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AN OVERVIEW OF ORGANOCHLORINATED POLLUTANTS IN AGRICULTURAL SOIL SAMPLES FROM ALBANIA

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Abstract: In this paper concentrations of organochlorine pesticides and polychlorinated biphenyls (PCB) in soil samples of Fushe-Kruja, Mamurras, Laci and Miloti areas are presented. These areas are located in central Albania and they are known for intensive agricultural activity. Twelve soil samples were selected in agricultural areas that are in use from local farmers. Sampling was realized in December 2017. Organochlorine pollutants have high stability, high bioaccumulation capacity and the ability to spread out of the application site. Generally, these compounds are difficult to degrade. In the soil or sediment, the speed of degradation is much lower. Although pesticides have been banned many years ago, they are reported frequently in different studies. Sample treatment procedure includes ultrasonic extraction with organic solvents followed by sulfuric acid hydrolysis and a Florisil column. GC-electron capture detection using a capillary column was implemented for isolation and determination of organochlorine pesticides and polychlorinated biphenyls in soil samples. The highest levels of chlorinated pollutants in study areas were found for organochlorine pesticides because of their previous uses for agricultural purposes. Volatile PCBs were found in higher concentrations because of their atmospheric origin. Found levels were comparable with reported studies for other agricultural areas in Albania.

INTRODUCTION

In this study, one of the most important agricultural and industrial areas of our country has been considered. Fushe-Kruja, Mamurras, Lac, and Miloti areas lies in the north-central part of Albania. These areas are used for agricultural purposes (Nuro and Marku, 2012). Fushe Kruja lies 21 km North-West of Tirana and 10 km from the town of Kruja and at the same time the Kruje-Dajt mountain. Also, Mamurrasi (43 km), Laci (52 km) and Miloti (57 km) are located in the same direction. Average altitude of these fields are 15 m above sea level. Altogether, they have an area of more than 200 km², and newly constructed houses in the field area have occupied a large area, thus affecting the agricultural land. The fields that lie in these areas are very fertile. They are used for cereals, fruits and vegetables. Many fruits tree grow in the surrounding hills in the east of the field areas. Kullas - Zeze areas are particularly good as agricultural units for fruit and grapes plantations. The main parts of these fields are irrigated by waters of Ishem and Mati rivers and those branches. Some rivers that lie in South-East (Zeza, Lana, Tirana and Terkuza rivers) which stems from the Kruja and Dajti mountains are not used for irrigation because they are highly polluted by industrial activity in Tirana-Kruja region. During the previous years, the state-run farming activity was at very high rates, making full use of the total area capacity. Currently, fruit trees are cultivated individually in almost all villages by farmers, in the field and hilly areas.

Pesticides, especially organochlorine pesticides, are kinds of chemical substances belonging to the so-called Persistent Organic Pollutants (POP) substances because they are persistent for many years after their application (Shayler *et al,* 2009). Their degradation is difficult and realized with lower rate in soil and sediments. Usually, they interrupt the reproduction pathway of the pathogens to the plants. Pesticides were used widely for many years in Albania until the 90s. Pesticides are very toxic substances. They can reach human body mainly through the daily foods. So, then pesticides can seriously damage human health. Researchers emphasize that they may be carcinogenic, causing genetic mutations, and impairing reproductive abilities. Also, these substances affect the immune system (Hildebrandt *et al,* 2009; Fernandez *et al,* 2008). Polychlorinated biphenyls (PCB) are organochlorine compounds with 1-10 chlorine attached to the biphenyl structure. Polychlorinated biphenyls were widely used as dielectric and coolant fluids in electrical apparatus, carbonless copy paper and in heat transfer fluids (Erikson, 1986; Kim *et al* 2004). Also, PCBs are part of POP because of their persistence and toxicity. Polychlorinated biphenyls were not used in agriculture but they are often reported in soil samples due to their ability to spread far away from their applications places because of atmospheric factors (wind, rain, snow, etc). Pesticides and PCBs analyzes in soil samples of Fushe-Kruja, Mamurras, Lac, and Miloti areas were performed using GC/ECD techique recomanded in literature (Gaw *et al,* 2006; Muir and Sverko, 2006; Schepens *et al,* 2001).

