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# Presence of DDT Residues in Agricultural Soils in Northwestern Part of Albania

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***Abstract*—Shkodra and Lezha areas, in the northwestern part of Albania, are well known for the production of agricultural crops like cereals, vegetables, potatoes, fruit trees, forage crops, industrial plants etc.. These regions are mostly developed in producing vegetables in greenhouses and also in cultivating medicinal and aromatic plants. Also, these areas have been flooded time after time. Organochlorine pesticides haven't been used in Albania since 1990. The mismanagement of organochlorine pesticides stocks after 90' is a source of pollution, not only in their storage areas but also in a wider range. As soil is a major source of pollution with pesticides, it is necessary to perform pesticide residues analyses in order to ensure the safety of food and health, and to preserve the qualities of the soil. In this study we have determined DDT (dichlorodiphenyltrichloroethane) residues in some agricultural soils in Shkodra and Lezha region. From the analysis of DDT residues, resulted that in 23 soil samples were not found DDT residues, in 11 soil samples were found DDT residues lower than 0.01mg/kg and in 9 of them were found residues slightly over 0.01mg/kg.**

***Keywords: Dichlorodiphenyltrichloroethane (DDT), Organochlorine pesticides (OCPs), residues, Gas Chromatography – Mass Spectrometer/***

## I. INTRODUCTION

In Shkodra region, agricultural land occupies approximately 13%. The main agricultural plants are field plants like wheat, maize, green beans, potatoes, vegetables, forage crops, tobacco etc.. Vegetables are cultivated in large inhabited areas and only in these last 10 years it is developed fruit-trees and especially vineyard cultivation mainly for industrial purposes [1]. The lowland of Nënshkodra (which lies between Shkodra and Lezha), as well as the Shkodra lake shore area, have been flooded time after time. After the construction of the Vau Dejes, Koman and Fierza hydro powers, the waters of Drini River are commanded by "the man", but still we have floods occurring in the lowland of Nënshkodra during intense rainfall [5].

Lezha's area is known for its production of field crops as well as arboriculture. Its plantation structure consists of field crops, vegetables potatoes, beans, industrial crops and fodder. Lezha area presents the greatest surfaces in the region where these crops are planted [3].

The Lushnja, Saranda and Shkodra areas have shown the most progress in developing market-driven production, especially on greenhouse vegetables, watermelon, citrus, and medicinal and aromatic plants [15].

Organochlorine pesticides have been used since in the early to mid-twentieth century. First DDT was used to fight fleas, lice, flies and mosquitoes and to reduce the spread of insect borne diseases such as malaria and yellow fever, but its potential impact on the environment is substantial due to its persistency in the environment [13]. Organochlorine pesticides (OCPs) were found to be very effective in controlling pests, so their adoption was extremely rapid [12]. Unfortunately, due to their highly persistency OCPs are still detectable in surface waters 20 years after their use has been banned, and once a persistent pesticide has entered in the food chain, it can undergo "bio-magnifications", i.e., accumulation in the body tissues of organisms, where it may reach concentrations many times higher than in the surrounding environment [4]. These pesticides cause contamination of not only the water environment, but also of crops grown in contaminated soil. High levels of these pesticides have been detected in a variety of crops around the world. These pesticides continue to be detected in different environments, especially agricultural fields where these pesticides were previously used [14]. A very toxic pesticide as DDT is still present in high concentration in biota of some areas [2]. DDT (Dichlorodiphenyltrichloroethane**)** consists two isomers 2-2'-DDT, 2-4'-DDT and their metabolites 2-2'-DDE, 2-4'-DDE (Dichlorodiphenyldichloroethylene), 2-2'-DDD and 2-4'- DDD (Dichlorodiphenyldichloroethane). The term ΣDDT refers to sixth above components [11]. It is known that p, p'- DDT is the principal isomer of technical DDT. Generally DDE and DDD resist further chemical and biological degradation. This

phenomenon is usually used as an indicator for the time lapse of DDT usage. If the ratio of p, p'-DDT/DDT metabolite is > 0.5, it indicates recent usage of DDT [6].

