



The Migration of Organic Chlorine Pesticide Residues in the Composition of the Soil Samples from Mirzaabad, Gulistan and Boyovut Districts of Syrdarya Region

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ABSTRACT: The thin layer chromatography gas chromatography ECD detector was employed to evaluate soil samples and wheat stalks collected during the spring season for the presence of chlorine organic pesticides, namely DDT, DDE, DDD, HCH alpha, and gamma isomers. The study revealed that the uppermost concentration of pesticides is constrained within the depth interval of 0–10(20) cm, with their infiltration extending to a depth of 2.0–2.5 m. The initial investigation focused on examining the dynamics and movement of OCP, including substances such as DDT, DDD, DDE, alpha HCH, and gamma HCH, throughout the Syrdarya region. This page provides an overview of organochlorine pesticides, their residual presence, their application in agricultural regions, and the constituent makeup of wheat stalks. In April 2023, a collection of samples was obtained from several districts within the Syrdarya region. Subsequently, a comprehensive analysis was conducted on a total of 15 samples. The gas chromatography technique with an electron capture detector (GC/ECD) was employed for the investigation of organic chlorine insecticides. The isolation and quantification of organic chlorine insecticides with low to medium polarity were achieved using a capillary column.

KEYWORDS: Gulistan, Syrdarya region, Mirzaabad, Boyovut, soil samples, organochlorine pesticides (OCP), DDT, DDE, DDD, HCH alpha, beta and gamma isomers soil sample, ECD detector, gas chromatography technique.

INTRODUCTION

The primary route of human exposure to organochlorine contaminants is via the contamination of food. Fish, meat, fruits, vegetables, and dairy products are considered significant dietary sources of pesticides and their metabolites for human consumption. The presence of these pollutants in food has been well-acknowledged for a significant period of time.

The implementation of tasks outlined in various decisions and normative legal documents, such as the Decree of the President of the Republic of Uzbekistan dated December 16, 2018 No. PD-5303 “On measures to further ensure the food security of our country”, Decree No. PD-5853 of the President of the Republic of Uzbekistan dated October 23, 2019 “On approval of the strategy of agricultural development of the Republic of Uzbekistan for 2020–2030”, and the Decree of the President of the Republic of Uzbekistan dated June 17, 2019 No. PD-5742 “On measures for the effective use of land and water resources in agriculture”, is facilitated [1, – p. 54–55].

At present, the utilization of pesticides is prevalent in order to achieve a substantial crop output in the agricultural sector. In light of this, it is estimated that around 80–85% of pesticide residues are introduced into the human body through the consumption of food. Due to this rationale, significant emphasis is directed towards this particular industry with the objective of supplying the populace with food goods of high quality. In order to mitigate potential adverse impacts on human health, it is imperative to possess comprehensive and dependable data that facilitates the formulation of strategies pertaining to the extent of pesticide contamination in agricultural commodities [2, – p. 84–85]. The establishment of protocols aimed at maintaining the hygienic integrity of pesticides plays a crucial role in safeguarding the overall food safety of the general population. This endeavor is intricately linked to the development and validation of consumer market identification techniques, as well as the precise quantification and regulation of residual pesticide levels.

The persistence of chlorine compounds in the environment and their tendency to accumulate in the food chain have emerged as significant issues of concern. The utilization of DDT and numerous other chlorinated pesticides has been prohibited in the majority of countries since the 1970s.



The escalation in pesticide utilization for agricultural purposes has resulted in a corresponding rise in environmental pollution, specifically affecting soil, water, and air quality. The primary attributes exhibited by chlorine-based organic pesticides include low polarity, limited solubility in aqueous solvents, and high lipophilicity, indicating a strong affinity for fat-soluble solvents. The user provided a numerical reference [3]. The characteristics shown by pesticides, including their notable stability, extended half-life, and capacity for long-distance migration, have resulted in the persistent contamination of air, water, and soil over prolonged periods, notwithstanding their extensive historical utilization. A scientific investigation has revealed that a minimal fraction (0.3%) of the pesticides applied effectively reach their intended targets, with the overwhelming majority (99.7%) being dispersed into other environmental compartments such as soil, water, air, and other locations.

