

RESEARCH PAPER

Determination of organochlorine pesticides residues in environmental samples from the republic of Azerbaijan

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Highlights

- Determination of organochlorine pesticide residues in soil and water and in agricultural products was performed in this study.
- The concentration of organochlorine pesticides in samples was investigated by gas chromatography-mass spectrometry (GC-MS).
- The analytical process was carried out according to the method QOST 32194-2013.
- The predominant residue in the agricultural products and soil samples was endosulfan I.

Article Info

Receive Date: 15 October 2022

Revise Date: 17 November 2022

Accept Date: 27 November 2022

Available online: 09 December 2022

Keywords:

Organochlorine pesticides

Soil

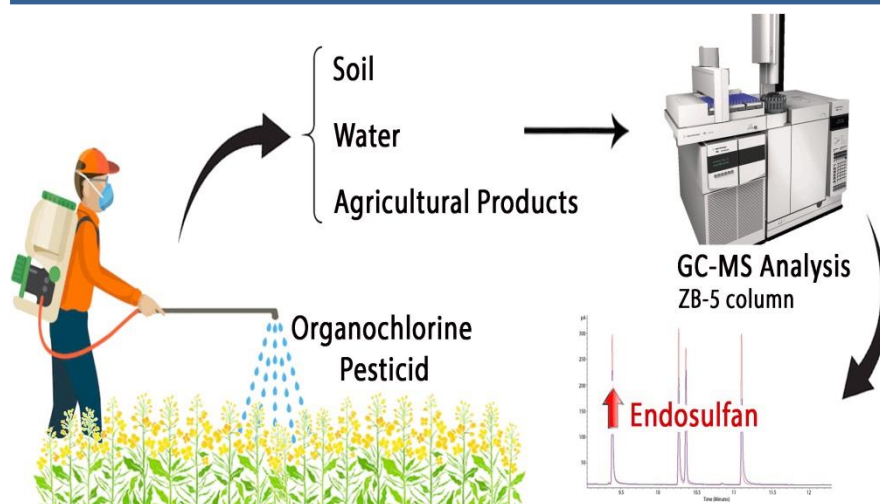
Water

Fruit

GC-MS

Republic of Azerbaijan

Graphical Abstract



Abstract

The objective of this study was to determine the residues of organochlorine pesticides widely used in the past, such as α -BHC, β -BHC, δ -BHC, lindane, aldrin, dieldrin, endrin, endrin-aldehyde, 4,4-DDE, 4,4-DDD, 4,4-DDT, endosulfan I, endosulfan II, endosulfan sulfate, heptachlor, heptachlor epoxide, metoxychlor in environmental objects such as soil and water, and in agricultural products from Republic of Azerbaijan. The concentration of organochlorine pesticides in samples was investigated by the method of gas chromatography-mass spectrometry (GC-MS). For this purpose, soil samples were collected from the cotton plantation and samples of irrigation water, as well as samples of potatoes and apples grown in the surrounding area. The preparation of vegetables and fruits (extraction of pesticides and purification of the extract) for analysis was carried out according to the method QOST 32194-2013. The predominant residue in the agricultural products and soil samples was endosulfan I. It was concluded that the detection of pesticides in the samples could be due to the amount of pesticide residues in the soil resources resulting from intensive agricultural use in the recent past.



