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Türkiye, Ergene Nehir Havzası'nda, Çevre Kirliliğinde Biyomonitör Olarak Kullanılan Çeşitli Bitki Yapraklarındaki Organoklorlu Pestisitlerin Gaz Kromatografisi-Kütle Spektroskopisi ile Tayini

Cemile ÖZCAN

Kırklareli Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölümü, Kırklareli

e-posta: cemilebal.ozcan@klu.edu.tr

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Özet

Ergene Havzası Türkiye'de sınırları belirlenmiş olan 23 havzadan birisidir. Ergene Havzası, Tekirdağ, Edirne ve Kırklareli illerinin büyük bir kısmını kapsamaktadır. 2012 yılı süresince Ergene Nehir Havzasında on noktadan toplanan çeşitli bitki örnekleri (*Urtica dioica* L., *Melissa officinalis*, *Verbascum sinuatum*, *Typha latifolia* L., *Pinus nigra* L., *Cupressus arizonica* L., *Populus nigra* L., *Cedrus libani* L., *Paliurus aculeatus* L., *Mentha pulegium* L., *Plantago major* L., *Laurus nobilis* L.) hızlı, kolay, ucuz, etkili, dayanıklı ve güvenli (QuEChERS) ekstraksiyon metodu kullanılarak ekstrakte edilmiştir. Yüksek toksisiteye sahip organik klorlu pestisitlerin konsantrasyonları gaz kromatografi-kütle spektroskopisi-elektron impact iyonlaştırma-pozitif mod (GC-MS-EI (+)) kullanılarak tayin edilmiştir. Pestisitler için sırasıyla LOD, LOQ ve RSD% değerleri 0.02-0.21 $\mu\text{g L}^{-1}$, 0.06-0.71 $\mu\text{g L}^{-1}$ ve altında %10 bulunmuştur. Bitki örneklerindeki pestisitlerin geri dönüşüm çalışmaları sırasıyla 78.9-99.9% aralığında değişmektedir. İnsan sağlığını tehlikeye sokan ΣHCH ve Dieldrin konsantrasyonlarında izin verilen günlük alım sınırını aşmadığı belirlenmiştir.

Anahtar kelimeler

Ergene Nehir Havzası;
bitki örnekleri;
pestisitler; GC-MS;
QuEChERS.

Gas Chromatography-Mass Spectrometry Determination of Organochlorine Pesticides in Various Plant Leaves Used as Biomonitors in Environmental Pollution, Ergene River Basin, Turkey

Abstract

Ergene Basin is one of the 23 basins which identified the borders in Turkey. This Basin covers a large part of the province of Tekirdağ, Edirne and Kırklareli. The various plant samples (*Urtica dioica* L., *Melissa officinalis*, *Verbascum sinuatum*, *Typha latifolia* L., *Pinus nigra* L., *Cupressus arizonica* L., *Populus nigra* L., *Cedrus libani* L., *Paliurus aculeatus* L., *Mentha pulegium* L., *Plantago major* L., *Laurus nobilis* L.) collected from ten point in Ergene River Basin during 2012 year were extracted by using the quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction method. The concentrations of organochlorine pesticides having high toxicity were determined by using gas chromatography-mass spectrometry with electron impact ionization-positive mode (GC-MS-EI (+)). The LOD, LOQ and RSD% were between 0.02-0.21 $\mu\text{g L}^{-1}$, 0.06-0.71 $\mu\text{g L}^{-1}$, below 10%. for pesticides, respectively. Recoveries of pesticides in plant samples ranged from 78.9% to 99.9%, respectively. The ΣHCH and Dieldrin concentrations were not exceeded the tolerable daily intake limit accordingly serving as likely threat to humans.

Keywords

Ergene River Basin;
plant samples;
pesticides; GC-MS;
QuEChERS.

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1. Introduction

After the World War II, men of science began to identify that, certain chemical pollutants were capable of persistent in the environment for a long time, migrating in air, water, soil, sediment and plant and amassing in levels being harm natural haunts of inhabiting (Barr 2008, Sarigiannis et al.

2013, De'vier et al. 2011, El-Shahawi et al. 2010). The pesticides are likely chemical pollutants widely used for agriculture goals because of lower costs and upper the quality of being effective. They may accumulate as decomposition in living creature, which can remain or less degradate in the environment (Barr 2008, Barriada-Pereira et al.

2005, Darko et al. 2008). However, pesticides are hazardous because of their chemical, physical or biological properties in food with probable to cause an adverse health effect. El-Shahawi et al., organochlorine pesticides (OCPs) have demonstrated very important acute toxicity, mutagenic and carcinogenic effects as well as endocrine devastating effects (El-Shahawi et al. 2010).

Among the most important sources of pesticides originating from industrial and agricultural pollutants, such as the inorganic and organic fertilizers, sewage sludge, irrigation waters and fungicides can be counted (Ozcan 2015, Singh 2001, Nerin et al. 2002). In general, factory and agricultural pollutants, when released into plants, bind to particulate matter, and are incorporated into the water and sediment. Thus, plant is an important reservoir of pesticides and other contaminants in the environment. Nowadays, toxic OCPs were restricted or prohibited in the majority of the industrialized nations and in Turkey since the late 90s because of toxicity to organisms and bioaccumulation in environment. Therefore, in studies concerning with OCPs, their residues have been found in soil, water, plant, food and air samples (Sarigiannis et al. 2013, Yeo et al. 2004, Lu et al. 1998, Beard et al. 2000, Smeds and Saukko 2001, Borga et al. 2004, Ozcan, 2015, Ratola et al. 2014). Hexachlorobenzene is a selective fungicide used with food crops, because of a seed dressing and as a wooden protective. It also arises as a result of waste incineration and as a byproduct of several industrial processes. Lindane is generally used as an insecticide on food crops, in forestry and to treat industrial and household pesticides.