In the past, OCP insecticides demonstrated efficacy in managing malaria and typhus; but, their usage has been prohibited in the majority of developed nations. The statistical data pertaining to the utilization of different pesticides indicates that around 40% of the total pesticides employed fall within the category of organic chlorine pesticides. Several organochlorine insecticides, including DDT, hexachlorocyclohexane, aldrin, and dieldrin, are extensively utilized as pesticides in emerging Asian countries to combat a range of pests.

The study observed a significant and enduring presence of the gamma-isomer of HCH in soil, with a concentration of one-tenth mg/kg. Several researchers have observed that the beta-isomer of HCH exhibits greater resistance when compared to DDT. Numerous categories of pesticides undergo degradation processes resulting in the formation of persistent metabolites that possess potential hazards to both the environment and living organisms. Typically, the concentration of DDE (*p,p*-dichlorodipenyldichloroethylene), the primary metabolite of DDT (*p,p*-dichlorodipenyltrichloromethylmethane), surpasses the original substance in agricultural soils where DDT has been employed. The user has provided a numerical sequence consisting of the numbers 5 and 6.

The perception of pesticides as hazardous to human health or the environment did not emerge until the late 1950s. Nevertheless, the extensive utilization of pesticides around the middle of the 20th century prompted inquiries over their level of safety. Numerous studies have demonstrated the profound toxicity of DDT towards various mammalian, piscine, and avian species. Upon entering the soil, the animal remains undergo a process of preservation within the human adipose tissue for an extended period. Furthermore, these remains tend to amass within the liver, and subsequently, they are expelled through the secretion of milk and eggs.

For instance, the application of organochlorine pesticides to soil leads to their proliferation in crops, subsequently resulting in their presence in the human body by the consumption of the product cultivated therein [7]. As per the findings of V.P. Vasilev [8], the process of DDT accumulation in fruits, such as apple trees, is absent due to the absence of fruit evaporation. In a study conducted by Riskieva [9], it was shown that the concentration of DDT in fruits was significantly higher compared to the concentration of this substance in the soil, with a ratio of ten to one.

The distribution of organochlorine pesticides in the environment can occur as a result of pesticide application, the release of contaminated waste into natural ecosystems, and the discharge of industrial waste that contains these chemical compounds. The presence of volatile and stable compounds enables their adherence to both soil and air, hence augmenting the probability of prolonged persistence within the environment. Consequently, chronic exposure to these substances has been associated with the emergence of several diseases in both animal and human populations. This study demonstrates the presence of toxicity, practical application, and environmental stability.

The presence of DDT (as shown by the combined metabolites) and HCH (as indicated by the combined isomers of 3 alpha, beta, and gamma) was identified in the soil, along with herbicides and organochlorine insecticides.

Pesticides, chemical substances developed to combat pests and pathogens, pose a significant global environmental challenge within the realm of agricultural production. These substances exert adverse effects on the environment and human health, manifesting directly within the agricultural sector as well as in various other domains of the national economy.

The materials and methods. In the spring season of Mirzaabad, Gulistan, Boyovut, and Dehkanabad agricultural of Boyovut district, soil samples were obtained from a depth range of 70–150 cm. The study focused on the Chromatek Kristallyuks 4000 M (Russia) PID (Proportional–Integral–Derivative controller) and ECD, which are electronic capture detector devices used in the chemical analysis department of the “Experimental Biology” laboratory.



