻⁷ at 20	0.025	6.91	5.18
4,4'-DDE	72-55-9	C ₁₄ H ₈ Cl ₄	318.03	White	89	336	6.0x10 ⁻⁶ at 25	0.12	6.51	4.70
4,4'-DDD	72-54-8	C ₁₄ H ₁₀ Cl ₄	320.05	Colorless crystals	109	350	1.35x10 ⁻⁶ at 25	0.090	6.02	5.18
Metolachlor	51218-45-2	C ₁₅ H ₂₂ ClNO ₂	283.79	colorless	-62.1	100 at 0.001 mmHg	4.2x10 ⁻⁵ mmHg at 25 °C	488	2.9	No data

Appendix III. The soil group map for Bolu (BİGEP, 2003)



Generally, sampling region of Bolu contain colluvial soil, brown forest soil and brown forest soil lacking in lime. Colluvial soils were accumulated by the surface flow, moving from a short distance by the side streams. For this reason, those soils show same property with the soils in the top of the hills. Brown forest soil has a high content of lime (Anonymous 17). Almost high places covered with brown forest soil in sampling region. Therefore, colluvial soil and brown forest soil have the same property.

REFERENCES

Agency for Toxic Substances and Disease Registry, 1989, Toxicology profile for alpha-, beta-gamma-, and delta-hexachlorocyclohexane, Clement and Associates, 205-88-0608, 1-133

Anonymous 1, Access: www.epa.gov/oia/toxics/pop.htm, Access date: 9 March 2011.

Anonymous 2, Access: www.epa.gov/pesticides/about/index.htm, Access date: 9 March 2011

Anonymous 3, Access: www.epa.gov/reg5rcra/wptdiv/p2pages/water.pdf, Access date: 9 March 2011

Anonymous 4, Access: <http://www.atsdr.cdc.gov/ToxProfiles/tp12-c9.pdf> , Access date: 9 March 2011

Anonymous 5, Access: <http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/metolachlor.pdf>, Access date: 9 March 2011

Anonymous 6, Access: <http://www.inchem.org/documents/pims/chemical/pimg001.htm>, Access date: 9 March 2011

Anonymous 7, Access: <http://en.wikipedia.org/wiki/Talk%3APesticide>, Access date: 9 March 2011

Anonymous 8, Access: <http://www.cee.vt.edu/ewr/environmental/teach/smprimer/gc/gc.html>, Access date: 9 March 2011

Anonymous 9, Access: <http://www.chemistry.adelaide.edu.au/external/soc-rel/content/ecd.htm>, Access date: 9 March 2011

Anonymous 10, Access: <http://pan-europe.info/Issues/index.html>, Access date: 9 March 2011

Anonymous 11, Access: http://pan-europe.info/Issues/Pesticide_Pollution.html, Access date: 9 March 2011

Anonymous 12, Access: http://otrans.3cdn.net/c1f04293317b797427_gsm6i2ei7.pdf, Access date: 9 March 2011

Anonymous 13, Access: <http://www.agnet.org/library/ac/1998e/>, Access date: 9 March 2011

Anonymous 14, Access: http://www.zmo.org.tr/genel/bizden_detay.php?kod=6391&tipi=24&sube=0, Access date: 9 March 2011

Anonymous 15, Access: [http://www.ttgiv.org.tr/content/docs/ envanter-ozet-raporu.doc.](http://www.ttgiv.org.tr/content/docs/envanter-ozet-raporu.doc.), Access date: 9 March 2011

Anonymous 16, Access: <http://www.atsdr.cdc.gov/toxprofiles/index.asp>, Access date: 9 March 2011

Anonymous 17, Access: http://www.tarimziraat.com/faydali_bilgiler/toprak/408-toprakcesitlirinelerdir.html, Access date: 9 March 2011

Antonious, G.F., Byers, M.E., Snyder-Conn E., 1998, Residues and fate of endosulfan on fieldgrown pepper and tomato, *Pesticide Science*, 54, 61–7

Agency for Toxic Substances and Disease Registry, 1996, Toxicological Profile for Endrin and Endrin Aldehyde (Update). August. Prepared by Research Triangle Institute under Contract No. 205-93-0606 for U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Atlanta, Georgia: ATSDR, CDC.

Ayas, Z., Barlas Emir, N., Kolankaya, D., 1997, Determination of organochlorine pesticide residues in various environments and organisms in Göksu Delta, Turkey, *Aquatic Toxicology*, 39, 171-181

Banksa, K. E., Huntera, D. H., Wachala, D. J., 2005, Chlorpyrifos in surface waters before and after a federally mandated ban, *Environment International*, 31, 351-356

Bolu İl Gelişme Planı (BİGEP), 2003.

