Global Journal of Agricultural Research

Vol.4, No.5, pp.39-47, November 2016

Published by European Centre for Research Training and Development UK (www.eajurnals.org)

# STATUS OF SOIL ORGANIC MATTER AND LEVELS OF DDT RESIDUES IN SOME AGRICULTURAL SOILS IN ALBANIA

**[1]Mimoza Mukaj, [1]Sofiana Mai, [1]Magdalena Cara, [2]Rolf-Alexander Düring**
[1]Faculty of Agriculture and Environment, Agricultural University of Tirana
[2]Institute of Soil Science and Soil Conservation Justus Liebig University, Giessen, Germany

**ABSTRACT:** *Soil Organic Matter (SOM) plays an important role in sorption of pesticides. If SOM content is high, the pesticide residues, as they are nonpolar, can be bound to particulate SOM, otherwise they present a risk to the flora, fauna and human health. Persistent Organic Pollutants (POPs) are chemical substances that remain in the environment, bioaccumulate through the food chain, and can cause negative effects on the environment and human health. This study was aimed to estimate soil organic matter and persistent organochlorine pesticide residues in some organic and conventional greenhouses/farms in areas of central Albania. Soil organic matter was determined by the gravimetric determination of ignition loss. Analysis of organochlorine pesticide residues were performed by gas chromatography - mass spectrometry. Organic matter contents were in a range of 1.96 % to 5.41 %. The minimum of ΣDDT residues was 0.10 µg/kg and the maximum of ΣDDT residues was 13.33 µg/kg.*

**KEYWORDS**: Organic Carbon (OC), pesticide residues, gas chromatography-mass spectrometry (GC-MS).

## INTRODUCTION

### Soil organic matter

SOM is defined as the sum of plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and well-decomposed substances (Salehi, et al., 2011). The Pedo - Transfer Rule 21 (PTR21) defined by Van Ranst is used to estimate OC (Organic Carbon) in the topsoil horizon, and the soils can be categorized according to the content of OC. From this point of view, soils are divided in four groups as following: "**V**ery low OC"- soils that have < 1 % OC, "**L**ow OC" - soils that have 1.1 – 2 % OC, "**M**edium OC" - soils that have 2.1- 6% OC and "High OC" - soils that have > 6% OC. In most cases, organic matter content in soils is measured as organic carbon (OC) and this value is converted to the organic matter (OM) content using a standard conversion ratio OC : OM of 1 : 1.72 (Jones, R.J.A., et al., 2004). In Albania, about 75.2 % of total land (not only agricultural) exert an organic carbon (OC) content ≤ 2% and 23.6% of total land have organic carbon (OC) > 2% (Hinsinger, 2014).

SOM acts as a non-polar phase or surface, and consequently is the main sorbent for pesticides of low polarity (Rada & Gajić-Umiljendić, 2009). Ecotoxicological effects



ISSN 2053-5805(Print), ISSN 2053-5813(Online)

depend on soil organic matter content. When SOM content is low the residues remain bioavailable, and are intensely absorbed by biota and therefore are hazardous to the flora and fauna (Langenbach, 2013).

**Chlorinated Pesticides as Persistent Organic Pollutants (POPs)**

The Food and Agriculture Organization (FAO) defines pesticides as any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease (Anzene, et al., 2014). Persistent organic pollutants are chemical substances that remain in the environment, bioaccumulate through food chain and cause negative effects on the environment and human health (FFTC Annual Report, 2009). Their persistence in the environment still makes them to be detected in different environmental matrices, such as soil and sediments, despite the fact that their use has been banned (Okoya, et al., 2013). Organochlorine insecticides were still detectable in surface waters 20 years after their use, and once a persistent pesticide has entered the food chain, it can undergo "bio-magnification", i.e., accumulation in the body tissues of organisms, where it may reach concentrations many times higher than in the surrounding environment (Ghabbour, et al., 2012). Studies have shown that DDT is still in the highest concentration in the biota of some areas (Enbaia, et al, 2014) 4,4'-DDT (Dichlorodiphenyltrichloroethane**)** consists of 2,2' -DDT, 2,4'-DDT and their metabolites 2,2' –DDE, 2,4'-DDE, 2,2'-DDD and 2,4'-DDD. The term ΣDDT refers to the six above components (Nirwal, 2001). The impact of pesticides and other toxic chemicals on the environment depends on the interaction with soil particles. In recent years, there has been a growing concern about the possible release of bound pesticide residues from soil. Important to know is whether released residues are of toxicological and/or ecological significance. Bound residues can be released by physicochemical mechanisms or through biochemical processes. The primary factor for the release of the bound residues is the activity of micro-organisms. Also, the changes in agricultural practices and new introduced chemicals can affect the chemistry of soil. Soil bound pesticide residues can enter into the aquatic environment, be released, and subsequently be accumulated in aquatic food chains (Gevao et al., 2000).

