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# Persistent Organochlorine Pesticides Residues In Soils Samples From Agricultural Area Of Myzeqeja, Albania

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***Abstract* — Organochlorine Pesticides (OCPs) are prevalent contaminants, which were applied worldwide against pests in fruits, horticultural and arable crops. Studies have reported the detection of the OCPs, which are retained in soil and are insoluble in water, but also are decomposed very slowly and may persist for several years. The most important groups of OCPs, are DDTs and HCHs, which use was restricted in 1970s, due to high persistence and toxicity. The long-range transport and biomagnification of DDT and its metabolites, cause high level of pollution even in places where the DDT was never applied. The production and use of lindane, contaminates the environment with about 12-30% of it being volatized into atmosphere. The aim of this study was to determine the concentration of OCPs residues in agricultural soil. We have analyzed 33 samples collected in this area, in May 2016. OCPs residues are determined with Gas chromatography techniques.**

**The analysis showed presence of DDT (Dichlorodiphenyltrichloroethane), its metabolites products DDE (Dichlorodiphenyldichloroethylene) and**

**DDD (Dichlorodiphenyldichloroethane), as well as α, β, γ and δ isomers of HCH (Hexachlorocyclohexane) residues. With small exceptions, from this study, resulted that concentrations of OCPs residues in soil samples were in significant levels, higher than 10 μgKg$^{-1}$.**

***Keywords—Organochlorine pesticides (OCP); residues; Gas chromatography***

## I. INTRODUCTION

Organochlorine pesticides (OCP) are persistent contaminants which were applied worldwide against pests in fruit growing, horticultural and arable crops. The residues of pesticides in soil can be absorbed by plants, entering the food chain, leading to bioaccumulation. In Swiss legislation, there is a guide value of 20 μgkg$^{-1}$, and this trigger value indicates a potential health risk for humans [11]. Several studies have reported the detection of pesticides in soil especially the OCPs group, which are retained in soil and are insoluble in water. They decompose very slowly and persist for several years in the environment [12]. OCPs have been shown to have acute and chronic health effects, that's why in May 2004, Stockholm Convention on POPs entered in force with the main purpose to reduce and eliminate these pollutants. DDT was listed as 1 of 12 persistent organic pollutants (POPs), while α-HCH, β-HCH, and γ-HCH (lindane) were added to the list in 2009 [10]. The most important groups of OCPs are DDTs and HCHs, which use was restricted in 1970s, due to high persistence and toxicity. High prevalence of DDE, shows for predominance of aerobic transformation processes [9]. Although the use of DDT and its metabolites have been banned, they are still present in the environment. The presence of DDT and its degrading products in crop growing areas/ground water/ drinking water, even in low concentration, shows for a potential of long term persistence and wide spread exposure to public [1]. Lately the focus has been on historic inputs and the evaluations of long-term changes in remote sites has been barely considered [4]. The high DDE/DDT ratio shows old pollution, but low DDE/DDT ratio is evidence of recent DDT pollution. The long-range transport and biomagnification of DDT and its metabolites cause high level of pollution even in places where the DDT was never applied like in Artic Area [7]. Sometimes,

the levels of soil contamination with DDTs are greater than 10 μgkg$^{-1}$, which exceeds the "Total Threshold Limit Concentration" (TTLC) for DDTs [2]. Under aerobic conditions, much of the DDT in soils is degraded to DDE, and most of the DDT in well-aerated soils may be degraded as DDE [13]. The high concentration of DDTs than DDE in some areas shows for a minimal degradation of DDT or shows for a recent input of DDT. Technical HCH consists principally of four isomers, α-HCH (60-70%), β-HCH (5-12%), γ-HCH (10-15%), δ-HCH (6- 10%), while lindane contains >99% of γ-HCH [10]. The production and use of lindane contaminates the environment, and about 12-30 % of it, is volatized into atmosphere. Lindane is very immobile in the soil and can be adsorbed easily by organic matter [3]. Among the HCH isomers, α HCH is more likely to partition to the air and transport over long distances, while β HCH is more resistant to hydrolysis and environmental degradation and is the dominant isomer in soils, animal tissue, and fluids. δ HCH has the longest half-life of HCH isomers, and it was the most heavily polluted isomer, although its original level was not higher.