Soil samples were collected from each respective region utilizing the envelope method. Soil samples were obtained utilizing a stainless steel spade at a depth ranging from 70 to 150 cm from the surface layer, employing the envelope approach. The soil sample was pulverized and subsequently measured using an analytical balance (XYSSALE, FA 2204N) to obtain a weight of 10 g. The soil sample obtained from Haver blocker 59302 OELDE (Germany) was subjected to sieving using a 200 μm mesh size. The soil sample was placed in a solution containing 1% ammonium chloride salt, and the samples were allowed to sit for a duration of one day. The soil solution was obtained by utilizing a combination of 30 ml of acetone and 30 ml of hexane (chemical reactive supply (CRS) S6N14, chda, batch 4–160153). The extraction procedure involved subjecting the mixture to ultrasonic agitation using a UT SONIS Professional ultrasonic cleaner from China for a duration of 1 hour. The solution component of the soil extract was separated from the centrifuge and subsequently filtered. Following this, 30 ml of acetone and hexane solvents were introduced to the sediment portion, which was then subjected to agitation on a shaker for a duration of 30 minutes. The samples were subjected to extraction, filtration, and subsequently transferred into a separatory funnel. The mixture was then vigorously agitated with 180 ml of distilled water for a duration of 5–7 minutes. The lower portion was extracted. In order to exclude extraneous compounds, the upper phase containing hexane was subjected to treatment with anhydrous sulfuric acid. The hexane phase was extracted from the sulfuric acid phase using a separatory funnel. The hexane was subjected to heating in a water bath at a temperature of 40°C until its volume reduced to 10 ml. Subsequently, 1 g of anhydrous sodium sulfate (Na_2SO_4) was introduced to the hexane in order to absorb any remaining water. The mixture was then allowed to stand for a duration of 1 hour. A volume of 1 ml of the filtrate was transferred into the auto-sampling vial for subsequent analysis.

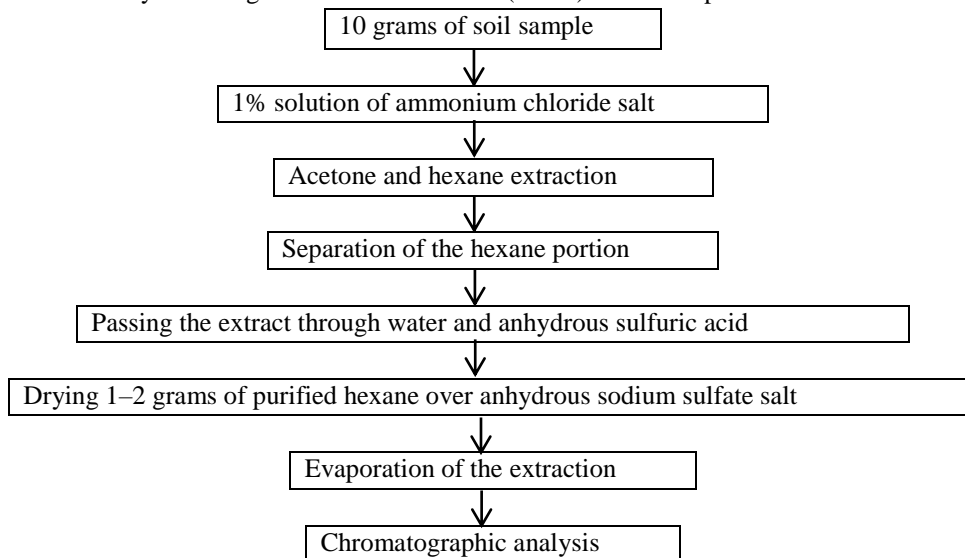
No traces of chlorine organic pesticides were observed in the soil sample when compared to the established standards in the aforementioned experimental procedure. The bleaching process involved the utilization of a solution comprising silver nitrate dissolved in ammonia.