Extraction of multiple pesticides from complex environmental matrices have been a challenge because of their different physiochemical naturally essential. For the separation of pesticides from plant matrix, solid phase extraction (SPE) has been preferentially used, because of its easy, robustness and simplicity automation (Balkis et al. 2015, Borga et al. 2004, Ozcan 2015, Chowdhury et al. 2011, Anonymous 1980a). By many researchers have been reported a quick, easy, cheap, effective,

rugged and safe extraction method (QuEChERS) for sample preparation in pesticide multi-residue analysis (Mantzou et al. 2013, Bruzzoniti et al. 2014, Pastor et al. 1997). Various analytical methods, GC-MS, HPLC-MS and atomic spectroscopic techniques, have been reported for determinations of organic compounds including pesticide residues and toxic metals in dissimilar matrices like natural and drinking water, biological, food crops soil and environmental (Barriada-Pereira et al. 2005, Borga et al. 2004, Ozcan et al. 2012, Ozcan and Yaman 2013, Ozcan and Yaman 2015, Chowdhury et al. 2011, Pastor et al. 1997, Ozen et al. 2003, Yaman and Gucer 1998, Yaman 2000, Ozcan et al. 2010, Ozmen et al. 2008). However, molecular weight, fragmentation products and molecular structures can also be defined by GC-MS (Ozcan 2015, Lino et al. 1997).

Ergene River Basin in Thrace region of Turkey, has an area of 17,323 km². A large part of Ergene Basin covers the cities of Tekirdağ, Edirne and Kırklareli. Agricultural area and industrial activities have been the cause of increase of toxicity and pollution in the ecological environment (Tokatli 2015, Yilmaz et al. 2017, Ordu and Demir 2009). Although there are many pesticide and heavy metals studies related to soil, sediment and water (Erarslan et al. 2014, Güyer et al. 2016, Nikolaou et al. 2008, Güneş et al. 2008) in the Ergene Basin, there have been no studies with this plants in literature studies.

The goal of this study is to determine the concentrations of OCPs in *Utica dioica* L., *Melissa officinalis*, *Verbascum sinuatum*, *Typha latifolia* L., *Pinus nigra* L., *Cupressus arizonica* L., *Populus nigra* L., *Cedrus libani* L., *Paliurus aculeatus* L., *Mentha pulegium* L., *Plantago major* L., *Laurus nobilis* L. from Thrace Basin of Ergene River by GC-MS-EI (+).The examined pesticides are Σ BHC (hexachlorocyclohexane) (α -BHC, β -BHC, γ -BHC, δ -BHC), Σ DDT (dichlorodiphenyltrichloroethane) (4,4'-DDD, 4,4'-DDE, 4,4'-DDT), α -Endosulfan, β -Endosulfan, Endosulfan sulfate, Heptachlor, Heptachlor-endo-epoxide, Aldrin, Dieldrin, Endrin aldehyde, Endrin ketone, Endrin and Methoxychlor. In order to improve the cleanliness of the plant

samples the QuEChERS extraction method was adapted for the selected pesticides and matrix.

2. Materials and Methods

2.1. Instrumentation

The OCPs were analyzed by gas chromatography-mass spectrometry, using an Agilent 7890A model and Agilent 5975C MSD system at Kırklareli University. HP-5 MS-IU column (30m x 250 μ m x 0.25 μ m) was used together with Helium as carrier gas. Injection volume, injector temperature and split flow were 1 μ L, 250 °C and 1 mL min⁻¹, respectively. The GC oven temperature was kept fixed at 110 °C for 5 min and rised to 320 °C at a rate of 8 °C min⁻¹ (Ozcan 2015). Fragmentation voltage and scan range (m:z) of MS were taken at 70 eV and 50-500, respectively. Data acquirement was fulfilled under selected ion monitoring (SIM) mode. Component identification was performed to using spectrometric electronic libraries of the National Institute of Standards and Technology (NIST) (Kurt et al. 2004).

2.2. Chemicals and materials

The standard stock solutions of OCP Mix 2, (2000 ng μ L⁻¹ in toluene), including α -BHC, β -BHC, δ -BHC, δ -BHC, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, α -Endosulfan, β -Endosulfan, Endosulfan sulfate, Heptachlor, Heptachlor-endo-epoxide, Aldrin, Dieldrin, Endrin aldehyde, Endrin ketone, Endrin and Methoxychlor were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All solvents and other chemicals were HPLC grade and analytical reagent grade, respectively. Ultrapure water (18.2 M Ω) acquired with a purification system (ELGA) was used for all preparations.

The standard solutions were prepared in toluene from dilution of their stock standard solutions at concentrations of 250, 100, 50, 25, 10, 5 and 1 μ g L⁻¹. Standard identification, analysis and quantification have been done by GC-MS (Ozcan 2015, Ozcan 2016).

2.3. Collection of Plant Samples

The various chemicals and fertilizers are applied to soil and plants as a result of development agricultural techniques. Therefore, the pollution dimension in soil and plants be also increasing (Yilmaz et al. 2017). The agriculture and industry are situated primarily along the Ergene River Basin and is concentrated in Thrace, among Edirne, Tekirdag (especially Corlu) and Kırklareli. Ergene River Basin that was selected as the study area (Fig.1) is a place having intensive industrial and agricultural activities. The examination of OCPs was studied in the plant samples (*Urtica dioica* L. (UD), *Melissa officinalis* (MO), *Verbascum sinuatum* (VS), *Typha latifolia* L. (TL), *Pinus nigra* L. (PN), *Cupressus arizonica* L. (CA), *Populus nigra* L. (PoN), *Cedrus libani* L. (CL), *Paliurus aculeatus* L. (PA), *Mentha pulegium* L. (MP), *Plantago major* L. (P), *Laurus nobilis* L. (LN)) collected from Ergene River Basin in 2012 year. The studied ten points including the distribution of the sample sites are shown in Fig. 1 and Table 1.

Table 1. The coordinates of the sampling locations.