Binici, B. 2007, Yağmur suyunda PAH ve Pestisit Tayini Alıcı ortam Modellemesi, Ms. Thesis, GIT

Bloomfield, J. P., Williams, R.J., Gooddy R. J., Cape J. N , D. C., Guha, P., 2006, Impacts of climate change on the fate and behaviour of pesticides in surface and groundwater—a UK perspective, *Science of the Total Environment*, 369, 163-177

Bozlaker, A., Muezzinoglu, A., Odabasi, M., 2009, Processes affecting the movement of organochlorine pesticides (OCPs) between soil and air in an industrial site in Turkey, *Chemosphere*, 77, 1168-1176

Calhoun, Y., 2005, *Water Pollution*, Chelsea House Publisher

Carabias- Martíneza, R., Rodríguez-Gonzaloa, E., Fernández-Laespadaa, M.E., Calvo Seroneroa, L., Sánchez-San Román, F. J., 2003, Evolution over time of the agricultural pollution of waters in an area of Salamanca and Zamora (Spain), *Water Research*, 37, 928–938

Cerejeiraa, M.J., Vianab, P., Batistaa, S., Pereiraa, T., Silvaa, E., Valerioa, M.J., Silvaa, A., Ferreirab M., Silva-Fernandesa A. M., 2003, Pesticides in Portuguese surface and ground waters, *Water Research*, 37, 1055-1063

Chan, C., Bruce, G., Harrison, B., 1994, Wet deposition of organochlorine pesticides and polychlorinated biphenyls to the Great Lakes, *Journal of Great Lakes Research*, 20, 546–60

Chan, C., Williams, D., Neilson, M., Harrison, B., Archer, M., 2003, Spatial and temporal trends in the concentrations of selected organochlorine pesticides (OCs) and polynuclear aromatic hydrocarbons (PAHs) in Great Lakes Basin precipitation, 1986 to 1999, *Atmospheric Environment*, 40, 1563–1578

Claver, A., Ormad, P., Rodríguez, L., Ovelheiro, J. L., 2006, Study of the presence of pesticides in surface waters in the Ebro river basin (Spain), *Chemosphere*, 64, 1437–1443

Covacia, A., Hurab, C., Schepensa, P., 2001, Selected persistent organochlorine pollutants in Romania, *The Science of Total Environment*, 280, 143–152

Dong, C., Zeng, Z., Yang, M., 2005, Determination of organochlorine pesticides and their derivations in water after HS-SPME using polymethylphenylvinylsiloxane-coated fiber by GC-ECD, *Water Research*, 39, 4204–4210

Doong, R.A., Peng, C.K., Sun, Y.C., Liao, P.L., 2002, Composition and Distribution of Organochlorine Pesticide Residues in Surface Sediments from The Wu-Shi River Estuary, Taiwan, *Marine Pollution Bulletin*, 45, 246–253

DPT, 2002, Bolu İli Raporu

Ecobichon, D. J., Amdur, M. O., Doull, J., and Klaassen, C. D., Eds., 1991, Toxic effects of pesticides, In Casarett and Doull's Toxicology, 4th ed. Pergamon Press, New York

EPA, 1993, Revised Draft Lake Michigan Lakewide Management Plan for Toxic Pollutants

EPA 1998, Great Lakes Binational Toxics Strategy Pesticide Report

Ghadiri, H., Rose, C.W., 2001, Degradation of endosulfan in a clay soil from cotton farms of western Queensland, *Journal of Environmental Management*, 62, 155–69.

Golfinopoulos, S. K., Nikolaou, A. D., Kostopoulou, M. N., Xilourgidis, N. K., Vagi, M. C., Lekkas, D. T., 2003, Organochlorine pesticides in the surface waters of Northern Greece, *Chemosphere*, 50, 507–516

Graham, W.H, Miley, M.K., DeNoyelles, F., Smith, V.H., Thurman, E.M., Carter, R., 2000, Alachlor transformation patterns in aquatic field mesocosms under variable oxygen and nutrient conditions, *Water Research*, 34, 16, 4054–4062

Guan, Y. F., Wang, J. Z., Ni, H. G., Y. Zeng, E. Y., 2009, Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: Assessment of mass loading, input source and environmental fate, *Environmental Pollution*, 157, 618–624

Guruge, K. S. , Tanabe, S., 2001, Contamination by persistent Organochlorines and Butyltin Compounds in the West coast of Sri Lanka, *Marine Pollution Bulletin*, 42, 3, 179–186