Table 1. The state of the chromatogram of the soil sample in the Electron Capture Detector (ECD)

Evaporator temperature	230°C
Temperature detector	250°C
Column temperature	200°C
Carrier gas consumption, gas nitrogen	1.cm ³ /min 20, 2.cm ³ /min 17
Flow division coefficient	1:5
Ionization energy	70 eV;
Detector operation delay	7 min
Total analysis time	14 min
Column title	ZB–5
Column length, meters	30
Column diameter mm	0,32
Column type	Capillary
Detector	Electron Capture Detector (ECD)



Table 2. The scheme of the analysis of Organochlorine Pesticides (OCPs) in the composition of soil



Analysis and results

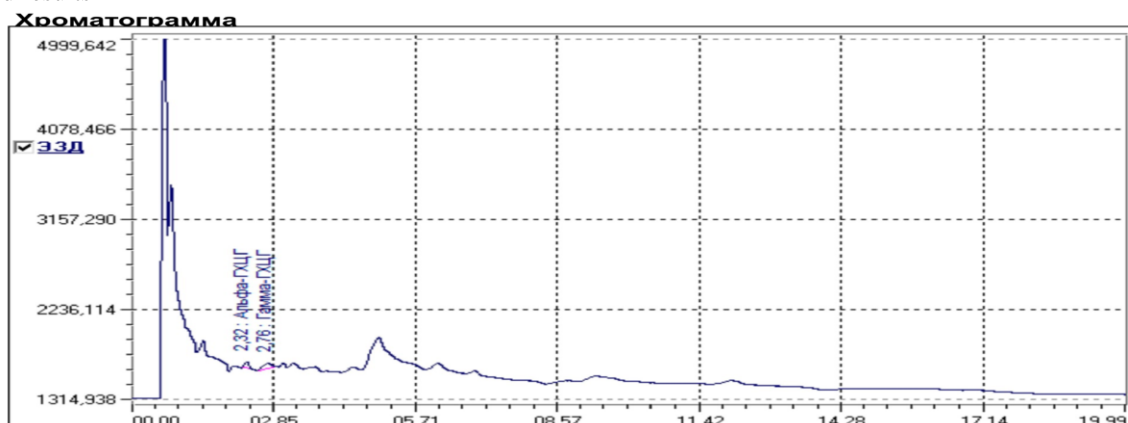


Figure 1. The chromatogram of the soil sample of Dehkanabad farm area of Boyovut district of Sirdarya region

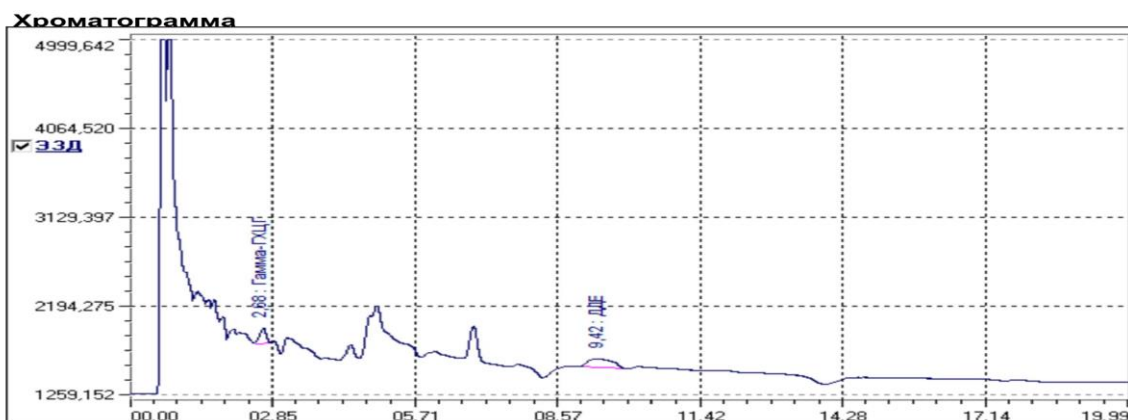


Figure 2. The chromatography of wheat grass of Dehkanabad farm area of Boyovut district of Sirdarya region



Table 3

The title of organochlorine pesticides (OCPs)	Time, minute	Concentration mg, kg	Height, mV	Area, mV, minute	Width, second
Alpha Hexachlorocyclohexane (HCH)	2,32	0,001	63,875	5,6111	4,16
Gamma Hexachlorocyclohexane (HCH)	2,76	0,001	43,978	8,0167	13,12