doi 10.22034/CAJESTI.2022.06.02

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E-ISSN: 2717-0519

P-ISSN: 2717-4034

1. Introduction

Pesticides have become an integral part of agriculture and have played an important role in protecting crops from yield loss for many years. The use of pesticides is still considered the most effective. However, only a portion of the pesticides applied reaches the target pest (Pimentel, 1995), and the rest ends up in water, soil, and air. The amount that is lost from agricultural fields and reaches surface waters depends on various factors such as the chemical properties of each pesticide, soil characteristics, topography, weather, and agricultural practices (Konstantinou et al., 2006). Pesticides that accumulate in the ecosystem enter the food chain and affect non-target species. They reach the sea or lake via groundwater or surface water and affect life forms such as phytoplankton and zooplankton, shrimp, oysters, and fish (Weber, 2018; Mahmood et al., 2016). It is estimated that there are about one million chronic illnesses and deaths due to pesticide poisoning worldwide each year (van der Werf, 1996). The majority of people are affected by eating food contaminated with pesticides (Sladen et al., 1966). Organochlorine pesticides (OC) are volatile and can contaminate remote areas where they have not been applied by reaching other areas through the air and surface runoff. For example, traces of DDT (dichlorodiphenyltrichloroethane) were found in the Antarctic ecosystem as early as the 1960s (Agbeve et al., 2014). Organochlorine pesticides have a long residual effect and remain in the environment for a long period of time without losing their toxic properties. They have the property of bioconcentration. As polytrophic poisons, these pesticides have a pronounced effect on the central nervous system (CNS) and internal organs (liver, kidneys) (Bempah et al., 2012).

According to the Stockholm Convention, ratified in 2004, DDT, heptachlor, endrin, aldrin and other representatives are banned in a number of countries in Europe, North and South America. Nevertheless, their residual amounts remain in the soil, in natural waters, and thus in plants. Therefore, the development of methods for the determination of pesticides in agricultural products is not only an analytical but also an important social task. It is known that in the recent past Azerbaijan was one of the cotton-producing republics of the Soviet Union. Large parts of Azerbaijani territory were extensively treated with DDT, heptachlor and other OC pesticides. The aim of this work is to study the processes of migration of OC pesticides into the environment and to determine their residual levels in environmental objects such as soil, water and agricultural products from Republic of Azerbaijan (Downie and Templeton, 2013).

2. Materials and Methods

The analysis was performed using a gas chromatograph HP6890 (Agilent, USA) equipped with a column ZB-5 (Phenomenex, USA) and a mass selective detector HP5975. Length of the column - 60 m, inner diameter 5 mm, surface thickness 0.25 μm , copolymer of 5% biphenyl and 95% dimethylpolysiloxane. The volume of injected sample and standard solutions - 1 μL . Helium was used as a carrier gas. The following reagents were used for the analysis: Pentachloronitrobenzene (Supelco); SS TCL Pesticides Mix (Supelco); hexane, HPLC grade; acetone, HPLC grade; dichloromethane, HPLC grade; sodium sulfate, reagent grade; sodium chloride, reagent grade; deionized water; nitrogen, QOST 9293.

2.1. Sample Collection

To study the migration of OC pesticides into the environment and the residual amounts of these pesticides in the environment, soil samples collected from the cotton fields, water used to irrigate these fields, and samples of potatoes and apples grown nearby (Republic of Azerbaijan). The soil and fruit samples were placed in plastic bags, and the water samples were placed in a glass container. The samples were brought to the laboratory in a portable icebox.

2.2. Sample Extraction

2.2.1. Soil

Soil samples were extracted according to EPA 3515C. The soil was homogenized, and stones and plant debris were sorted out before analysis. A 40 g soil sample was placed in a glass conical flask. An internal

standard solution was added to the sample before extraction. The sample was extracted with 50 ml methanol and 60 ml methylene chloride on an ultrasonic bath for 30 minutes. The extract was then transferred through a CF/C filter (Whatman) into a separatory funnel. Previously, 100 ml of solvent-purified deionized water was poured into a separatory funnel. The mixture was shaken for 1 minute, and then the organic phase was separated by draining into a flask. The extraction was repeated twice more for 15 minutes with the addition of 50 ml of dichloromethane. All three extracts were combined and then evaporated to a volume of 2 ml on a rotary evaporator at a temperature of $30\pm 5^{\circ}\text{C}$. The extract was then concentrated under nitrogen to 1 ml.

2.2.2. Water

The extraction was performed according to EPA 3510C. Approximately 1 liter of the water sample is poured into a separatory funnel. An internal standard solution was added to the sample before starting the extraction. The water sample was extracted with dichloromethane (50 ml) by vigorous shaking for 1-2 minutes. Then the organic phase was separated by draining into a flask. This procedure was repeated two more times with fresh portions of the solvent and the soil phase was collected. All three extracts were combined and evaporated on a rotary evaporator at a temperature of $30\pm 5^{\circ}\text{C}$ to a volume of 2 ml. The obtained extract was then concentrated to 1 ml under nitrogen addition (Liang et al., 2020).