The organochlorine pesticides are not in use in our country since 90'. It was expected that levels for this class

of organic pollutants to be decreasing due to the degradation process. This comes as a result of old industries in the country (the Lindane chemical plant in Porto-Romano, Durrës) as the major polluting factor and mismanagement of pesticides [7]. Mismanagement of oddments pesticides, for some years after 90', was a source of pesticides contamination not only in area of chemical plant in Porto Romano, but in a higher diameter; including the waters of Adriatic Sea [13].

The monitoring of residues in various parts of the environment is still inadequate. The monitoring of soils for pesticide residues is much more sporadic and limited to the agricultural soils. Among other environmental components, soil is the largest source of pesticides residues. The analysis for pesticide residues in soil would be useful in assuring the safety food and public health as well as soil quality [12]. This study includes these areas: Velipojë, Shtoj, Stajkë, Mjedë, Kosmaç, Zejmen, Piraj (Zadrimë) and Grykëzezë in the region of Shkodra and Lezha.

## II. MATERIALS AND METHODS

### A. Study area and soil sampling

Our study area consists of 43 greenhouses and farms in Shkodra and Lezha region. Shkodra and Lezha are located in the northwestern part of Albania with respective coordinates N 42° 11' 00", E 19° 45' 00" and N 41° 47' 01" E 19° 38' 37".

Sampling was done on December 2015 and in compliance with Standard ISO10381-1, 2: 2002 [8], [9]. The soil samples were collected from each greenhouse or farm in a depth of 0-25 cm, using a soil auger. Each soil sample was result of 10 -15 subsamples, using random sampling method. These 10 - 15 subsamples were collected in a bucket and after being homogenized thoroughly were put in bag of polyethylene. The samples were labeled with place with code number and were stored at 4 $^{o}$C.

In the Fig. 1 is presented sampling sites map in the Shkodra and Lezha regions.

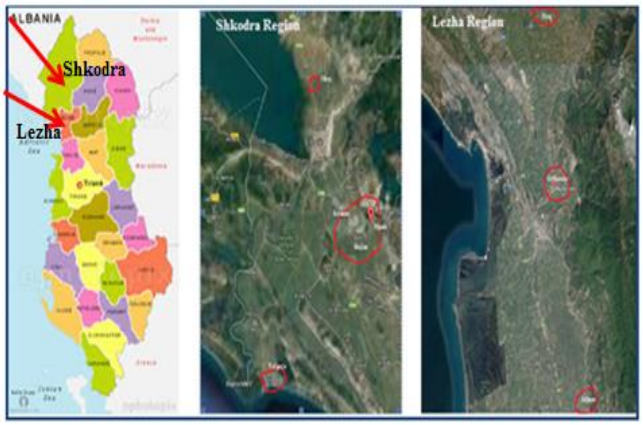


*Figure 1*. Map of Albania and Sampling sites

### B. DDT Residue analysis

Extraction and analysis of soil samples were performed according to the ISO 10382:2002 [10], in Faculty of Agriculture Laboratory, University of Novi Sad, Serbia.

### C. Instrumentation

*Gas chromatograph:* Configure the GC / MSD system Agilent Technologies, model 7890N Network GC System, auto sampler Agilent 7683 Series Injector, Agilent 5977 MSD; *Capillary column:* HP-5MSI, 5% phenyl methyl siloxane, HP 19091S-433, maximum temperature of 325 ° C, column length 30.0 m, column diameter 250.00 μm, film thickness 0:25 μm; *The flow of carrier gas:* helium; *Injector temperature*: 300 $^{o}$C; *Mode:* split less; *Purge flow to split vent*: 50 ml / min, 2min; *Gas saver*: 20 ml / min, 2min; *The temperature program of the column:* starting temperature: 70 $^{o}$ C, start time: 2:00 min. changes in temperature: 25 $^{o}$C / min to 150 $^{o}$C, 0 min, 3 $^{o}$C / min to 200 $^{o}$C, 0 min. 8 $^{o}$C / min to 280 $^{o}$C, final temperature: 280 $^{o}$ C for 10 minutes, Total analysis time: 41.87 minutes;
*Ionization type*: EI; *Transfer line temperature:* 280 $^{o}$C; *MS quadrupole temperature*: 150 $^{o}$C, maximum 200 $^{o}$C; *Ion source temperature*: 230 $^{o}$C, maximum 250 $^{o}$C; *File tune with the parameters settings MS*: atune. u; *Acquisition mode*: SCAN / SIM.