The sampling point	Coordinates	
	N	E
1E	41° 31' 12"	27° 54' 36"
2E	41° 16' 0.7926"	27°43'48.9"
3E	41° 11' 20.3"	27° 28' 32.6"
4E	41°15'12.6"	27°27'08.7"
5E	41° 20' 8.4"	26° 55' 15.6"
6E	41°16'40.7"	26°40'30.6"
7E	41° 1' 36.3"	26° 21' 37.7"
8E	41° 38' 23.2"	27° 29' 52.6"
9E	41° 41' 14.9"	27° 22' 00.7"
10E	41° 42' 00.0"	27° 12' 00.0"

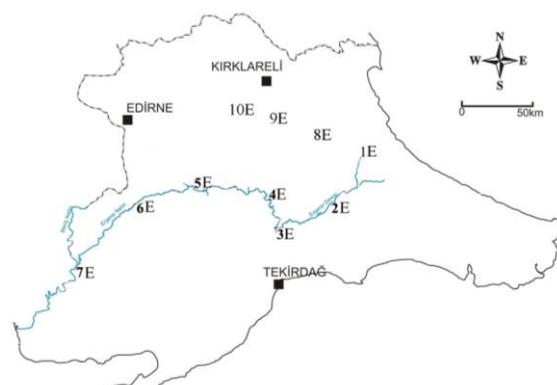


Figure 1. A map of Ergene River showing the sampling locations.

The plant samples were transferred to the laboratory in plastic bags, washed with tap

water, and rinsed with distilled water. After drying at room temperature, the samples were ground using an agate mortar and homogenously mixed and stored in refrigerator until analysis. Each sample was analyzed in the minimum triplet and the mean was reported.

2.4. Extraction of plant samples

After homogenization of plant samples, nearly 5 g portion were added 10 mL dichloromethane into a 50 mL PTFE centrifuge tube. The sample was centrifuged in a 50 mL polypropylene centrifuge tube. Sodium acetate 1.5 g and anhydrous magnesium sulfate 6.0 g in supernatant were added to remove moisture and the compound was stirred for 3 min using the vortex. The sample was then centrifuged again at 5 °C and 5 min at 7000 rpm. The supernatant extraction was followed by a clean-up step using a SPE (with 400 mg PSA, 1200 mg MgSO₄) (Ozcan 2016, Ozcan 2015, Mantzos et al. 2013, Anonymous 2007, Anonymous 1980a, Ahlborg et al. 1995, Stefanelli et al. 2009, USEPA, 2007, Bruzzone et al. 2014). OCPs in the supernatant were concentrated for dryness in 35 °C using a gentle nitrogen stream. This was dissolved in 1 mL of hexane and filtered through a syringe filter of 0.45 µm (Ozcan 2016). Afterwards, the extracts (1 µL injection volume) were quantified by GC-MS.

2.5. Quantitation

The mean concentration was calculated as the arithmetic average of the results from a set of samples analysed. Linearity, accuracy, precision, recovery parameter, limit of detection (LOD) and limit of quantitation (LOQ) were determined for OCPs. Seven level (1-250 µg L⁻¹) calibration series with three analyses at every concentration level were determined for the calibration curve and linearity were drawn to automatically (Ozcan 2015). LOD and LOQ had a signal to noise ratio of ≈3 and ≈10, respectively (Jacobsen et al. 2004, Shrivastava and Gupta 2011).

$$\text{LOD}=\text{SDX3}$$

$$\text{LOQ}=\text{SDX10}$$

Calibration graphs for α-BHC; β-BHC; γ-BHC; δ-BHC; 4,4'-DDD; 4,4'-DDE; 4,4'-DDT; α-Endosulfan; β-Endosulfan; Endosulfan sulfate; Heptachlor; Heptachlor-endo-epoxide; Aldrin; Dieldrin; Endrin aldehyde; Endrin ketone; Endrin and Methoxychlor were established in a range of 1-250 µg L⁻¹ with correlation of coefficients from 0.994; 0.995; 0.993; 0.993; 0.986; 0.993; 0.998; 0.994; 0.994; 0.989; 0.992; 0.994; 0.996; 0.993; 0.990; 0.991; 0.996 and 0.996 for all analytes, respectively. The LODs, LOQs and RSDs are shown in Table 2. LOD ranged from 0.02 to 0.21 µg L⁻¹ for OCPs. LOQ ranged from 0.06 to 0.71 µg L⁻¹ for pesticides. The RSDs were ≤10% in all the pesticides. RSDs of the migration time ranged from 0.1% to 9.5% for the analytes, indicating the good repeatability of the method.

Table 2. The LOD (µg L⁻¹), LOQ (µg L⁻¹), recovery% and RSD% of OCPs.

Pestisit	LOD	LOQ	Recovery (%)	RSD%
α-HCH (1)	0.06	0.21	92.3 ± 4.2	6.3
β-HCH (2)	0.21	0.71	85.2 ± 6.9	9.5
γ-HCH (3)	0.06	0.21	90.8 ± 6.6	5.3
δ-HCH (4)	0.02	0.06	85.2 ± 8.2	9.2
Heptachlor (5)	0.06	0.19	91.9 ± 5.8	2.5
Aldrin (HHDN) (6)	0.03	0.10	78.9 ± 9.7	9.3
Heptachlor-endo-epoxide (7)	0.18	0.60	96.2 ± 5.1	2.4
α-Endosulfan (8)	0.14	0.46	98.0 ± 3.9	1.9
4,4'-DDE (9)	0.03	0.10	92.4 ± 5.1	3.1
Dieldrin (10)	0.12	0.40	99.5 ± 3.9	0.5
Endrin (11)	0.06	0.21	92.2 ± 5.2	1.9
β-Endosulfan (12)	0.03	0.10	98.5 ± 3.3	1.2
4,4'-DDD (13)	0.04	0.13	98.8 ± 4.8	0.9
Endrin-aldehyde (14)	0.06	0.21	89.4 ± 7.2	6.9
Endosulfan-sulfate (15)	0.06	0.21	88.4 ± 7.2	7.1
4,4'-DDT (16)	0.03	0.10	95.7 ± 5.1	1.9
Endrin-ketone (17)	0.12	0.40	85.3 ± 8.1	7.7
Methoxychlor (18)	0.03	0.10	99.9 ± 2.2	0.1

The method was checked for recovery efficiencies by analyzing uncontaminated of plant samples spiked with OCP standard (n=5). The solvent blanks, spike blanks and duplicate samples were analyzed in each 10 samples. In addition, surrogate standard was added to each of the sample to

monitor procedural performance and matrix effects. The recoveries of surrogate spiked in the plant samples ranged from 78.9% to 99.9%, respectively.