After a long period of weathering, α and γ HCH can be transformed into δ HCH. The greater relative proportion of β HCH than α and γ HCH indicates that the HCH is due to historical use and that technical HCH has not recently been used. The relatively small proportion of γ HCH further supports the conclusion that there are few new inputs of

HCH [5]. In general, α- and γ-isomer have higher degradation rates than the β- and δ- isomers. The isomeric pattern of contaminated soil changes over time to the favor of β- HCH [8]. Canadian limit value for Lindane in agricultural soils is 10 μg·kg$^{-1}$ [9]. The levels of the pesticides in the vegetables and soil samples require a special attention and laws to regulate the use and circulation of chemicals [6].

In this study, we have taken into consideration some greenhouses and farms in Myzeqeja area. In the present study, we aimed to determine concentrations of persistent organochlorine pesticide residues in soil.

## II. MATERIALS AND METHODS

### *A. Study area and Sample collection*

Study area included greenhouses and farms from Lushnja (Kemishtaj Goricaj, Mertish, Karbunare), and Fier (Cakran). All the samples were randomly collected (33 samples) from selected areas, using a soil auger in a depth of 0-25 cm. Sampling was done in May 2016 in compliance with Standard ISO10381-1, 2: 2002. These subsamples were collected in a bucket and after being thoroughly homogenized were transferred in a polyethylene bag. Each sample was labeled with its own identification code and send to the laboratory.

The figure 1 shows the geographical position of the sampling locations.

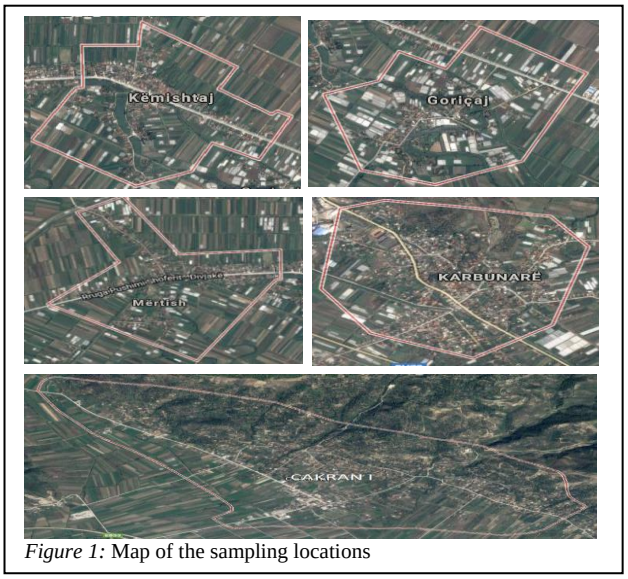


*Figure 1:* Map of the sampling locations

The collected soil samples were sieved in a 2mm sieve and were stored at 4 $^{o}$ C until the analysis were performed. The moisture content was determinated in Customs Laboratory (Customs General Directorate of Albania). Extraction and analysis of soil samples of OCPs pesticides were performed at the Institute of Soil Science and Soil Conservation Justus Liebig University, Giessen, according to the Standard DIN ISO 10382:2002.

### *B. Analysis of OCPs pesticides residues*

*Extraction of soil samples*

Extraction and analysis of OCPs pesticides were performed based on Standard DIN ISO 10382: 2002. Each soil sample was extracted twice. The first extract was used for qualitative analysis and the second extract was used for quantitative analysis. The soil samples (0.5 g) were weighted in a clear SPME vial. 5 ml of acetone and 5 ml petroleum ether were added in the vial, then it was shaken for 15 min and centrifuged. After that, the supernatant was transferred in the amber SPME vial. Extraction was repeated with 5 ml petroleum ether. The second supernatant was transferred to the supernatant obtained previously. The supernatant was shaken in the Vortex. From the amber vial, an aliquot (1 ml) was taken and evaporated under a gentle flow of N2. 4 μl Internal Standard, 100 μl methanol, 10 ml saline (735,10 mg CaCl2 and 50g NaCl in 500 ml MQ water) were added. Then it was shaken briefly in the Vortex.