2.2.3. Vegetables and Fruits

Extraction of fruit and vegetable samples was performed according to QOST 32194-2013. The vegetable and fruit samples were crushed using a blender until a homogeneous mass was obtained. The obtained sample (100 ± 0.1 g) was placed in a 1000 ml conical flask and made up to a total volume of 100 ml with deionized water. The sample was allowed to stand for about 5 minutes until it was well saturated with water. Then 200 ml of acetone was added to the same flask, tightly sealed, and shaken on a mechanical shaker for 2 hours. A blank sample was prepared in a similar manner. The suspension was filtered with a vacuum pump through a Buchner funnel with medium-porosity filter paper into a 500-ml Bunsen flask. The Erlenmeyer flask and the residue on the filter paper were washed with two 25-ml portions of acetone, with the wash liquids collected in the same flask. The volume of the filtrate was measured with a cylinder and 1/5 of this filtrate was transferred to a 500-ml separatory funnel. Then 250 ml of deionized water, 50 ml of saturated sodium chloride solution, and 100 ml of dichloromethane were added to a separatory funnel containing the filtrate.

The mixture was shaken for 2 minutes. After separation of the phases, the lower phase (dichloromethane) was poured into another separatory funnel. The procedure was repeated twice with 50 ml of dichloromethane, and the phases were then combined. The combined extract was washed with two 100 ml portions of deionized water, and the aqueous fraction was discarded. Then the extract was filtered through filter paper containing about 20 g of sodium sulfate into a round bottom flask with a capacity of 500 ml. The extract was evaporated in a rotary evaporator at a temperature not exceeding 35°C to a volume of about 2 ml. The solution was quantitatively transferred to a 10 ml volumetric vessel with 1-2 ml of hexane and evaporated to about 1 ml under a gentle stream of nitrogen. The extracts were purified with an eluent - a mixture of dichloromethane and hexane (20% by volume). The eluent was prepared by mixing 1 volume of dichloromethane with 4 volumes of hexane (Ebadi and Shokrzadeh, 2006a).

3. Results and Discussion

In this study, we investigated the possibility of determining the residues of organochlorine pesticides in soil, water and agricultural products. Samples were analysed for a total of 17 OC pesticides (α -BHC, β -BHC, δ -BHC, lindane, aldrin, dieldrin, endrin, endrin aldehyde, 4,4-DDE, 4,4-DDD, 4,4- DDT, endosulfan I, endosulfan II, endosulfan sulphate, heptachlor, heptachlor epoxide, metoxychlor) Pentachloronitrobenzene was used as an internal standard for quantification of each OC pesticide (Fig. 1).

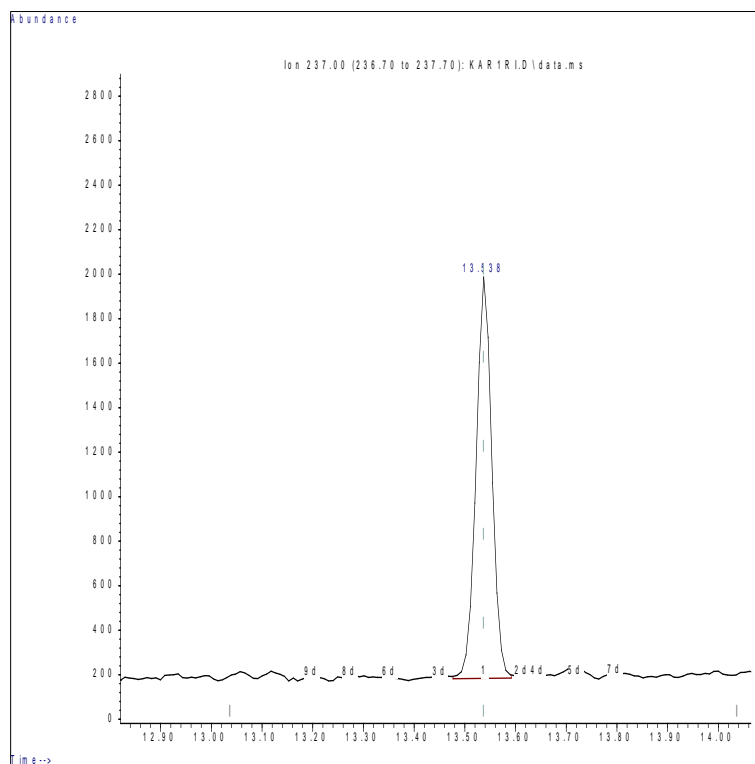


Fig. 1. Chromatogram of internal standard – pentachloronitrobenzene.