3. Results and Discussion

Ergene River Basin is under strong influence of the industrial and agricultural activities. For example, chemistry industries such as textile, agriculture, battery, and food (oil, flour, etc.) in Ergene River Basin have undergone extremely rapid development during the last forty decades (Ordu and Demir 2009). Though use of eighteen OCPs has been prohibited in Turkey by a decision made by the Turkish government since the late 80s, they banned for use in Turkey in the late 90s (Kurt et al. 2004). But, unfortunately, it was observed that illegal use of OCPs continues nonetheless in agricultural areas.

The results obtained for plant samples are summarized in Table 3-5, respectively. The target OCPs were analyzed with a good reproducibility and low detection limits by using GC-MS-EI (+). After elution-cleaning with SPE cartridge for pesticides in plant samples has been developed as a simultaneous method for analysis by GC-MS. The main vantage of this method is that extraction and clean-up are performed in less time with a low volume of solvent. In addition, the proposed method is a sensitive, reproducible and reliable alternative to the normally used methods; furthermore, it is QuEChERS method. This study was demonstrated that the method using QuEChERS and GC-MS is very influential in analyzing the OCPs in the plant samples. Moreover, in the classical QuEChERS method, PSA and anhydrous MgSO₄ were added in the extracts. PSA is a structure that has a high chelating effect owing to the presence of the secondary amine functional group, as well as the primary one. As a result, it can retain co-extractives such as sugars, fatty acids, other organic acids, some polar pigments and other polar compounds of the matrix (Mantzios et al 2013).

The concentrations of α -HCH, β -HCH, γ -HCH, δ -HCH, Heptachlor, Aldrin, Heptachlor-endo-epoxide,

α -Endosulfan, 4,4'-DDE, Dieldrin, Endrin, β -Endosulfan, 4,4'-DDD, Endrin-aldehyde, Endosulfan sulfate, 4,4' DDT, Endrin-ketone and Methoxychlor for *Urtica dioica* L., *Melissa officinalis*, *Verbascum sinuatum* in 1E point were ranged from 11.9 to 14.1 $\mu\text{g kg}^{-1}$, 14.3 to 16.1 $\mu\text{g kg}^{-1}$, 12.3 to 20.8 $\mu\text{g kg}^{-1}$, 13.3 to 27.1 $\mu\text{g kg}^{-1}$, 28.1 to 55.7 $\mu\text{g kg}^{-1}$, 11.1 to 16.9 $\mu\text{g kg}^{-1}$, 15.6 to 175 $\mu\text{g kg}^{-1}$, 14.4 to 23.5, 11.4 to 12.1 $\mu\text{g kg}^{-1}$, 19.6 to 65.9 $\mu\text{g kg}^{-1}$, 46.3 to 88.1 $\mu\text{g kg}^{-1}$, 13.1 to 16.3 $\mu\text{g kg}^{-1}$, 13.8 to 14.8 $\mu\text{g kg}^{-1}$, ND to 22.7 $\mu\text{g kg}^{-1}$, 15.3 to 16.3 $\mu\text{g kg}^{-1}$, 16.4 to 17.7 $\mu\text{g kg}^{-1}$, 14.3 to 64.0 $\mu\text{g kg}^{-1}$, 18.8 to 19.7 $\mu\text{g kg}^{-1}$, respectively (Table 3-5).

Table 3. Concentrations of OCPs detected in plant samples in Ergene River Basin, $\mu\text{g kg}^{-1}$ (n=5), (S-L: Sampling location).

S-L	Sample	(1)	(2)	(3)	(4)	(5)	(6)
1E	UD1	14.1 ± 1.1	16.1 ± 1.1	20.8 ± 1.9	20.3 ± 1.5	55.0 ± 3.8	13.9 ± 0.9
	UD2	11.9 ± 0.8	14.3 ± 0.5	12.3 ± 0.8	27.1 ± 1.8	55.7 ± 3.2	16.4 ± 0.7
	MO	12.9 ± 0.9	15.5 ± 1.1	13.0 ± 0.2	13.7 ± 0.8	49.7 ± 3.1	11.3 ± 0.3
	VS	12.7 ± 0.9	15.1 ± 1.1	12.9 ± 0.2	13.3 ± 0.9	28.1 ± 1.9	11.1 ± 0.3
2E	TL1	12.1 ± 0.8	15.5 ± 0.9	13.4 ± 0.3	12.7 ± 0.9	27.0 ± 1.9	10.5 ± 0.1
	TL2	12.5 ± 1.1	14.8 ± 1.1	13.9 ± 0.3	13.0 ± 0.9	17.6 ± 1.1	11.1 ± 0.2
3E	TL1	12.6 ± 1.1	15.0 ± 0.9	12.8 ± 0.1	13.2 ± 0.5	42.4 ± 3.3	10.9 ± 0.3
	TL2	12.3 ± 0.9	14.9 ± 1.1	12.9 ± 0.8	13.0 ± 0.5	40.6 ± 3.0	10.8 ± 0.2
4E	TL1	13.0 ± 0.9	15.8 ± 0.9	14.5 ± 0.4	13.9 ± 0.9	33.5 ± 2.2	11.9 ± 0.2
	TL2	12.3 ± 1.1	14.8 ± 0.9	12.9 ± 0.1	13.4 ± 1.1	35.1 ± 2.5	10.6 ± 0.2
5E	PN	12.9 ± 0.9	15.2 ± 0.2	13.3 ± 0.9	13.5 ± 0.9	19.7 ± 1.1	11.2 ± 0.3
	TL	12.8 ± 1.2	15.2 ± 0.5	13.0 ± 0.2	13.3 ± 1.1	18.3 ± 0.9	11.2 ± 0.3
	CA	12.8 ± 1.2	15.5 ± 0.5	13.1 ± 0.1	13.2 ± 1.1	20.3 ± 1.1	11.3 ± 0.3
6E	PoN	ND	17.6 ± 0.6	18.9 ± 0.7	13.8 ± 1.1	57.9 ± 3.6	14.0 ± 0.8
	TL1	12.3 ± 1.2	14.5 ± 0.5	12.5 ± 0.1	12.8 ± 1.1	28.5 ± 2.2	10.8 ± 0.5
7E	TL2	12.8 ± 1.2	15.6 ± 0.9	14.9 ± 0.4	13.5 ± 1.1	73.4 ± 6.7	11.3 ± 0.5
	TL	11.8 ± 1.1	ND	11.9 ± 0.1	12.3 ± 1.1	27.5 ± 2.2	11.9 ± 0.4
8E	PN	25.4 ± 1.1	31.6 ± 1.3	13.4 ± 0.9	15.5 ± 0.5	20.8 ± 2.1	15.2 ± 0.8
	CL	12.6 ± 1.1	15.5 ± 0.9	13.3 ± 0.2	13.3 ± 0.9	35.8 ± 2.7	11.3 ± 0.1
	CA	12.4 ± 1.1	ND	12.5 ± 0.1	ND	17.5 ± 1.1	13.9 ± 0.1
9E	PA	12.7 ± 1.2	14.9 ± 0.5	12.8 ± 0.2	13.2 ± 0.9	17.4 ± 0.8	11.1 ± 0.2
	MP	13.2 ± 1.3	15.7 ± 0.5	14.7 ± 0.3	ND	22.7 ± 1.6	11.6 ± 0.1
	TL	12.3 ± 1.1	14.8 ± 0.5	13.0 ± 0.1	12.8 ± 0.6	18.9 ± 0.6	10.8 ± 0.1
10E	P	23.3 ± 2.1	16.2 ± 0.9	16.9 ± 0.5	13.2 ± 0.9	18.5 ± 0.9	11.3 ± 0.1
	TL	12.9 ± 1.1	16.1 ± 0.8	ND	13.9 ± 0.9	24.5 ± 1.3	11.5 ± 0.1
	LN	12.6 ± 0.9	17.4 ± 0.6	17.6 ± 0.3	12.8 ± 0.8	20.4 ± 0.11	11.9 ± 0.2
	LN2	13.7 ± 0.9	19.4 ± 0.7	20.5 ± 1.1	13.1 ± 0.9	21.7 ± 0.11	68.3 ± 3.2