- Hao, H., Sun, B., Zhao, Z., 2008, Effect of land use change from paddy to vegetable field on the residues of organochlorine pesticides in soils, *Environmental Pollution*, 156, 1046-1052
- Hilber, I., Mäder, P., Schulin, R., Wyss, G. S., 2008, Survey of organochlorine pesticides in horticultural soils and there grown Cucurbitaceae, *Chemosphere*, 73, 954-961
- Hill, M. K., 2004, *Understanding Environmental Pollution*, Second Edition, Cabridge University Press
- Hong, H., Chen, W., Xu, L., Wang, X., Zhang, L., 1999, Distribution and Fate of Organochlorine Pollutants in the Pearl River Estuary, *Marine Pollution Bulletin*, 39, 376-382
- Jergentz, S., Mugni, H., Bonetto, C., Schulz, R., 2005, Assessment of insecticide contamination in runoff and stream water of small agricultural streams in the main soybean area of Argentina, *Chemosphere*, 61, 817-826
- Jones, K. C., Voogt, P., 1999, Persistent organic pollutants (POPs): state of the science, *Environmental Pollution*, 100, 209-221
- Kim, J. H. and Smith, A., 2001, Distribution of organochlorine pesticides in soils from South Korea, *Chemosphere*, 43, 137-140
- Lee, K.T., Tanabe, S., Koh, C.H., 2001, Distribution of organochlorine pesticides in sediments from Kyeonggi Bay and nearby areas, Korea, *Environmental Pollution* 114, 207-213
- Manahan, S. E., 2000, *Environmental Chemistry*, Seventh Edition, CRC Press, USA
- Martin, E. W., 1971, *Hazards of Medication: A Manual on Drug Interactions, Incompatibilities, Contraindications, and Adverse Effects*. Lippincott, Philadelphia, PA
- Metcalf, R. L., Kapoor, I. P., Lu, P., Schuth, C. K., Sherman, P. 1973, Model ecosystem studies of environmental fate of six organochlorine pesticides, *Environ. Health Perspect.* 4, 35-44
- Miglioranza, K. S. B., Aizpun de Morenoa, J. E., Morenoa, V. J., Osterrieth, M. L., Escalante, A. H., 1999, Fate of organochlorine pesticides in soils and terrestrial biota of "Los Padres" pond watershed, Argentina, *Environmental Pollution*, 105, 91-99
- Nash, R.G., Harris, W.G., 1973, Chlorinated hydrocarbon insecticide residues in crops and soil, *Journal of Environmental Quality*, 2, 267-273
- National Academy of Sciences, 2000, *The Future Role of Pesticides in US Agriculture*, National Academy Press, Washington, D.C
- Office of Environmental Health Hazard Assessment California Environmental Protection Agency, 1999, Public Health Goal for Endrin In Drinking Water

Ozmen, M., Ayas, Z., Abbas, Güngördü A., Ekmekci, G. F., Yerli, S., 2008, Ecotoxicological assessment of water pollution in Sariyar Dam Lake, Turkey, *Ecotoxicology and Environmental Safety*, 70, 163-173

Öztaş, N.B., 2008, Pesticide pollution in surface and ground water of an agricultural area, Kumluca, Turkey, Ph.D. Thesis, METU

Öz, M., 2009, Characterization of PCBs, PAHs, and Organochlorine Pesticides in the Atmosphere of Bolu and Source Apportionment: Gas to Particle, Soil to Particle, Soil to Gas Exchanges, Msc. Thesis, AIBU

Rissato, S. R., Galhiane, M. S., Ximenes, V. F., M. B. de Andrade, R., Talamoni, J. L. B., Libanio, M., V. de Almeida, M., Apon, B. M., Cavalari, A. A., 2006, Organochlorine pesticides and polychlorinated biphenyls in soil and water samples in the Northeastern part of São Paulo State, Brazil, *Chemosphere*, 65, 1949-1958

Sankararamakrishnan, N., Sharma, A. K., Sanghi, R., 2005, Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Uttar Pradesh, India, *Environment International*, 31, 113-120

Shegunova, P., Klanova, J., Holoubek, I., 2007, Residues of organochlorinated pesticides in soils from the Czech Republic, *Environmental Pollution*, 146, 257-261

Shukla, G., Kumar, A., Bhanti, M., Joseph, P. E., Taneja, A., 2006, Organochlorine pesticide contamination of ground water in the city of Hyderabad, *Environment International*, 32, 244-247

Skoog, D.A., West, D.M., Holler, F.J., 1996, *Fundamentals of Analytical Chemistry*, Saunders College Publishing, Seventh Edition, USA

Supelco Technical Resources, 1998, Guide to Solid Phase Extraction, Bulletin 910, Sigma Aldrich Co., T197910

Suslick, K. S., 1988, *Ultrasound: Its Chemical, Physical and Biological Effects*, VCH Publishers, Weinheim, Germany

Suslick, K. S., Didenko, Y., Fang, M. M., Hyeon, T., Kolbeck, K. J., McNamara, W. B., M. Mdeleleni, M., Wong M., 1999, *Philosophical Transactions of the Royal Society, London, Ser. A*, 357-335.