The adsorption of DDT by various types of soils has been investigated, and found to be less in sandy loam, intermediate in clay soil, and greatest in organic soils. Adsorption of DDT is closely related to the organic matter content (Nirwal, 2001). Increase of organic matter content in soil can increase the amount of microbial biomass and thus can induce the degradation of organochlorine pesticides (Fang et al., 2007).

Organic marketing should allow only up to a level of 0.01 mg/kg for each substance and only for a minimum of two detected substances (Speiser, et al., 2013). Before 1990, organochlorine pesticides were widely used in Albania for agricultural purposes. The main agricultural areas were in the western part of the country (Shkodra, Durresi, Tirana, Fieri, Lushnja, Vlora). Until 1990, the former chemical plant in Porto Romano, Durres produced pesticides, such as lindane ($\gamma$-HCH) and thiram (Nuro & Marku, 2008). In our study, we have included only some greenhouses and farms from Tirana and Durres areas.



ISSN 2053-5805(Print), ISSN 2053-5813(Online)

## MATERIALS AND METHODS

### Study area and soil sampling

Soil samples were randomly collected (depth of 0-25 cm) from some conventional-farms and organic-farms, belonging to agricultural soils in the areas of central Albania. Sampling was done in compliance with Standard ISO10381-1, 2: 2002.