*Parameters of GC MS*

MS (Headspace) Thermo Trace GC

*Injector:* Mode: split less, inlet: temp.: 260 °C, split flow: 30 ml/min, split less time: 3 min constant temperature purge, carrier gas: helium flow: 1 ml/min, transfer line: 270 °C.

*Column:* Fused-silica capillary column: Thermo TG-XLB-MS: 60 m, 0.25 mm inner diameter; 0,25 µm coating thickness.

*Needle heater:* 270 $^{o}$C - for determination of DDT, DDD and HCH - PDMS (Polydimethylsiloxane) fiber. 300$^{o}$C - for determination of DDE with PA (Polyacrylate) fiber.

*Gas chromatography analysis*

The extracted samples were analyzed in GC-MS, full scan mode, in order to qualitatively check a broad range of chlorinated pesticides. Only DDTx and HCHx pesticide residues were detected. Quantitative analysis was performed in the SIM mode, based on the use of one target and two qualifier ions.

OCPs pesticides were identified according to their retention times, target and qualifier ions. The quantitation was based on the peak area ratio of the targets to that of internal standards. The concentration of pesticide residues in soil samples was determined by interpolation of the relative peak areas for each pesticide to IS peak area in the sample on the calibration curve.

## III. RESULTS AND DISCUSSION

From gas chromatography analysis, the following OCPs residues were found in the soil: DDT and its metabolites products (DDE and DDD), and α, β, γ and δ isomer of HCH.