Maximum concentration of δ -HCH, Heptachlor, Endrin-aldehyde, Endrin ketone, Heptachlor-endo-epoxide and Dieldrin in *Urtica dioica* L.2 was

detected as 27.1, 55.7, 22.7, 64.0, 175 and 65.9 $\mu\text{g kg}^{-1}$ in point of 1E, respectively. It was thought that this result may be sourced from evaporate of pesticide used in agriculture.

Therefore, these results show that toxicity and bioaccumulation effect of the plant can lead to toxic effect, especially the of agricultural applications and due to evaporation of industrial waste water (especially, sourced waste from production of chemical and chemical products).

Table 4. Concentrations of OCPs detected in plant samples in Ergene River Basin, $\mu\text{g kg}^{-1}$, (S-L: Sampling location).

S-L	Sample	(7)	(8)	(9)	(10)	(11)	(12)
1E	UD1	101 ± 5	19.5 ± 1.1	11.9 ± 0.9	42.6 ± 1.9	88.1 ± 7.1	16.3 ± 0.9
	UD2	175 ± 11	23.5 ± 1.3	11.4 ± 0.5	65.9 ± 4.8	81.0 ± 6.9	14.6 ± 0.6
	MO	16.0 ± 0.2	15.4 ± 0.6	12.1 ± 0.5	19.6 ± 1.1	73.6 ± 6.5	13.3 ± 0.3
	VS	15.6 ± 0.3	14.4 ± 0.6	12.1 ± 0.5	21.2 ± 1.3	46.3 ± 3.8	13.1 ± 0.3
2E	TL1	12.5 ± 0.9	ND	11.4 ± 0.9	15.2 ± 0.9	34.8 ± 2.6	13.3 ± 0.1
	TL2	14.8 ± 0.4	ND	11.8 ± 0.3	15.3 ± 1.1	36.4 ± 2.2	12.8 ± 0.1
3E	TL1	34.8 ± 1.1	14.8 ± 0.6	11.9 ± 0.5	15.7 ± 0.9	62.5 ± 4.1	13.1 ± 0.1
	TL2	20.5 ± 0.9	14.4 ± 0.6	11.6 ± 0.2	14.3 ± 0.9	51.4 ± 4.4	13.1 ± 0.2
4E	TL1	21.0 ± 0.9	ND	12.2 ± 0.1	16.0 ± 0.9	61.0 ± 5.2	17.6 ± 0.3
	TL2	17.3 ± 0.5	ND	11.8 ± 0.2	14.9 ± 1.1	54.8 ± 4.9	15.1 ± 0.3
5E	PN	44.1 ± 1.9	97.9 ± 5.9	12.1 ± 0.9	15.9 ± 0.9	710 ± 21	14.5 ± 0.3
	TL	14.7 ± 0.1	ND	12.1 ± 0.2	17.0 ± 1.3	45.2 ± 3.3	13.5 ± 0.2
	CA	119 ± 7	74.4 ± 4.9	12.1 ± 0.2	31.0 ± 2.1	234 ± 18	19.5 ± 0.9
6E	PoN	22.3 ± 1.1	ND	12.2 ± 0.3	31.8 ± 1.9	103 ± 8	24.1 ± 1.1
	TL1	15.1 ± 1.1	ND	11.6 ± 0.3	16.3 ± 0.7	62.2 ± 4.9	16.8 ± 0.5
7E	TL2	14.9 ± 0.9	ND	12.1 ± 0.3	18.1 ± 0.9	69.2 ± 5.3	14.1 ± 0.3
	TL	14.4 ± 0.9	ND	11.2 ± 0.1	15.3 ± 0.9	80.4 ± 7.1	12.9 ± 0.2
8E	PN	330 ± 22	21.1 ± 1.3	12.0 ± 0.3	31.3 ± 2.2	81.3 ± 7.1	23.4 ± 1.4
	CL	85.3 ± 5.9	46.7 ± 3.2	12.1 ± 0.3	31.4 ± 2.5	64.8 ± 5.2	15.3 ± 0.2
9E	CA	30.3 ± 1.9	14.7 ± 0.7	12.5 ± 0.3	29.4 ± 1.8	182 ± 11	14.8 ± 0.1
	PA	12.2 ± 0.1	ND	12.0 ± 0.5	15.3 ± 1.3	20.6 ± 1.6	12.8 ± 0.1
10E	MP	30.2 ± 1.8	ND	12.1 ± 0.3	15.1 ± 1.1	76.4 ± 6.5	14.7 ± 0.2
	TL	22.1 ± 0.9	ND	11.6 ± 0.2	14.3 ± 1.1	45.7 ± 3.8	12.6 ± 0.1
10E	P	26.1 ± 0.2	13.6 ± 0.4	11.9 ± 0.2	18.2 ± 1.2	44.5 ± 3.3	14.4 ± 0.2
	TL	15.8 ± 0.5	ND	12.3 ± 0.1	23.7 ± 1.9	84.1 ± 6.9	13.8 ± 0.1
	LN	15.7 ± 0.9	ND	11.7 ± 0.9	34.7 ± 0.9	31.6 ± 1.8	13.2 ± 0.2
	LN2	18.3 ± 0.9	ND	12.1 ± 0.9	59.3 ± 0.9	68.2 ± 4.9	15.7 ± 0.2