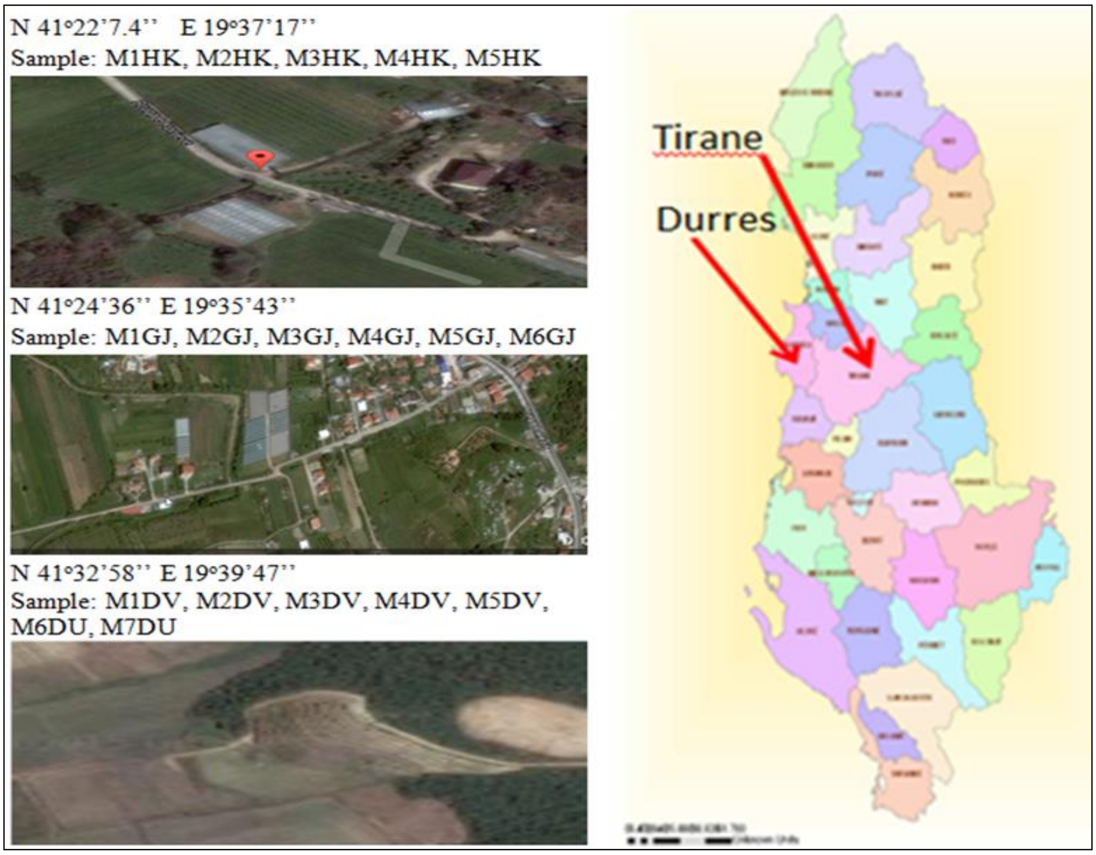

Figure 1. Coordinates of sampling sites and map

Analysis of moisture and organic matter content were performed in Albanian Customs Laboratory. Extraction and analysis of soil samples for pesticides were performed at the Institute of Soil Science and Soil Conservation Justus Liebig University, Giessen, Germany.

### Determination of Moisture and Organic Matter in soil samples

Determination of moisture and organic matter content was done according to the Standard ASTM 2974 - 14. For moisture and organic matter analyses, the soil samples were sieved through a 2 mm sieve. Subsequently the samples were oven dried at 105 $^{o}$ C overnight, cooled in a desiccator, and weighted before they were combusted. Gradually, the temperature was brought in a muffle furnace (Nabertherm - Model LV 5/11) to 540 $^{o}$ C and the samples were hold until they were completely ashes. After


ISSN 2053-5805(Print), ISSN 2053-5813(Online)

combustion, the samples were cooled in a desiccator and weighted again. The difference in weight, before and after ignition, represented the amount of the OM that was present in the sample.

**Organochlorine pesticides analysis**

**Extraction of samples (Solid - Liquid Extraction)**

The method used was based on Standard DIN ISO 10382: 2002. Soil samples were extracted twice. The soil sample (1 g) was weighted in a clear SPME vial. In the vial were added 5 ml of acetone and 5 ml petroleum ether, 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, it was taken an aliquot (12 ml) and was evaporated under a gentle flow of $N_2$. It was added IS TCN (1 ppb; 2 µl 5 ppm Standard), 100 µl methanol, 10 ml saline (735,10 mg $CaCl_2$ and 50g NaCl in 500 ml MQ water), 1 ppb $^{13}C$ HCB (2 µl at 5 ppm), 1 ppb $^{13}C$ 2,4´-DDT (2 µl at 5 ppm). Then it was shaken briefly in the Vortex.

The first extract for each sample was used for SPME GC MS analysis in full scan mode. The second extract was used for SPME GC MS analysis with SIM (Single Ion Monitoring).

**Gas Chromatography–Mass Spectrometry Analysis**

**Parameters**

GC-MS (Headspace) Thermo Trace GC Ultra

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

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

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

**Full Scan Mode Determination**

The extracted samples were analyzed in GC-MS, full scan mode, in order to qualitatively check a broad range of chlorinated pesticides. Only DDT and DDT transformation products pesticide residues were detected.

**Single Ion Monitoring (SIM) Determination**

Quantitative analysis was performed in the SIM mode based on the use of one target and two qualifier ions. 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.


ISSN 2053-5805(Print), ISSN 2053-5813(Online)

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.

## RESULTS AND DISCUSSION

### Organic matter

The minimum of organic matter content was found in greenhouse M6Gj (1.96 %) and the maximum of organic matter content was found in greenhouse M3HK (5.41 %).
Organic matter content of the soil samples expressed in %, are shown in the following figure.