### D. Extraction, concentration and clean-up of the extract

For each soil sample was weighted 20 g of wet soil samples to an Erlenmryer 50 mL of acetone was added and was shaken for 15 minutes. Then was added 50 mL of petroleum etherand was shaken again for 15 minutes. The extraction was repeated again with 50 mL of petroleum ether. The extracts were collected into a separator funnel of two litres capacity and acetone was removed by shaking twice with 500 mL water. After that, the extract was dried over sodium sulfate and was transferred in the evaporator to reduse

volume of extract to to 10 Ml. The concentrated extract was transferred in a calibrated tube and was concentrated to 1 mL, in a gentle stream of nitrogen. 2 mL of TBA reagent sulfite was added in 1 mL of the concentrated extract and was shaken in 1 minute. 10 mL of water was added and was shaken qgain for about 1 minute. The organic layer was separated from aqueous layer with a Pasteur pipette, than were added a few crystals of anhydrous sodium sulfate to remove residual tracec of water. The entire concentrated extract was separated by column chromatoghraphy on silica gel in two fractions to separate the nonpolar pesticides from the polar pesticides. Into each of the two fractions was added 10 µL of the standards solution injection to each extracted soil samples. Identification and quantitative analysis of DDT residues were performed by using Gas Chromatography Mass Spectrometry (GC/MS) in multiple reactions monitoring (MRM).

### E. Gas chromatographic analysis

**Calibration Curves for DDT and its metabolites**

In the Fig. 2 are presented calibration curve for each internal standards used.

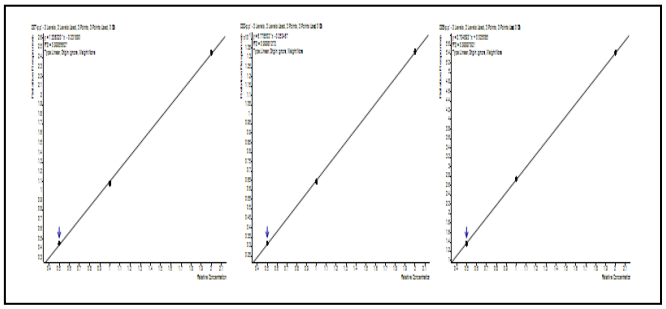

*Figure 2.* Calibration curves for DDT, DDD and DDE standards

For calibration curves were injected three levels of calibration standards DDT, DDD and DDE. Coefficient of determination $R^2$ for calibration curves of DDT, DDD and DDE were 0.9996, 0.9998 and 0.9999 respectively. Limit of quantification (LOQ) for DDT, DDD and DDE was 20 µgkg$^{-1}$.

**Measurements of soil samples**

The extracted soil samples were injected on GC-MS. With the absolute retention time, were identified the peaks of the internal standards. For other relevant peaks in the gas chromatogram, were determined the relative retention times compared to the standards injection. In the fig. 3 are presented the chromatograms of some soil samples.

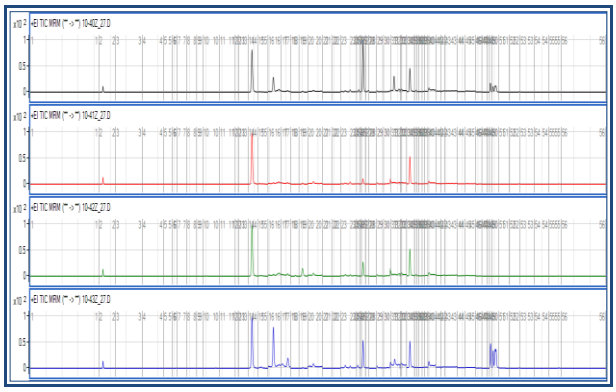

*Figure 3.* Samples Multiple Reaction Monitoring (MRM) chromatograms.