According to the findings presented in Table 3 (Figure 1), an analysis was conducted on soil samples collected from the Dehkanabad farm area, Boyovut district, Sirdarya region. The analysis involved examining 10 grams of soil samples. The experiment revealed the presence of the alpha isomer of HCH (α -hexachlorocyclohexane) at a concentration of 0.001 mg–ml, detected within a time frame of 2.32 minutes. Additionally, the experiment detected the presence of the gamma isomer of HCH (γ -hexachlorocyclohexane) at the same concentration of 0.001 mg–ml, and the alpha and beta isomers of HCH (α -hexachlorocyclohexane, β -hexachlorocyclohexane) were identified within 2.76 minutes. No other forms of OCPs were identified in the soil composition.

Table 4

The title of organochlorine pesticides (OCPs)	Time, minute	Concentration mg, kg	Height, mV	Area, mV, minute	Width, second
Gamma Hexachlorocyclohexane (HCH)	2.68	0.003	156.167	20.4224	10.60
DDE	9.42	0.008	90.048	53.4356	26.96

As shown in Table 4 (Figure 2), after the analysis of the soil sample taken in March of the spring season, wheat grass planted in Dehkanabad farm, Boyovut district, Sirdarya region, contained HCH (γ -hexachlorocyclohexane) Gamma isomer in the amount of 0.003 mg–ml in 2.68 minutes, 9 HCH (γ -hexachlorocyclohexane) Gamma isomer and DDE were detected in soil at 0.008 mg–ml of DDE at 42 min and no other OCP was detected.