A mixture of seventeen OC pesticides, containing 2000 mg/L of each component (α -BHC, β -BHC, δ -BHC, Lindane, Aldrin, Dieldrin, Endrin, Endrin Aldehyde, 4,4-DDE, 4,4-DDD, 4,4-DDT, Endosulfan I, Endosulfan II, Endosulfan sulfate, Heptachlor, Heptachlor epoxide, Metoxychlor) was used as a standard solution. The calibration standard samples were prepared by dissolving a mixture of OC pesticides in dichloromethane. Quantification of pesticides in the samples was performed with 8-points linear calibration curve (Fig. 2).

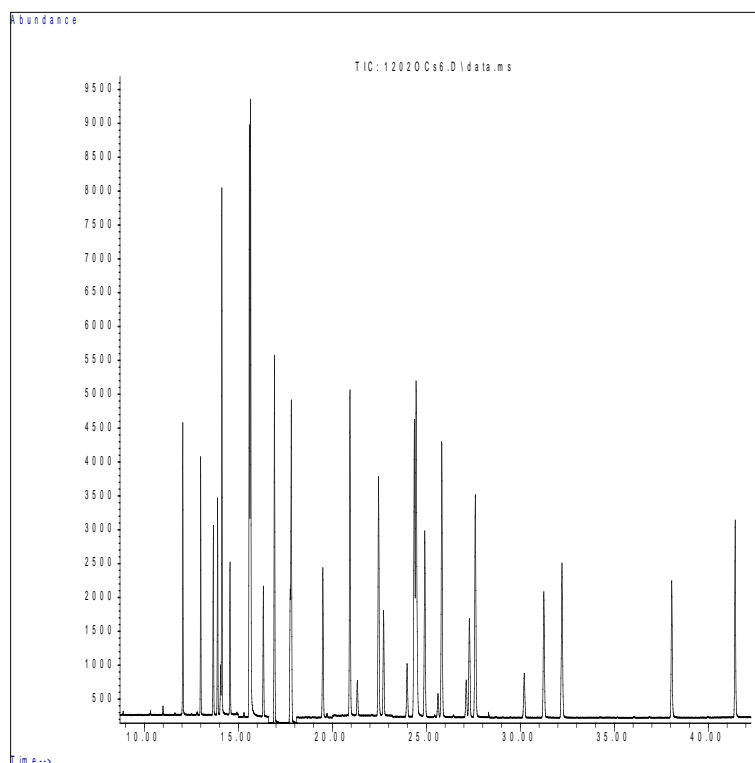


Fig. 2. Ion chromatogram of seventeen OC pesticides in calibration standard solution.

Retention times and Detection limit of method are presented in [Table 1](#).

Table 1. Retention times and detection limits of method.

OC pesticides	Retention Time (min)	Detection Limit (mg/kg)
α - BHC	12	0,005
Lindane	13	0,005
β - BHC	14	0,005
Heptachlor	15,5	0,005
δ - BHC	17	0,005
Aldrin	17,9	0,005
Heptochlor epoxide	19,5	0,005
Endosulfan I	21	0,005
4,4-DDE	22,6	0,01
Dieldrin	24,5	0,005
Endrin	25	0,005
4,4-DDD	26	0,01
Endosulfan II	27,3	0,005
4,4-DDT	27,6	0,01
Endrin Aldehyde	32,3	0,005
Endosulfan sulfate	38,1	0,005
Metoxychlor	41,4	0,05

Soil and water samples chromatograms are presented in [Figs. 3](#) and [4](#) correspondingly.