*Table 1*. Results of DDTs and HCHs residues of soil samples

| Sample code | 2.4 DDE | 4.4 DDE | 2.4 DDD | 4.4 DDD | 2.4 DDT | 4.4 DDT | ∑DDTs | α HCH | β HCH | γ HCH | δ HCH | ∑HCHs | ∑OCPs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M48 | 0.58 | 36.52 | 0.38 | 0.32 | 2.03 | 3.74 | 43.56 | n.d | 17.06 | n.d | n.d | 17.06 | 60.62 |
| M49 | 0.41 | 23.40 | 0.34 | 0.34 | 1.22 | 3.65 | 29.03 | n.d | n.d | n.d | 15.63 | 15.63 | 44.66 |
| M50 | 0.99 | 60.57 | 0.44 | 0.37 | 3.84 | 6.72 | 72.93 | n.d | n.d | 22.19 | 25.7 | 47.89 | 120.82 |
| M51 | 0.31 | 21.94 | 0.14 | 0.17 | 0.86 | 2.39 | 25.51 | n.d | 95.93 | 13.67 | 5.39 | 19.06 | 44.57 |
| M52 | 0.55 | 36.77 | 0.31 | 0.31 | 2.16 | 4.70 | 44.49 | n.d | 27.14 | 22.85 | 23.72 | 73.71 | 118.20 |
| M53 | 0.19 | 15.42 | 0.13 | 0.17 | 0.76 | 2.91 | 19.28 | n.d | n.d | n.d | 10.13 | 10.13 | 29.41 |
| M54 | 0.12 | 7.01 | 0.08 | 0.13 | 0.40 | 1.83 | 9.36 | n.d | 32.75 | 49.8 | 9.04 | 91.59 | 100.95 |
| M55 | 0.14 | 8.92 | 0.10 | 0.14 | 0.60 | 2.43 | 12.10 | n.d | 11.87 | n.d | 20.42 | 32.3 | 44.40 |
| M56 | 0.38 | 25.78 | 0.14 | 0.23 | 1.35 | 4.54 | 32.28 | n.d | 11.15 | n.d | 19.51 | 30.66 | 62.94 |
| M57 | 0.22 | 13.71 | 0.15 | 0.22 | 0.77 | 3.29 | 18.21 | n.d | n.d | 40.52 | 21.79 | 62.31 | 80.52 |
| M58 | 0.21 | 14.71 | 0.10 | 0.19 | 0.84 | 3.57 | 19.51 | n.d | 26.33 | n.d | 13.29 | 39.62 | 59.13 |
| M59 | 0.08 | 5.89 | 0.04 | 0.06 | 0.31 | 1.25 | 7.53 | n.d | n.d | n.d | 13.61 | 13.61 | 21.14 |
| M60 | 0.06 | 4.02 | 0.06 | 0.12 | n.d | 1.58 | 5.66 | n.d | 14.93 | n.d | 18.08 | 33.01 | 38.67 |
| M61 | 0.02 | 1.56 | n.d | n.d | n.d | 0.30 | 1.88 | n.d | n.d | n.d | 13.7 | 13.7 | 15.58 |
| M62 | 2.60 | 23.60 | 0.13 | 0.32 | 1.00 | 4.68 | 32.20 | n.d | n.d | n.d | 22.57 | 22.57 | 54.77 |
| M63 | 11.78 | 285.61 | 4.01 | 2.50 | 41.56 | 89.49 | 59.85 | n.d | 16.52 | n.d | 6.31 | 22.83 | 82.68 |
| M64 | 3.43 | 59.39 | 0.63 | 0.79 | 5.86 | 17.86 | 87.97 | n.d | n.d | n.d | 5.63 | 5.63 | 93.60 |
| M65 | 2.25 | 3.07 | n.d | 0.09 | n.d | 0.78 | 6.10 | n.d | n.d | 26.25 | 9.08 | 35.33 | 41.43 |
| M66 | 2.34 | 2.11 | n.d | 0.13 | n.d | 0.44 | 4.88 | n.d | n.d | 27.09 | n.d | 27.09 | 31.97 |
| M67 | 2.21 | 1.93 | n.d | 0.06 | n.d | 0.59 | 4.72 | 9.49 | n.d | n.d | 16.34 | 25.84 | 30.56 |
| M68 | 2.38 | 4.56 | n.d | 0.11 | 0.15 | 1.27 | 8.22 | n.d | 19.14 | n.d | 12.6 | 31.74 | 39.96 |
| M69 | 2.17 | 4.04 | n.d | 0.14 | n.d | 1.41 | 7.63 | n.d | n.d | n.d | n.d | n.d | 7.63 |
| M70 | 2.15 | 5.43 | n.d | 0.77 | 1.55 | 2.56 | 12.47 | n.d | 88.5 | n.d | 6.49 | 6.49 | 18.96 |
| M71 | 2.30 | 8.59 | 2.29 | 0.87 | 2.30 | 4.20 | 20.55 | n.d | 15.58 | 31.13 | 11.91 | 58.63 | 79.18 |
| M72 | n.d | 14.56 | n.d | 0.88 | n.d | 2.82 | 18.26 | n.d | n.d | 158.69 | 14.87 | 14.87 | 33.13 |
| M73 | 2.26 | 12.65 | n.d | 0.85 | 1.63 | 3.15 | 20.55 | n.d | n.d | n.d | n.d | n.d | 20.55 |
| M74 | 2.35 | 21.87 | 2.23 | 0.89 | 1.75 | 4.27 | 33.37 | n.d | n.d | n.d | 6.13 | 6.13 | 39.50 |
| M75 | n.d | 2.44 | n.d | n.d | n.d | n.d | 2.44 | n.d | n.d | 19.07 | 16.35 | 35.41 | 37.85 |
| M76 | n.d | 2.25 | n.d | n.d | n.d | n.d | 2.25 | n.d | 7.44 | n.d | 5.3 | 12.74 | 14.99 |
| M77 | n.d | 2.33 | n.d | n.d | n.d | n.d | 2.33 | n.d | n.d | 80.74 | n.d | - | 2.33 |
| M78 | n.d | 2.40 | n.d | n.d | n.d | n.d | 2.40 | n.d | n.d | 15.36 | 3.54 | 18.89 | 21.29 |
| M79 | n.d | 3.09 | n.d | n.d | n.d | 1.84 | 4.93 | n.d | n.d | 18.76 | n.d | 18.76 | 23.69 |
| M80 | 21.94 | 8.58 | n.d | 0.83 | 1.66 | 2.51 | 35.52 | n.d | n.d | n.d | 11.47 | 11.47 | 46.99 |

n.d. - not detected;
below scope of application (lower limit of calibration concentration); above scope of application (upper limit of calibration concentration)