The concentrations of α -HCH, β -HCH, γ -HCH, δ -HCH, Heptachlor, Aldrin, Heptachlor-endo-epoxide, α -Endosulfan, 4,4'-DDE, Dieldrin, Endrin, β -Endosulfan, 4,4'-DDD, Endrin-aldehyde, Endosulfan sulfate, 4,4' DDT, Endrin-ketone and Methoxychlor

in *Typha latifolia* L. plant of all points were found among 11.8 to 13.0 $\mu\text{g kg}^{-1}$, ND to 16.1 $\mu\text{g kg}^{-1}$, ND to 14.9 $\mu\text{g kg}^{-1}$, 12.3 to 13.9 $\mu\text{g kg}^{-1}$, 17.6 to 73.4 $\mu\text{g kg}^{-1}$, 10.5 to 11.9 $\mu\text{g kg}^{-1}$, 12.5 to 34.8 $\mu\text{g kg}^{-1}$, ND to 14.8 $\mu\text{g kg}^{-1}$, 11.2 to 12.3 $\mu\text{g kg}^{-1}$, 14.3 to 23.7 $\mu\text{g kg}^{-1}$, 34.8 to 84.1 $\mu\text{g kg}^{-1}$, 12.9 to 17.6 $\mu\text{g kg}^{-1}$, 13.6 to 15.0 $\mu\text{g kg}^{-1}$, ND to 127 $\mu\text{g kg}^{-1}$, 15.4 to 18.9 $\mu\text{g kg}^{-1}$, 16.9 to 17.9 $\mu\text{g kg}^{-1}$, 13.6 to 15.1 $\mu\text{g kg}^{-1}$ and 17.9 to 19.9 $\mu\text{g kg}^{-1}$, respectively (Table 3-5 and Fig. 2-7).

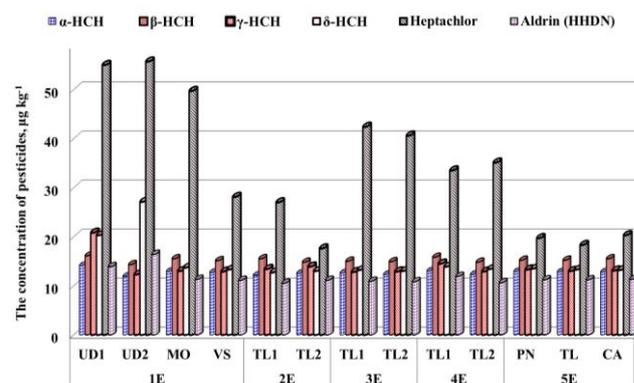


Fig. 2. The concentration graph of α -HCH, β -HCH, γ -HCH, δ -HCH, Heptachlor and Aldrin of plant samples in 1E-5E points.

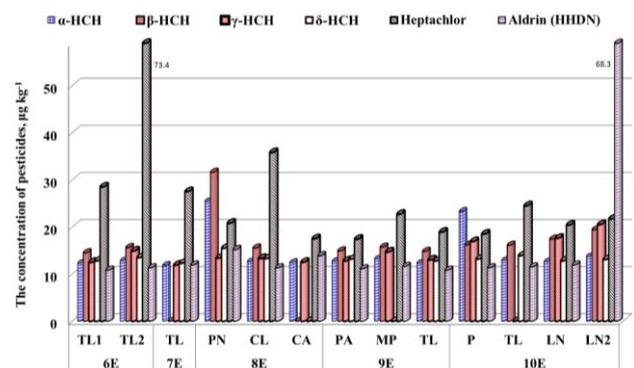


Fig. 3. The concentration graph of α -HCH, β -HCH, γ -HCH, δ -HCH, Heptachlor and Aldrin of plant samples in 6E-10E points.

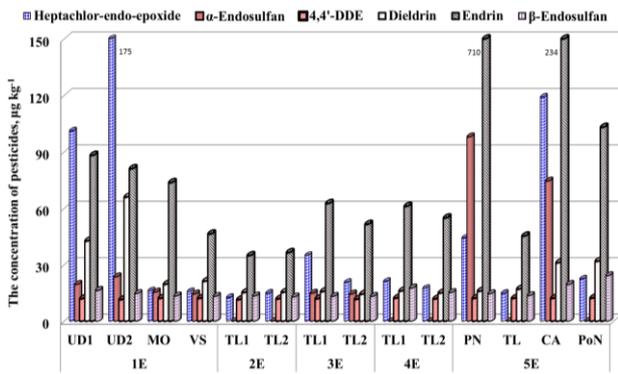


Fig. 4. The concentration graph of Heptachlor-endo-epoxide, α -Endosulfan, 4,4'-DDE, Dieldrin, Endrin and β -Endosulfan of plant samples in 6E-10E points.