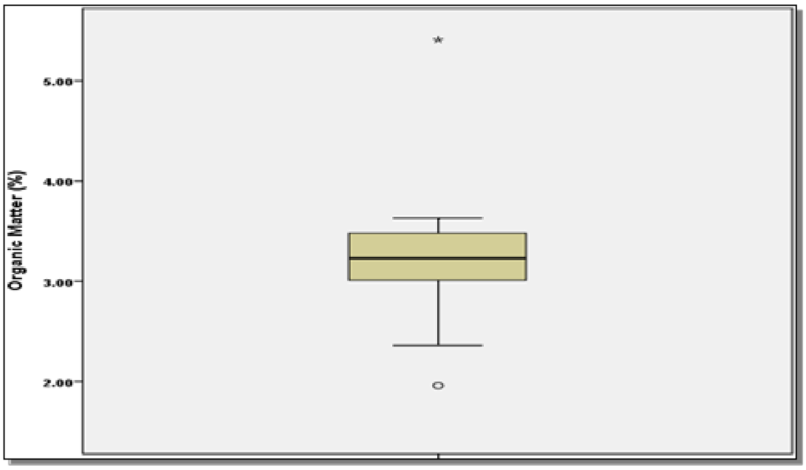


Figure 2. Organic matter content in soil samples

Considering the coefficient 1.72 for converting OC to OM content and the Pedo - Transfer Rule 21 (PTR21) defined by Van Ranst, it is clearly evident that the soils that ranged from 1.96 - 3.58 % of OM should be considered as soil with low organic matter content, and soils that ranged from 3.63 - 5.41 % of OM should be considered as soil with medium organic matter content.

### DDT and metabolites

Identification and quantitative analysis of DDT and HCH were performed by using Gas chromatography coupled to mass spectrometry (GC/MS). The detection limit of this method was at 0.01 µg/kg. All DDT residue concentrations are expressed on dry matter basis. In Table 1, it is evident that in the samples M3DV, M4DV, M5DV which belong to one farm in Durres area, and in the sample M4HK, which belongs to one farm in Tirana area, there were not found any DDT residues. From Table 1, we can see that the DDT residues higher than 10 µg /kg were found in the soil of greenhouses M1GJ, M4GJ, M5GJ, and M6GJ in Tirana area. In the other greenhouses and farms the ΣDDT residues were lower than 10 µg /kg.


ISSN 2053-5805(Print), ISSN 2053-5813(Online)

Table 1. Results of DDT residues for 18 analysed soil samples, calculated in dry matter.

| Sample code | 2.4´-DDE µg/kg | 4.4´-DDE µg/kg | 2.4´-DDD µg/kg | 4.4´-DDD µg/kg | 2.4´-DDT µg/kg | 4.4´-DDT µg/kg | Σ DDT µg/kg |
|---|---|---|---|---|---|---|---|
| M1GJ | n.d. | 10.78 | n.d. | 0.95 | n.d. | 1.6 | 13.33 |
| M2GJ | n.d. | 2.98 | n.d. | 0.47 | n.d. | n.d. | 3.45 |
| M3GJ | n.d. | 8.32 | n.d. | 1.02 | n.d. | n.d. | 9.34 |
| M4GJ | [1]0.08 | 7.45 | n.d. | 0.95 | 0.46 | 1.95 | 10.81 |
| M5GJ | [1]0.13 | 6.92 | n.d. | 1.05 | 0.55 | 1.96 | 10.48 |
| M6GJ | n.d. | 7.05 | n.d. | 0.88 | 0.41 | 2.15 | 10.5 |
| M1DV | n.d. | 0.25 | n.d. | n.d. | n.d. | n.d. | 0.25 |
| M2DV | n.d. | 0.16 | n.d. | n.d. | n.d. | n.d. | 0.16 |
| M3DV | n.d. | [1]0.05 | n.d. | n.d. | n.d. | n.d. | n.d. |
| M4DV | n.d. | [1]0.04 | n.d. | n.d. | n.d. | n.d. | n.d. |
| MSDV | n.d. | [1]0.05 | n.d. | n.d. | n.d. | n.d. | n.d. |
| M6DU | n.d. | 0.1 | n.d. | n.d. | n.d. | n.d. | 0.1 |
| M7DU | n.d. | 0.13 | n.d. | n.d. | n.d. | n.d. | 0.13 |
| M1HK | n.d. | 0.64 | n.d. | n.d. | n.d. | n.d. | 0.64 |
| M2HK | n.d. | 1.06 | n.d. | n.d. | n.d. | 1.56 | 2.62 |
| M3HK | n.d. | 0.46 | n.d. | n.d. | n.d. | n.d. | 0.46 |
| M4HK | n.d. | [1]0.17 | n.d. | n.d. | n.d. | n.d. | n.d. |
| M5HK | n.d. | 0.26 | n.d. | n.d. | n.d. | n.d. | 0.26 |

n.d. - Not detected (< detection limit);
[1]Values were below lowest concentration of calibration.