Table 1 shows the analytical results of DDT and its metabolites products DDE and DDD as well as α, β, γ and δ isomer of HCH isomers residues. ΣDDTs represents DDT and its metabolites products (DDE

and DDD), while ΣHCHs represents α, β, γ and δ isomer of HCH. Taken into consideration the results of the moisture of soil samples, the results are calculated in μgKg $^{-1}$ dry matter (d. m.). From table 1, we can see that the highest value of ∑DDT residues is 87.97 μgKg$^{-1}$, and the lowest value is 1.88 μgKg$^{-1}$, which belonged respectively to sample M61 and M64. Also, the highest concentration of ∑HCH residues was observed in M54 and was 91.59 μgKg$^{-1}$, while the lowest concentration was observed in sample M64 and was 5.63 μgKg$^{-1}$. We have not taken into consideration the contribution of all the values of DDTs and HCHs residues that were below the limit of calibration concentration. Also, we have not taken into consideration the contribution of 4.4 DDE and 4.4 DDT residues for sample 63 (285.61, 89.49 μgKg$^{-1}$, respectively), of β HCH for sample M51 (95.93 μgKg$^{-1}$), of β HCH for sample M70 (88.50 μgKg$^{-1}$), of γ HCH for sample M72 (158.69 μgKg$^{-1}$) and of γ HCH for sample M77 (80.74 μgKg$^{-1}$), because they were upper the limit of calibration concentration. From this point of view, considering these values the trend of ∑DDTs and ∑HCHs residues for these samples is increasing and the values tend to be the highest values among analyzed samples. From table 1, it is evident that the level of ΣHCHs residues for most analyzed soil samples were more than 10 μgKg$^{-1}$ except the 4 soil samples: M64, M74 (5.63 and 6.13 μgKg$^{-1}$), and M69, M73 (there were not found any ∑HCH residues).

The values of DDT and his transformed products DDE and DDD residues in μgKg$^{-1}$, are presented in figure 2.

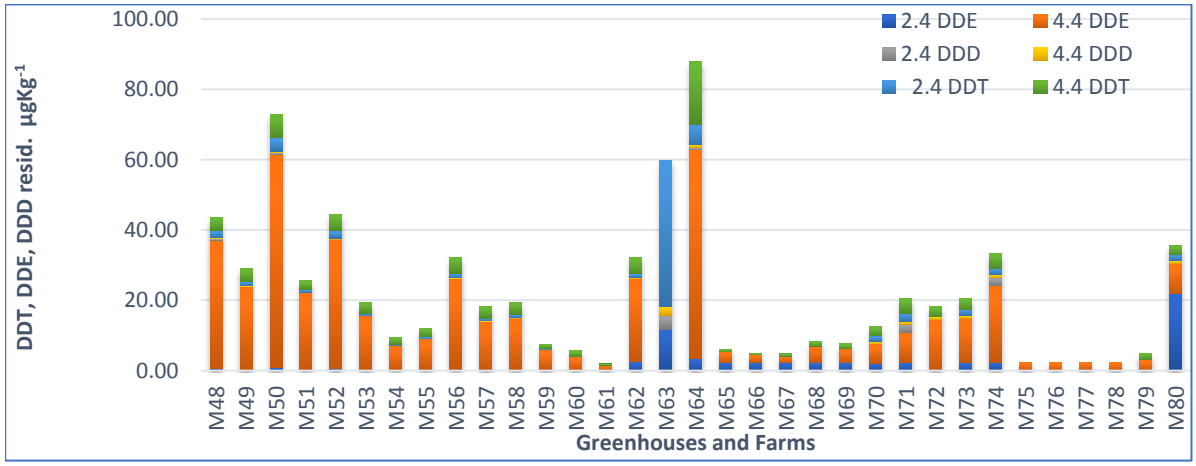


*Figure 2.* Results of DDTs residues in μgKg$^{-1}$ d. m. for analyzed soil samples