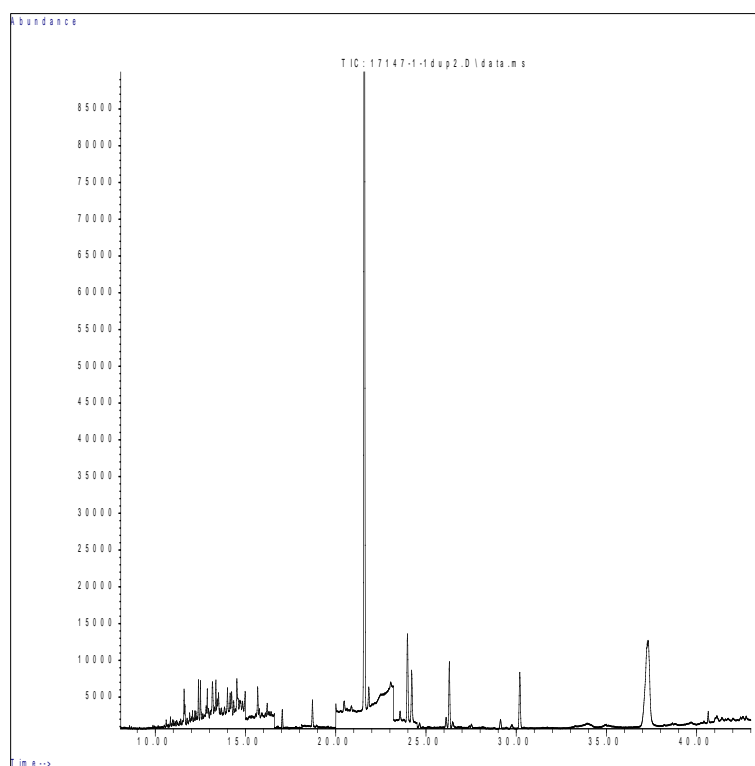


Fig. 3. GC-MS chromatogram of soil sample.

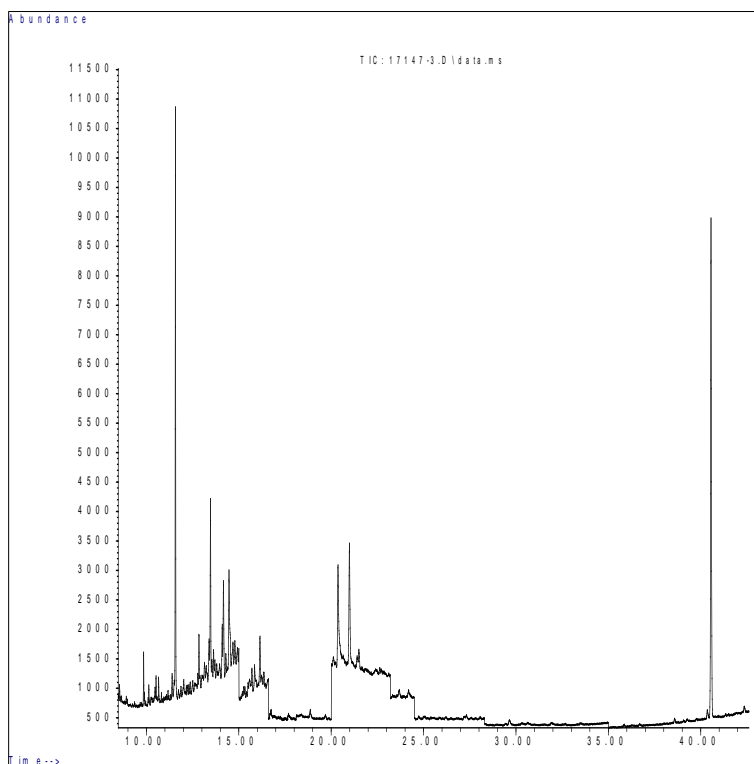


Fig. 4. GC-MS chromatogram of water sample.

It is known that pesticides accumulate in vegetables and fruits to varying degrees (Agarwal et al., 1986). Apples, strawberries, peaches, grapes and among vegetables potatoes, beets, carrots, tomatoes and cabbage have the greatest ability to accumulate pesticides (Chakraborty et al., 2016). We performed chromatographic determination of residues of OC pesticides in potato and apple samples. A matrix solution prepared by adding the appropriate standard intermediate solutions of pesticides to the blank sample was used. The GC- MS chromatograms of the potato and apple samples are shown in Figs. 5 and 6.