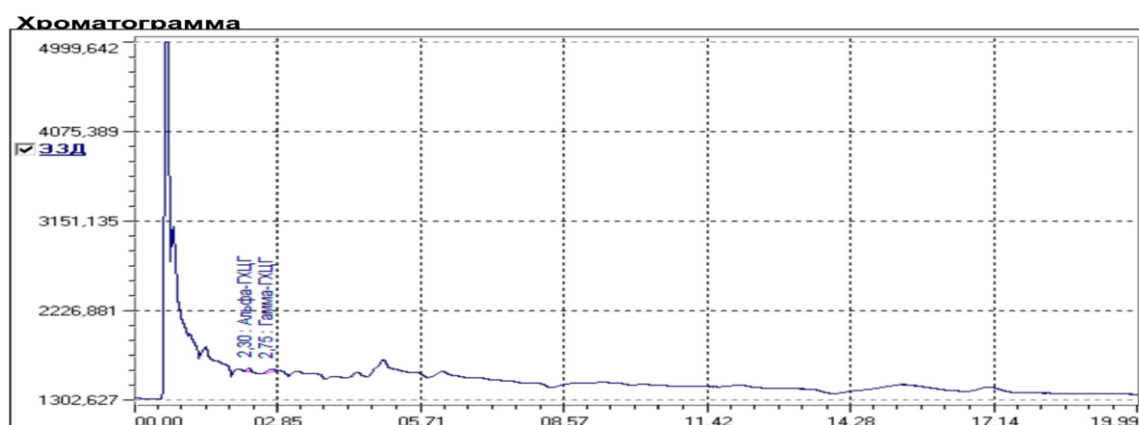


Figure 3. The soil samples of Boyovut district of Sirdarya region

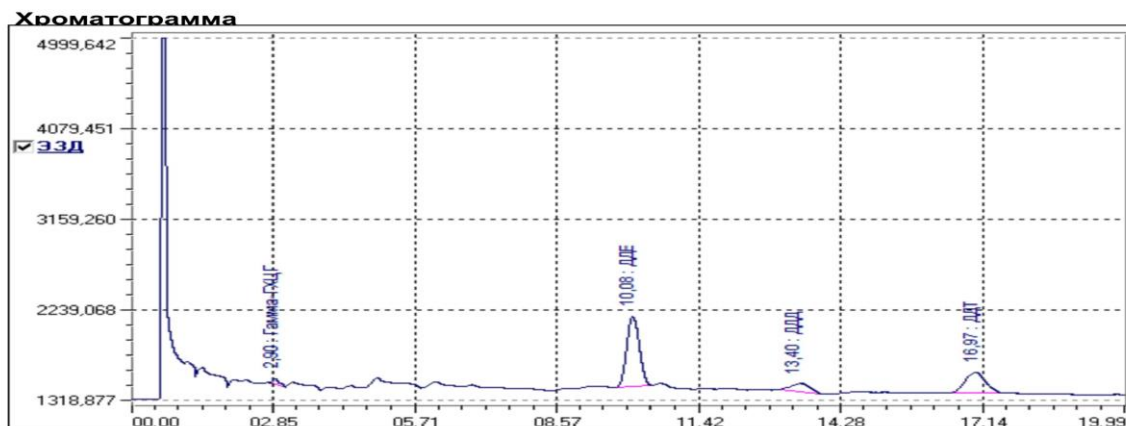


Figure 4. The soil samples of Gulistan district of Syrdarya region

Table 5

The title of organochlorine pesticides (OCPs)	Time, minute	Concentration mg, kg	Height, mV	Area, mV, minute	Width, second
Alpha Hexachlorocyclohexane (HCH)	2,30	0,001	40,385	3,3109	4,56
Gamma Hexachlorocyclohexane (HCH)	2,75	0,001	24,168	3,7659	9,44

According to the data presented in Figure 3 (Table 5), during the spring season, an analysis was conducted on soil samples weighing 10 g, which were obtained from the Gulistan district of the Syrdarya region. The results indicated the presence of the alpha isomer of HCH (α -hexachlorocyclohexane) at a concentration of 0.001 mg–ml, with a retention time of 2.30 minutes. Additionally, HCH was detected with a retention time of 2.75 minutes. The gamma isomer of gamma-hexachlorocyclohexane was found at a concentration of 0.001 mg/mL. Additional groupings of OCPs were not identified.

Table 6

The title of organochlorine pesticides (OCPs)	Time, minute	Concentration mg, kg	Height, mV	Area, mV, minute	Width, second
Alpha Hexachlorocyclohexane (HCH)	2,90	0,001	52,534	6,7887	4,56
Gamma Hexachlorocyclohexane (HCH)	2,90	0,001	52,534	6,7887	4,56
DDE	10,08	0,031	708,072	197,4585	21,80
DDD	13,40	0,007	72,985	33,7759	21,16
DDT	16,97	0,0037	204,114	91,1761	27,60

During the analysis of soil samples from the Boyovut district of the Sirdarya region, the composition of 10 g of soil was examined. Within a time span of 2.9 minutes, the presence of HCH (α -hexachlorocyclohexane) alpha and HCH (γ -hexachlorocyclohexane) gamma isomers was detected, with concentrations of 0.001 mg–ml. Subsequently, after 10.08 minutes, the presence of DDE (dichlorodipenyldichloroethylene) was observed, with a concentration of 0.031 mg–ml. Following this, after 13.4 minutes, DDD (dichlorodipenyldichloroethane) was found in the amount of 0.007 mg–ml. Finally, after 16.9 minutes, DDT (dichlorodipenyltrichloroethane) was detected, with a concentration of 0.037 mg–ml. Additionally, the presence of OCP was determined.