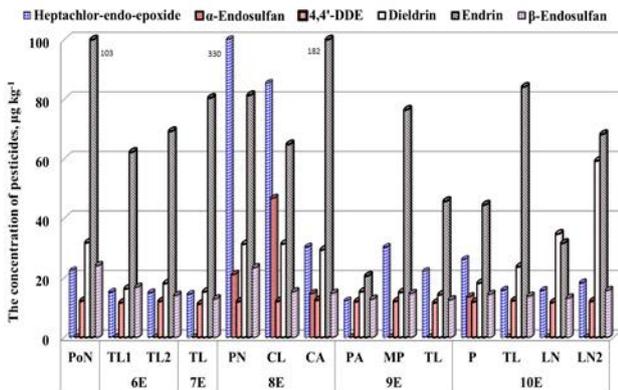


Fig. 5. The concentration graph of Heptachlor-endo-epoxide, α -Endosulfan, 4,4'-DDE, Dieldrin, Endrin and β -Endosulfan of plant samples in 6E-10E points.

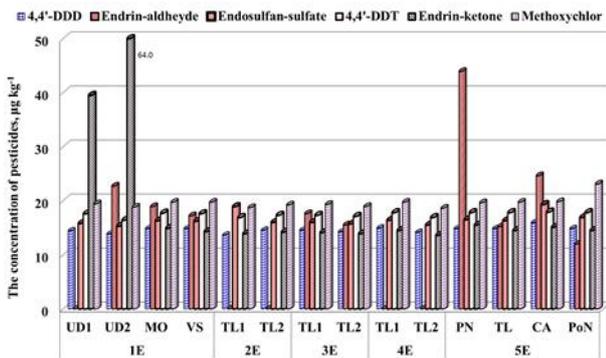


Fig.6. The concentration graph of, 4,4'-DDD, Endrin-aldehyde, Endosulfan sulfate, 4,4' DDT, Endrin-ketone and Methoxychlor of plant samples in 1E-5E points.

The concentrations of Heptachlor, Heptachlor-endo-epoxide, α -Endosulfan, Endosulfan sulfate, Endrin and Endrin-aldehyde in *Cyperus arizonica* L. of 5E and 8E points were found among 20.3 to 17.5 $\mu\text{g kg}^{-1}$, 119 to 30.3 $\mu\text{g kg}^{-1}$, 74.4 to 14.7 $\mu\text{g kg}^{-1}$, 234 to 182 $\mu\text{g kg}^{-1}$ and 24.6 to 325 $\mu\text{g kg}^{-1}$, respectively (Table 3-5 and Fig. 2-7). The use of pesticides can

be considered to be due to evaporation and agricultural the application processes.

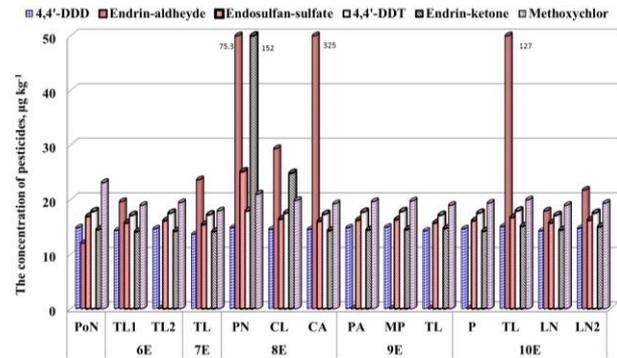


Fig. 7. The concentration graph of, 4,4'-DDD, Endrin-aldehyde, Endosulfan sulfate, 4,4' DDT, Endrin-ketone and Methoxychlor of plant samples in 6E-10E points.

Table 5. Concentrations of OCPs detected in plant samples in Ergene River Basin, $\mu\text{g kg}^{-1}$, (S-L: Sampling location).