MATERIALS AND METHODS

Sampling of soil from study area

Soil sampling stations are given in Figure 1. Sampling was carried out in December 2017 in 3 stations for each region (Fushe-Kruje, Lac, Mamuras and Klos). Sampling was done in agricultural parcels that are in use by farmers. Soil samples were collected in square shape (25 x 25 x 25 cm) based on ISO 10382

Method. They were transported at + 4°C. Soil samples were air-dried for some days in room temperature. After that, oven was used (4 hours in 105°C) for their final dry.

Fig. 1. Map of soil sampling from the Fushe – Kruje, Lac, Mamurras and Milot areas

Treatment of soil samples for analysis of pesticides and PCBs

An amount of 10 g dry soil samples was taken to determine the chlororganic pesticides and PCBs in the Fushe-Kruja, Laç, Mamurras and Milot areas. The sampled amount was placed in the erlermayer and a volume of 50 ml of Hexan / Dichloromethane extract to the 3:1 ratio in v/v mixture was added. Extraction of chlororganic compounds was performed in ultrasonic bath for 30 minutes at 30°C. By the filtration process, the extract was separated into a glass to which 5 g of silica gel with 45% sulfuric acid was added to enable the hydrolysis of the macromolecules. The final clean-up procedure was carried out by passing the respective extracts in the florisil column, which were activated in advance with a volume of 10 ml n-Hexan. The 20 ml volume of n-Hexan / Dichloromethane in 4 : 1 ratio was used as the eluent solvent to pass the chlorine-pollutants in a liquid phase, suitable for further analysis. The eluate was evaporated to a final volume of 2 ml and then injected the respective eluate into the GC/ ECD (Nuro and Marku, 2011).

Chromatography

Gas chromatographic analyses were performed with a HP 6890 Series II gas chromatography apparatus equipped with a 63Ni electron-capture detector and PTV injector. The column used was Rtx-5 [low/mid polarity, 5% (phenyl methyl siloxane)] (30 m x 33 mm I.D., x 25mm film). The split/splitless injector and detector temperatures were set at 280^{0}C and 300^{0}C, respectively. Carrier gas was

He at 1 ml/min and make-up gas were nitrogen at 24 ml/min. The initial oven temperature was kept at 60^0C for 4 min, which was increased, to 200^0C at 20^0C/min, held for 7 min, and then increased to 280^0C at 4^0C/min for 20 min. The temperature was finally increased to 300^0C, at 10^0C/min, held for 7 min. Injection volume was 2 μl, when splitless injections were made. Pesticide quantification was performed by internal standard method (Nuro and Marku 2011). Organochlorine pesticides and PCB markers were studied simultaneous in soil samples.

RESULTS AND DISCUSSIONS

Organochlorine pesticides in soil samples

The focus of this study has been one of the most important agricultural and industrial areas of Albania. Fushë-Kruja, Lac, Mamurras and Miloti areas continue to be used for agricultural purposes. The averages for the total of chlororganic pesticides, found in soil samples taken from the study areas are given in Figure 2. From these data it was noticed that chlorine-containing pesticides were found in all soil samples. The average level of pesticides was higher for the samples taken in the Laç area with a value of 193.4 μg/kg, while the average level of pesticides was lower in the samples taken in the Milot area with a value of 101.2 μg/kg. Presence of chlororganic pesticides found in the soil samples were due to previous uses of the compounds in these areas for agricultural purposes. Their absorbtion process on lands is relatively strong and consequently they will continue to be persistent for a long time.

Figure 2 shows the distribution of chlororganic pesticides, which is the same distribution of pesticides for all sampling stations, due to the same origin of pesticides in these samples. Higher levels were found for Heptachloropoxide, Endrin, Dieldrin and HCHs because of previous uses of these pesticides in agricultural areas.