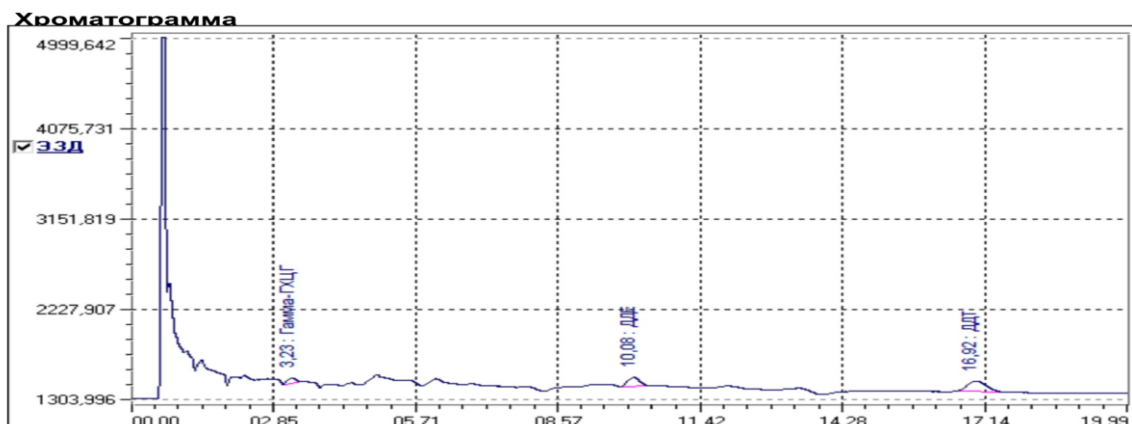


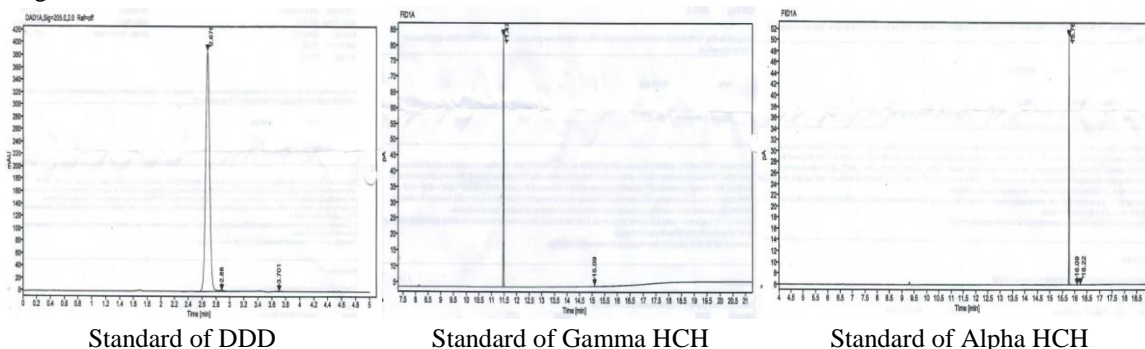
Figure 5. The soil samples of Mirzaabad district of Sirdarya region

Table 7

The title of organochlorine pesticides (OCPs)	Time, minute	Concentration mg, kg	Height, mV	Area, mV, minute	Width, second
Gamma Hexachlorocyclohexane (HCH)	3,23	0,002	50,101	8,8702	9,20
DDE	10,08	0,004	90,482	23,3175	14,16
DDT	16,92	0,018	104,454	44,1156	20,60

According to the findings presented in Figure 5 (Table 7), an analysis was conducted on soil samples weighing 10 g, collected from the Mirzaabad district of the Sirdarya region during the spring season. The experiment involved measuring the concentration of HCH (hexachlorocyclohexane) Gamma isomer, DDE, and DDT in the samples. The HCH Gamma isomer was detected at a concentration of 0.002 mg–ml after 3.23 minutes, while DDE was found at a concentration of 0.004 mg–ml after 10.08 minutes. Additionally, DDT was detected at a concentration of 0.018 mg–ml after 16.92 minutes. The presence of OCP was also determined during the experiment.