S-L Sample	(13)	(14)	(15)	(16)	(17)	(18)	
1E	UD1	14.4 ± 0.1	ND	15.8 ± 0.9	17.6 ± 0.9	39.5 ± 2.8	9.4 ± 0.2
	UD2	13.8 ± 0.3	22.7 ± 0.9	15.3 ± 0.6	16.4 ± 0.9	64.0 ± 4.8	8.8 ± 0.1
	MO	14.8 ± 0.3	18.9 ± 0.7	16.3 ± 0.6	17.7 ± 0.6	14.9 ± 0.9	9.7 ± 0.2
	VS	14.8 ± 0.3	17.2 ± 0.4	16.2 ± 0.6	17.6 ± 0.6	14.3 ± 0.6	9.7 ± 0.1
2E	TL1	13.6 ± 0.1	ND	18.9 ± 0.9	16.9 ± 0.8	13.9 ± 0.9	8.7 ± 0.1
	TL2	14.5 ± 0.1	ND	16.0 ± 0.6	17.3 ± 0.8	14.2 ± 0.6	9.2 ± 0.2
3E	TL1	14.5 ± 0.1	17.6 ± 0.9	16.0 ± 0.6	17.3 ± 0.1	14.1 ± 0.2	9.3 ± 0.1
	TL2	14.2 ± 0.3	15.5 ± 0.7	15.7 ± 0.6	17.1 ± 1.1	13.9 ± 0.9	8.9 ± 0.1
4E	TL1	14.9 ± 0.4	ND	16.4 ± 0.8	17.8 ± 0.9	14.5 ± 0.9	9.7 ± 0.1
	TL2	14.1 ± 0.2	ND	15.5 ± 0.6	16.9 ± 1.1	13.6 ± 0.9	8.6 ± 0.1
5E	PN	14.8 ± 0.1	43.9 ± 2.9	16.5 ± 0.9	17.8 ± 1.1	15.5 ± 0.5	9.6 ± 0.2
	TL	14.8 ± 0.1	15.2 ± 0.8	16.3 ± 0.6	17.8 ± 1.1	14.5 ± 0.3	9.7 ± 0.2
	CA	15.9 ± 0.3	24.6 ± 1.8	19.3 ± 0.6	17.9 ± 0.2	15.1 ± 0.8	9.8 ± 0.2
PoN	14.8 ± 0.1	12.0 ± 0.6	16.9 ± 0.5	17.8 ± 1.1	14.5 ± 0.3	13.1 ± 1.1	
6E	TL1	14.3 ± 0.4	19.6 ± 1.1	15.7 ± 0.5	17.1 ± 1.1	14.1 ± 0.4	8.9 ± 0.2
	TL2	14.6 ± 0.2	ND	16.1 ± 0.5	17.5 ± 1.1	14.2 ± 0.4	9.4 ± 0.1
7E	TL	13.6 ± 0.2	23.6 ± 1.5	15.4 ± 0.5	17.2 ± 1.1	14.1 ± 0.4	7.9 ± 0.1
8E	PN	14.8 ± 0.1	75.3 ± 4.8	25.1 ± 1.1	17.9 ± 1.3	152 ± 9	11.0 ± 0.9
	CL	14.5 ± 0.1	29.3 ± 1.9	16.4 ± 0.9	17.5 ± 1.6	24.8 ± 1.3	9.8 ± 0.1
9E	CA	14.5 ± 0.9	325 ± 28	16.0 ± 0.9	17.3 ± 1.3	14.3 ± 0.5	9.2 ± 0.1
	PA	14.8 ± 0.9	ND	16.2 ± 0.8	17.7 ± 1.1	14.4 ± 0.5	9.6 ± 0.2
	MP	14.9 ± 0.5	ND	16.3 ± 0.2	17.8 ± 1.1	14.5 ± 0.5	9.7 ± 0.2
10E	TL	14.2 ± 0.5	ND	15.7 ± 0.2	17.1 ± 1.2	14.7 ± 0.8	8.9 ± 0.1
	P	14.6 ± 0.9	ND	16.1 ± 0.9	17.5 ± 1.4	14.2 ± 1.1	9.3 ± 0.2
	TL	15.0 ± 0.6	127 ± 9	16.7 ± 0.8	17.9 ± 1.1	15.1 ± 0.9	9.9 ± 0.1
	LN	14.2 ± 0.5	17.9 ± 0.8	15.7 ± 0.9	17.1 ± 1.1	14.4 ± 0.5	8.9 ± 0.1
LN2	14.7 ± 0.5	21.7 ± 1.1	16.2 ± 0.9	17.5 ± 1.1	15.0 ± 0.6	9.3 ± 0.1	

β -Endosulfan concentrations were as much as about 3-6 fold lower than α -Endosulfan, which might reflect the composition of the technical mixture applied in agricultural areas as well as differences in physical properties. α -Endosulfan is more volatile than β -Endosulfan, and therefore typically has higher atmospheric concentrations. It is obvious that pine needles pollution according to other plants were high. There are publications in the literature about this plants biomonitoring features (Tremolada et al. 1996, Xu et al. 2004, Yao et al. 2008, Ratola et al. 2014, Sojinu et al. 2012). Other sources of OCP residues in the plants might be agricultural practices and industrial activities within the Ergene River Basin, in combination with rainfall. Therefore, total Hexachlorocyclohexane (HCH) and Endosulfan compounds were used as insecticide in agriculture during the summer. The information available in literature about levels of these pesticides in pine needles and other plant is almost inexistent. This study is important in terms of being the first study of determination of OCP levels in this plant samples Ergene River, Turkey. OCPs are resistant to degradation, which allows them to persist in the environment for long while and become extensive by way of atmospheric and water transport mechanisms (Sarigiannis et al. 2013, Attia et al. 2013, Pang et al. 2006, Koytar et al. 2002). This result suggests that atmospheric accumulation of Endrin-aldehyde to *Cupressus arizonica* L. of 8E point has been determined high increase ($325 \mu\text{g kg}^{-1}$). The ΣHCH and Dieldrin concentrations exceeded the allowable daily intake limit thereby serving as potential threat to humans. According to Canada the ΣHCH and Dieldrin concentrations allowable limit were 18 and $6 \mu\text{g kg}^{-1}$ day, respectively (Anonymous 1996). Whereas in this study were found range from ND to $31.6 \mu\text{g kg}^{-1}$ and 14.3 to $65.9 \mu\text{g kg}^{-1}$, respectively. According to Huo et al. (2016) have been reported concentration values under 0.05 mg/kg values at the MRL among ND-598 ng/g in green tea for Endosulfan. The same researchers have indicated that they are below the limit of detection of other pesticides in tea (Huo et al. 2016). The recoveries of the pesticides in this study ranged from 78.9 to

99.9% which were better than reported by Huo et al. (71.1 to 119.0%) and Huang et al (2007) (60.7 to 136.7%).

4. Conclusion

The persistent nature of many pesticides together with possible continued illegal use of banned organochlorine compounds raises the potential for continued long-term chronic exposure to people, plants and animals, of the Thrace. The data presented here represent the first survey of contemporary concentrations of toxic organochlorine pollutants in plant samples collected along the Ergene River Basin. The OCPs, which have been detected, were higher than the qualitative target set by European Economic Commission Standards (Anonymous 1980). The results obtained can be used to design an Integrated Management Program to control the concentration of pesticides for plant samples in Ergene River Basin. This investigation is being continued to provide more information on OCPs concentrations of plant samples in Ergene River Basin. In addition to, biological monitoring is a useful appliance for assessing exposure to pesticides. The data gleaned from biomonitoring studies can be used successfully, in conjunction with other data, in risk assessment and risk management. In this study, Endrin ($710 \mu\text{g kg}^{-1}$), Heptachlor-endo-epoxide ($330 \mu\text{g kg}^{-1}$) and Endrin-ketone ($152 \mu\text{g kg}^{-1}$) were determined in the maximum concentration of PN. The lowest pesticide rate among all the plants studied was observed in PA. In addition to, the results show that pollution can be tolerated in Ergene River Basin, but cleaning may take a long time for. Furthermore, this established method by GC-MS technology was proved to be precise, accurate, and applicable to the routine analysis of 18 pesticides in plants. Hopefully, this paper will contribute to the simultaneous determination of 18 pesticides in plants, since banned pesticides are subject to restriction according environmental quality standards.

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