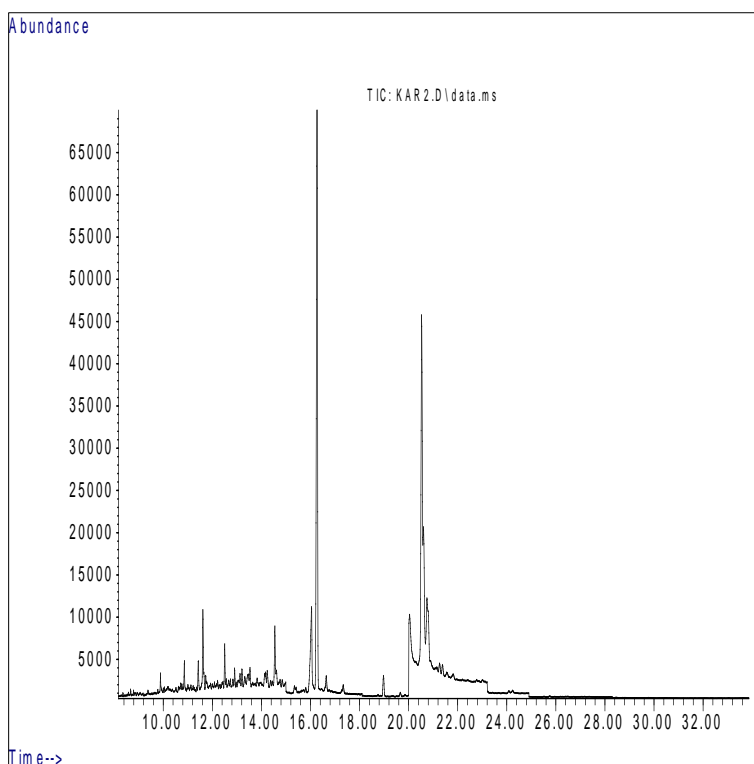


Fig. 5. GC-MS chromatogram of representative sample potato in SIM mode.

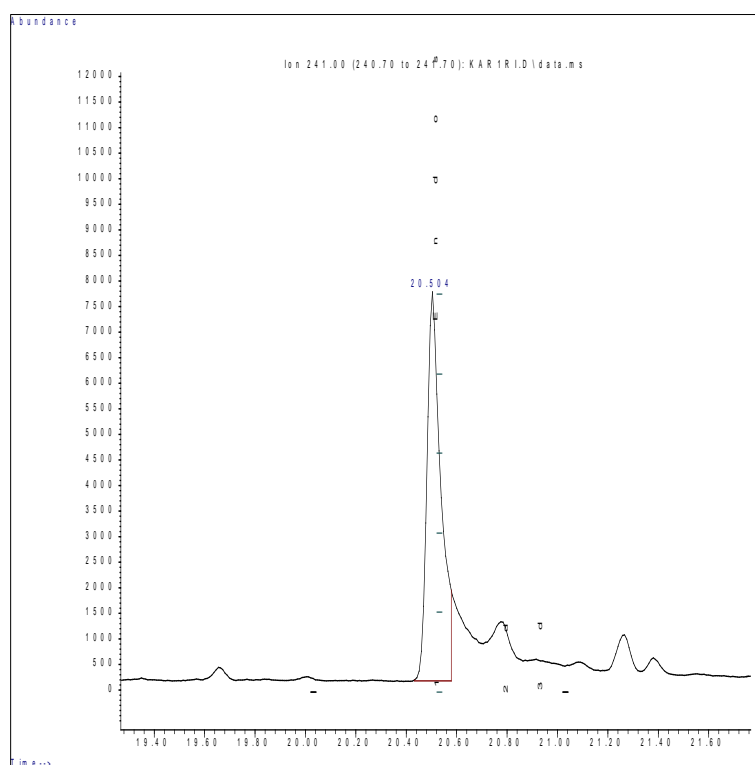


Fig. 6. GC-MS Chromatogram of a representative apple sample in SIM mode.

The results of the soil, water, potato and apple samples are shown in Table 2.