Tadeo, J. L., 2008, *Analysis of Pesticides in Food and Environmental Samples*, CRC Press.

Tanabe, S., Iwata, H. and Tatsukawa, R. 1994, Global Contamination by persistent Organochlorines and their ecotoxicological impact on marine mammals, *Science of the Total Environment*, 154, 163-177

Tanrivermis, H., 2003, Agricultural land use change and sustainable use of land resources in the mediterranean region of Turkey, *Journal of Arid Environments*, 54, 553-564

Thayer, A., 1999, Monsanto Expands Licensing Strategy for Flagship Herbicide, Chemical and Engineering News

Thomas, M. R., Wardman, O.L., 1999, Review of usage of pesticides in agriculture and horticulture throughout Great Britain 1986–1996, Pesticide Usage Survey Report, 150, York: CSL

Turgut, C., 2003, The contamination with organochlorine pesticides and heavy metals in surface water in Küçük Menderes River in Turkey, 2000–2002, Environment International, 29, 29-32

U.S. Environmental Protection Agency, 2003, Health Effect support Document for Aldrin/Dieldrin, Office of Drinking Water, Washington, D.C.

U.S. Environmental Protection Agency, 1998, Reregistration Eligibility Decision(RED) Alachlor, Washington, D.C.

Vega, A.B., Frenich, A. G., Vidal, J. L. M., 2005, Monitoring of pesticides in agricultural water and soil samples from Andalusia by liquid chromatography coupled to mass spectrometry, Analytica Chimica Acta, 538, 117–127

Vryzasa, Z., Vassilioub, G., Alexoudisb, C., Papadopoulou-Mourkidoua, E., 2009, Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece, Water Research, 43, 1-10

Wan, M.T., Kuo, J-N., Buday, C., Schroeder, G., Van Aggelen, G., Pasternak, J., 2005, Toxicity of α - and β -endosulfan and their formulated and degradation products to *Daphnia magna*, *Hyalella azteca*, *Oncorhynchus mykiss*, *Oncorhynchus kisutch*, and biological implications in streams, Environmental Toxicology and Chemistry, 24, 1146–1154

Wang, W., Meng, B., Lu, X., Liu, Y., Tao, S., 2007, Extraction of polycyclic aromatic hydrocarbons and organochlorine pesticides from soils: A comparison between Soxhlet extraction, microwave-assisted extraction and accelerated solvent extraction techniques, Analytica Chimica Acta, 602, 211-222

Wania, F., Mackay, D., 1993, Global fractionation and cold condensation of low volatility organochlorine compounds in Polar regions, Ambio, 22, 10–18

Wania, F., Mackay, D., 1996, Tracking the distribution of persistent organic pollutants, Environ Science and technology, 30, 390-6

Waxman, M.F., 1998, Agrochemical and Pesticide Safety Handbook, CRC Press, Florida.

Weber, J., Halsall, C. J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., Bidleman, T., 2009, Endosulfan, a global pesticide: A review of its fate in the environment and occurrence in the Arctic, Science of the Total Environment, Article in Press

Willet, K. L., Ulrich, E. M., Hites, R. A., 1998, Differential Toxicity and Environmental Fates of Hexachlorocyclohexane Isomers, *Environmental Science and Technology*, 32, 15, 2197-2207

Wilkinson, R. E., 1981, Metolachlor influence on growth and terpenoid synthesis, *Pesticide Biochemistry and Physiology*, 16, 63-71

Xue, N., Xu, X., Jin, Z., 2005, Screening 31 endocrine-disrupting pesticides in water and surface sediment samples from Beijing Guanting reservoir, *Chemosphere*, 61, 1594-1606

Zhang, G., Li J., Cheng, H., Li, X., Xu, W., Jones, K. C., 2007, Distribution of Organochlorine Pesticides in the Northern South China Sea: Implications for Land Outflow and Air-Sea Exchange, *Environmental Science and Technology*, 41, 3884-3890

Zhou, R., Zhu, L., Yang, K., Chen, Y., 2006, Distribution of Organochlorine Pesticides in Surface Water and Sediments from Qiantang River, East China, *Journal of Hazardous Materials*, 137, 68-75