From figure 2, it is observed that the concentrations of 4.4 DDE are higher than the concentration of 2.4 and 4.4 DDT residues and its transformed products 2.4 DDE, 2.4 and 4.4 DDD. The finding that 4.4 DDE was the major component of the ∑DDT residues, shows that the most part of DDT is transformed in aerobic condition, and the predominant reaction is de-hydro-chlorination of DDT to yield DDE. Also, from figure 2 we can see clearly that 19 samples (M48, M49, M50, M51, M52, M53, M55, M56, M57, M58, M62, M63, M64, M70, M71, M72, M73, M74 and M80) have DTTs residues in significant concentrations higher than 10 μgKg$^{-1}$.

Figure 3, presents the concentration of the of α, β, γ and δ isomer of HCH residues in soil samples, which have resulted positive, calculated in μgKg$^{-1}$ d. m. It shows that α HCH was found only in sample M67, while concentrations of the other isomers of HCHs found in other soil samples were different. According to the previous study, several explanations are possible, for example: α HCH has been converted naturally in the soil to β HCH, increasing the concentration for β HCH and decreasing it for α HCH; and/or the higher stability of β HCH compared with the other isomers (Hu, et al.). The soil analysis has revealed that the predominance of α HCH has changed over the years in favor of the β isomer. While, γ HCH isomer was not found in the soil samples M48, M49, M53, M55, M56, M58, M59, M60, M61, M62, M63, M64, M67, M68, M69, M70, M72, M73, M76, M77 and M80. Also, from figure 3 it is evident that the concentration of γ HCH isomer is higher than the other isomers of HCH for soil samples M51, M54, M57, M65, M66, M71, M74, M75, M78 and M79. We have found significant concentration of δ HCH in most of our analyzed samples.

In figure 4, are presented the results of OCPs residues, which are the sum of total DDTs and HCHs residues in μgKg$^{-1}$ d. m. As we can see from figure 4, we have found high concentration of OCPs residues in almost all analyzed soil samples. The level of concentration of OCPs residues was lower than 10 μgKg$^{-1}$ only for samples M69. For the samples M70 and M77, OPCs residues are 18.96 and 2.33, but we have not taken into consideration the contribute of the residues of HCHs and DDTs that have resulted in the upper limit of calibration concentration. In the other samples the concentration of OCPs residues were higher than 20 μgKg$^{-1}$. The highest concentration of OCPs residues was 120.82 μgKg$^{-1}$, which belonged to samples M50.