Table 2. Concentration of detected pesticides in samples (n = 3, P = 0.95).

Sample	Detected OC pesticide	Concentration in sample (ug.kg ⁻¹ , ug.l ⁻¹)	Injected (ug.kg ⁻¹ , ug.l ⁻¹)	Detected (ug.kg ⁻¹ , ug.l ⁻¹)	S _r (%)	Recovery (%)
Soil	4,4-DDE	1,9±0,1	10,0	9,0±1	4,98	73±9
	4,4-DDD	1,3±0,09	10,0	9,8±0,05	1,61	83±3
	4,4-DDT	4,6±0,2	10,0	12,0±1	3,33	85±7
	Endosulfan I	3,6±0,2	10,0	12±1	3,28	82±7
Water	4,4-DDT	2,2±0,15	10,0	9,8±0,4	1,8	84±3
Potato	Dieldrin	2,05±0,15	10,0	9,1±0,4	1,9	73±4
	Endosulfan I	10,4±0,4	10,0	31,5±2,52	3,04	85±6
Apple	Endosulfan I	2,1±0,15	10,0	9,8±0,4	1,61	83±3

The analyses included laboratory quality control procedures. Appropriate blanks and duplicates were analysed with each type of sample analysed. The studied pesticides have good selectivity and resolution parameters on a ZB-5 column (Phenomenex, USA). Experiments show that the retention time of pesticides (Table 1) can vary in the determination both in a mixture and individually; therefore, in the analysis of real objects, if there are difficulties in identifying peaks, the addition method should be used (Feng et al., 2011).

As is well known, DDT tends to metabolize, i.e., transform into other derivatives (Agarwal et al., 1986). The causes of metabolization are not yet fully understood. This phenomenon may occur during storage and preparation of samples as well as during gas chromatographic analysis. In addition, prolonged exposure in soil also contributes to the transformation of DDT. Studies conducted using special methods have shown that the major metabolite of DDT is 4,4'-dichlorophenyldichloroethane (DDE). Traces of both DDT and its metabolites were found in soil samples. DDT and its derivatives are very resistant; the half-life in soil can be up to 30 years. The concentration of endosulfan I and of DDT and its metabolites in soil and water samples does not exceed the

maximum permitted concentration (MPC), which is 0.1 mg/kg for soils and 0.1 mg/L for sanitary water. However, the content of endosulfan I (MPC in vegetables and fruits is 0.002 mg/kg) in potatoes exceeds the permissible limits by five times (Table 2). The high endosulfan content is due to the fact that endosulfan was extensively used in the past, especially in cotton fields. Endosulfan has no toxic effect on beneficial insects such as ladybugs, ichneumon wasps, and some mites, but is highly toxic to birds, poultry, bees, and fish (Guan et al., 2009; Peng et al., 2014; Rissato et al., 2006; Mohammadizadeh and Ebadi, 2006; Ebadi and Shokrzadeh, 2006b).

4. Conclusion

In the last fifty years, it is impossible to imagine the world of agriculture without pesticides. The demand for the production and distribution of pesticides that increase the quality and efficiency of agriculture is certain, but the possibility of improper and unreasonable use is very high. The increase in population and the consequent increase in food consumption, especially for agricultural products, has led farmers to increase the quantity of their products. Due to the negligence of farmers in the use of pesticides, atmospheric precipitation and various other factors, agricultural pesticides enter the waters of rivers and oceans. Pollution has become a global problem today.

For this reason, laws should be enacted to control the use of pesticides, and farmers should be trained to use pesticides wisely and to use biological pesticides and pesticides derived from natural products in order to protect the various components of the environment. give life assurance The purpose of this article, then, is to raise public awareness, especially in the Republic of Azerbaijan, of the dangers posed by these poisons and also to ensure the consumption of the samples under study. Of course, regular monitoring and recommendations for action by the relevant organizations are necessary.

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How to cite this paper:

Huseyinli, A.A., Hajieva, S., Mammadov, P., Sadikhova, L., 2022. Determination of organochlorine pesticides residues in environmental samples from the republic of Azerbaijan. *Cent. Asian J. Environ. Sci. Technol. Innov.*, **3**(6), 166-174.