## III. RESULTS AND DISCUSSION

The DDT residues concentrations are expressed on dried weights (d. w.) basis. From the 43 soil samples collected and analyzed, 20 of them resulted with DDT residues. In the table I, are presented DDT and its metabolites residues for the soil samples with their identification code. Also, in the table I is presented the ratio of p, p'-DDT and its metabolites p, p'- DDE and p, p' -DDD. From the table I, it is clear that in the soil samples M26, M31, M32, M34 and M39 p, p'- DDT were not detected, meanwhile in the other samples DDT residues concentrations varied from 2.04 to 4.83 µgkg$^{-1}$. Lack p, p´-DDT residues in these soil samples would seem to imply an earlier usage before several years of the ban, as it is highly persistent in soil media and its half-life is 2-15 years. Also, the rate of p, p'-DDT/DDT metabolites (p, p' -DDE and p, p'-DDD) for 7 soil samples was higher than 0.5. Based on previous studies and on the value of this ratio it is possible that DDT residues found in

TABLE I.
DDT residues and rate of p, p'-DDT/DDT metabolites residues

soil samples, residues of p, p´-DDD prevails compared to p, p´-DDT and p, p´-DDE. Meanwhile, for soil samples M26, M31, M32, M34 and M39, which belong to the these samples are due to the latest use of this pesticide from the farmers even though it was banned as toxic and dangerous for the environment and living beings [6].

As it is shown in the table I and fig. 4, for the most of greenhouses in Kosmaç, Zejmen, Piraj and Grykëzezë respectively, it is clear that DDT has fully degraded in its two metabolites p, p´-DDE and p, p´-DDD, but also in this case prevails p, p´-DDD compared to the p, p´-DDE metabolite.

According to the previous studies it was concluded that under aerobic conditions, the predominant reaction is de-hydro- chlorination of DDT to yield DDE. While, under anaerobic conditions transformation of DDT to DDD by reductive de-chlorination is considered to be the dominant reaction [11].

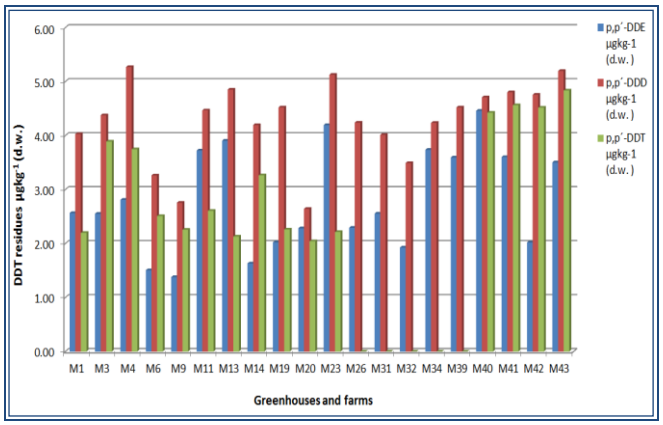


*Figure 4.* DDT and its metabolites residues in µgkg-1 dried weight.

In the fig. 5 it is shown the ΣDDT for all the samples who resulted in positive values.

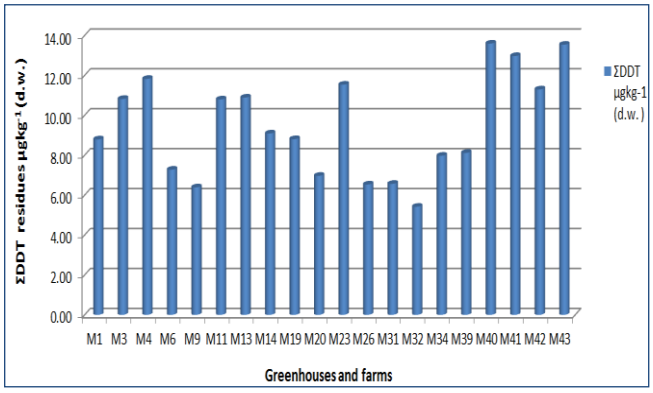


*Figure 5*. DDT residues for 20 soil samples in µgkg-1 (d.w)