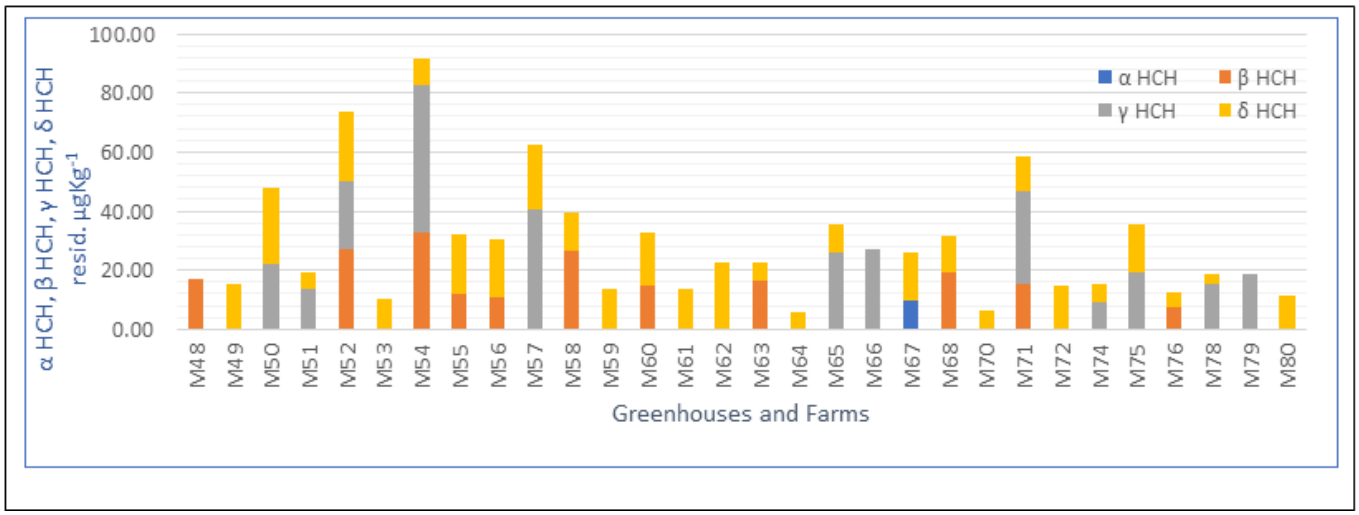


Figure 3. Results of HCH isomers residues in µgKg-1 d. m. for soil samples that have resulted positive

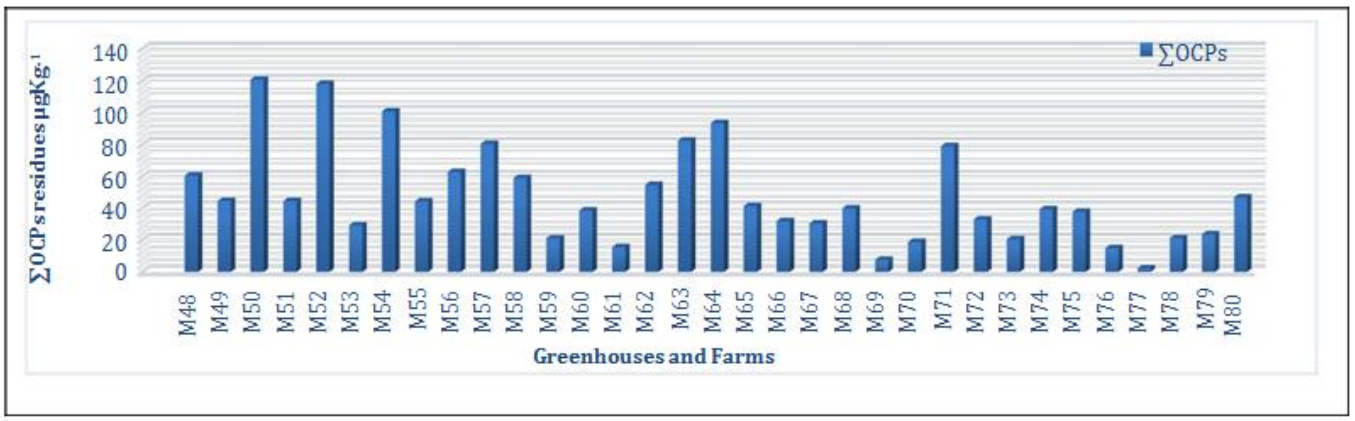


*Figure 4.* Results of OCPs residues in µgKg$^{-1}$ d. m. for analyzed soil samples

## IV.CONCLUSIONS

The results from this study show that persistent OCPs residues are present in all collected soil samples, and with small exceptions, the concentrations of Persistent OCPs, found in the soil samples were at high levels, much higher than 20 µgKg$^{-1}$.

High prevalence of DDE in all analyzed soil samples, shows reductive de chlorination of DDT to DDE in aerobic conditions.

The high concentration of β HCH compared with α and γ HCH indicates that the presence of HCH is mainly due to the past use and there has not been a new input of technical HCH.

Further monitoring of DDTs and HCHs residues is necessary in this area, to minimize health risk, as well as prevent, control and reduce environmental pollution.

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