In figure 3, there are presented the values of DDT residues and its related compounds in greenhouses and farms under this study.

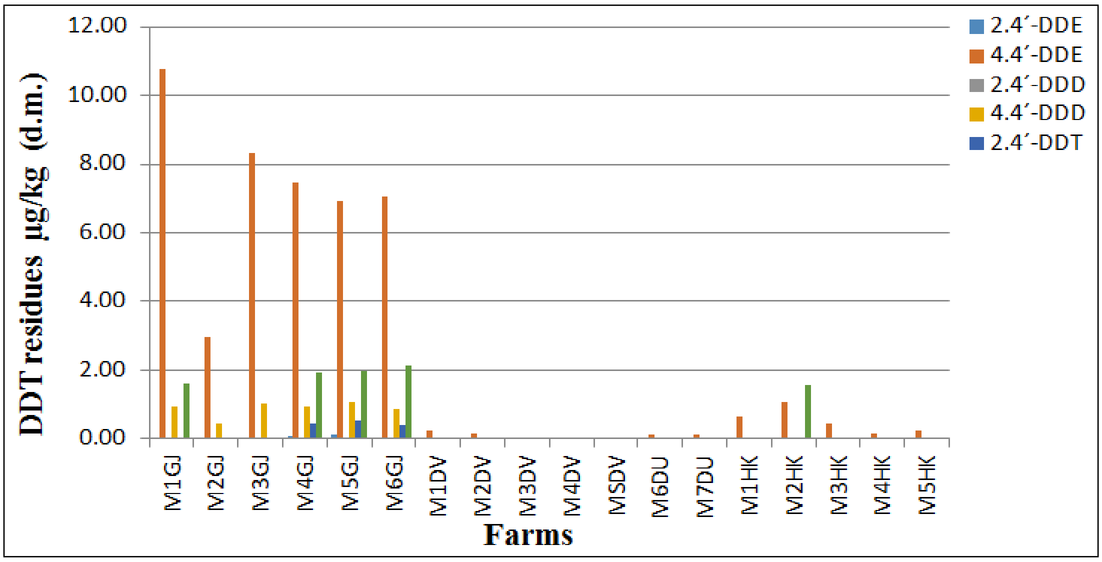


Figure 3. DDT residues and its metabolites in µg/kg (d.m.)


ISSN 2053-5805(Print), ISSN 2053-5813(Online)

From figure 3, it is clearly evident that the most part of DDT residues had transformed in its metabolite 4.4´-DDE. DDT and its related compounds DDE and DDD, bio-accumulate and bio-magnify in the environment. Under aerobic conditions, the predominant reaction is de-hydro-chlorination of DDT to yield DDE, and under anaerobic conditions transformation of DDT to DDD by reductive de-chlorination is considered to be the dominant reaction (Nirwal, 2001). This shows that in our case mostly DDT is transformed under aerobic conditions and only a small part of DDT is transformed under anaerobic conditions.

The sample M3HK which has the highest OM content (5.41 %), has low DDT residues (0.46 µg/kg), and the sample M1GJ which has 3.17 % OM content, has the highest DDT residues (13.33 µg/kg). M6GJ with lowest OM content (1.96%) has 10.50 µg/kg DDT residues. No positive correlation was found between DDT residue concentrations and OM content. Maybe, this is related to the fact that in the soils with more OM content, the amount of microbial biomass is higher and this probably can induce the degradation of organochlorine pesticides.

## CONCLUSIONS

- Status of Soil Organic Matter of the greenhouses and farms under this study is "Low" for 16 greenhouses and farms and "Medium" for 2 greenhouses.
- No positive correlation between the concentration of DDT and Organic Matter was found.
- The presence of DDT residues in the soils under this study is related to the past use of the pesticides in Albania.
- As in the past, in the areas like Shkodra, Tirana, Durres, Lushnja, Fier etc., POPs pesticides were widely used, a further study should be done to include all these areas.
- Furthermore, due to bio-accumulation and bio-magnification of POPs, it is necessary to perform analysis even in the products of the greenhouses and farms which had resulted in values higher than 10 µg/kg.

## ACKNOWLEDGEMENT

Authors thank for the support of this study: BioAgBal Project (funded by DAAD), Institute of Soil Science and Soil Conservation, of the Justus Liebig University of Giessen, and MSc. Laura Kunrath.

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