From the 43 soil samples under the study, DDT residues were present in about 20 of them or about 47 % of the samples. From the fig. 5, it is evident that DDT residues ranged from 5.4 to 13.59 µgkg$^{-1}$ and with a mean value 9.52 µgkg$^{-1}$. Also, for 45 % of soil samples which resulted in positive values, samples M3 M4 (Velipojë), M11 (Shtoj), M13 (Stajkë), M23 (Kosmaç), M40, M41, M42 and M43 (Grykëzezë), the values of DDT residue were slightly higher than 10 µgkg$^{-1}$ (0.01mgkg$^{-1}$).

## IV. CONCLUSIONS

- The residual concentration of ΣDDT was identified in a range of 5.4 - 13.59 µgkg-1 (0.005 - 0.014 mgkg$^{-1}$).
- Most of DDT residues are transformed into DDD, so it has degraded in anaerobic conditions. The anaerobic process is probably related to the fact that the area under the study is continuosly flooded.
- For the soil samples M3, M4 (Velipojë), M11 (Shtoj), M13 (Stajkë), M23 (Kosmaç), M40, M41, M42 and M43 (Grykëzezë), in which the values of ΣDDT were higher than 10 µgkg$^{-1}$ (0.01mgkg$^{-1}$), based on bio-magnification properties of persistent organic pollutants it is recommended to perform the analyses of the crops cultivated in this areas.
- As in 23 analysed soil samples were not found ΣDDT residues, in 11 samples were found ΣDDT residues lower than 0.01mgkg$^{-1}$, and in 9 of them were found residues slightly over 0.01mgkg$^{-1}$, we can conclude that the presence of DDT residues in the agricultural soils in the northwestern part of Albania, included in our study, in general is in low levels.

| Sample code | p, p´-DDE µgkg$^{-1}$ (d. w.) | p, p´-DDD µgkg$^{-1}$ (d. w.) | p, p´-DDT µgkg$^{-1}$ (d. w.) | p, p'-DDT/ DDT metabolites | ΣDDT µgkg$^{-1}$ (d. w.) |
|---|---|---|---|---|---|
| M1 | 2.56 | 4.03 | 2.20 | 0.33 | 8.79 |
| M3 | 2.55 | 4.38 | 3.89 | 0.56 | 10.82 |
| M4 | 2.81 | 5.27 | 3.75 | 0.46 | 11.83 |
| M6 | 1.51 | 3.26 | 2.51 | 0.53 | 7.28 |
| M9 | 1.38 | 2.76 | 2.26 | 0.55 | 6.39 |
| M11 | 3.72 | 4.47 | 2.61 | 0.32 | 10.80 |
| M13 | 3.91 | 4.85 | 2.13 | 0.24 | 10.89 |
| M14 | 1.63 | 4.20 | 3.26 | 0.56 | 9.09 |
| M19 | 2.02 | 4.52 | 2.26 | 0.35 | 8.81 |
| M20 | 2.28 | 2.64 | 2.04 | 0.41 | 6.97 |
| M23 | 4.19 | 5.13 | 2.21 | 0.24 | 11.53 |
| M26 | 2.29 | 4.24 | 0.00 | 0.00 | 6.53 |
| M31 | 2.55 | 4.01 | 0.00 | 0.00 | 6.57 |
| M32 | 1.93 | 3.49 | 0.00 | 0.00 | 5.42 |
| M34 | 3.74 | 4.23 | 0.00 | 0.00 | 7.97 |
| M39 | 3.59 | 4.52 | 0.00 | 0.00 | 8.12 |
| M40 | 4.46 | 4.71 | 4.42 | 0.48 | 13.59 |
| M41 | 3.60 | 4.80 | 4.56 | 0.54 | 12.97 |
| M42 | 2.02 | 4.76 | 4.52 | 0.67 | 11.30 |
| M43 | 3.50 | 5.20 | 4.83 | 0.56 | 13.54 |

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