The chromatogram of the standards



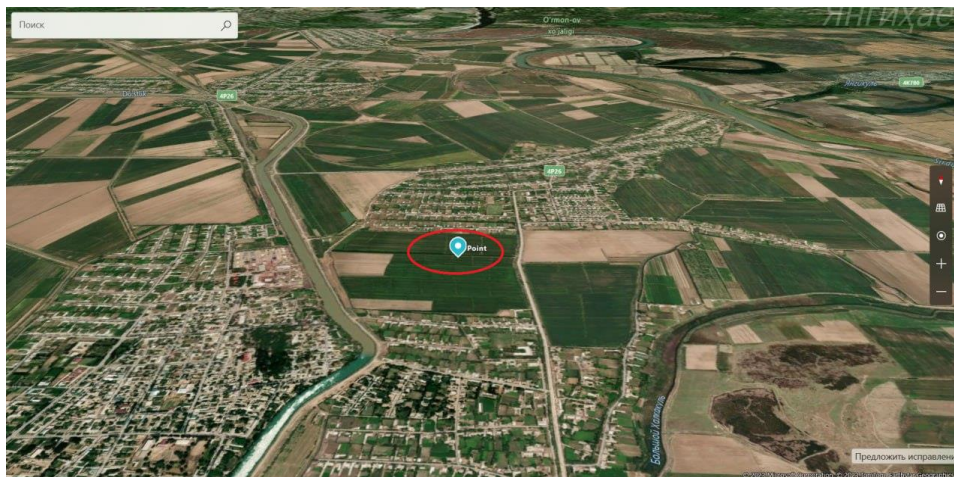


Figure 6. The geolocation map of Gulistan district of Syrdarya region

CONCLUSION

The absence of OCPs in the soil samples was attributed to their minimal presence and the limited sensitivity of thin-layer chromatography, which is a conventional analytical technique employed in this study. The Gas Chromatography method, namely the Electron Capture Detector (ECD), is widely recognized as a contemporary technique. This is primarily attributed to the remarkable sensitivity of the electron capture detector towards OCP, enabling the determination of concentrations that are 100 and 1000 times lower compared to the TLC (Thin-layer chromatography) method.

In the conducted analysis of soil samples obtained from the Mirzaabad district of the Sirdarya region, it was observed that the concentration of γ -HCH was 0.002 mg–ml within a duration of 3.23 minutes, DDE was 0.004 mg–ml within a duration of 10.08 minutes, and DDT was 0.018 mg–ml within a duration of 16.92 minutes, as determined using chromatographic analysis.

In the conducted analysis of soil samples collected from the Boyovut district of the Syrdarya region, a total of 10 g of soil was examined. The experiment revealed the presence of α -HCH at a concentration of 0.001 mg–ml, detected within a time frame of 2.9 minutes. Additionally, γ -HCH was observed at a concentration of 0.001 mg–ml, also detected within 2.9 minutes. Furthermore, DDE was found at a concentration of 0.031 mg–ml, with a detection time of 10.08 minutes. DDD was detected at a concentration of 0.007 mg–ml, taking 13.4 minutes for detection. Lastly, DDT was identified at a concentration of 0.037 mg–ml, with a detection time of 16.9 minutes. The chromatogram analysis also revealed the presence of OCP.

Upon analysis of soil samples collected from the Gulistan district of the Syrdarya region, it was seen that the α -HCH concentration was 0.001 mg–ml and the retention time was 2.9 minutes in the OCP chromatogram. Similarly, the gamma HCH concentration was determined to be 0.001 mg–ml with a retention time of 2.9 minutes.

During the analysis of soil samples obtained from the Dehqonabad farm area in the Boyovut district of the Sirdarya region, a concentration of α -HCH at 0.001 mg–ml was observed within a time frame of 2.32 minutes. Additionally, lower quantities of γ -HCH isomers were detected at a concentration of 0.001 mg–ml within a time frame of 2.76 minutes.

A study conducted at Dehkanabad farm, located in the Boyovut district of the Syrdarya area, revealed the presence of γ -HCH isomer at a concentration of 0.003 mg–ml in wheat grass. The detection of this isomer occurred within a time frame of 2.68 minutes. Additionally, the OCP chromatogram analysis identified the presence of DDE at a concentration of 0.008 mg–ml, with a detection time of 9.42 minutes.

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