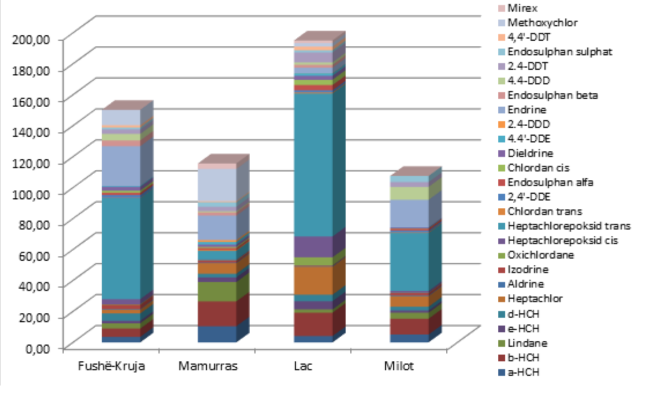

Fig. 2. Average for the total of chlorinated pesticides (μg/kg) in soil samples

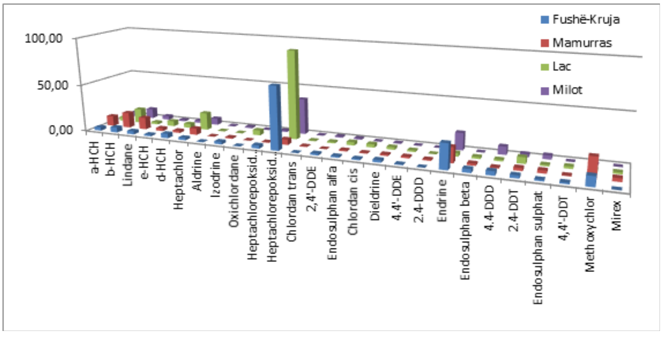

Fig. 3. Distribution of chlorinated pesticides (μg/kg) in soil samples

The total of HCH values found in the soil samples taken from the Laç - Mamurras - Fushe - Krujë - Milot areas are given in Figure 4. Total of Lindane and its isomers were higher in the Mamurras area with 45 μg/kg. In all the analyzed samples there is a similar distribution of HCHs. This was related to the same origin of Lindane in this area, due to its uses as insecticide in agricultural. The profile of all samples analyzed is given by the following descending scale: beta-HCH> alpha-HCH> Lindan> delta-HCH> e-HCH, which is mainly related to the physico-chemical properties of HCH isomers. Found levels are related to the previous use of Lindane for agricultural purposes in these areas. However, HCH levels for all samples were lower than the allowed values in the soil based on Albanian legistation (Anonymous 1994, 1998, 2009; ISO 2002).

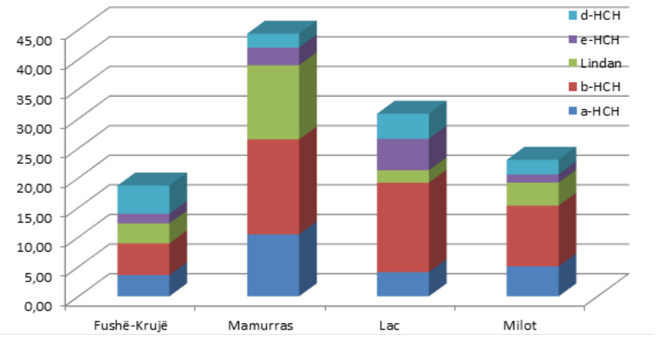

Fig. 4. Lindane and its isomers (μg/kg) on soil samples

In Figure 5 the total values of the Heptachlors found in soil samples taken from the Laç - Mamurras - Fushe - Krujë - Milot areas are shown. The average level of these compounds in the soil samples was displayed at maximum value for the Laç region with 118.5 μg/kg. Heptachlors distribution was the same for all samples due to their same origin. Heptachlorepoxide trans, which is one of Heptachlor degradation product, was found in higher level for all samples. Heptachlor could have been used earlier in these areas. Heptachlors concentrations were higher than permited levels in soil samples for Laci area.

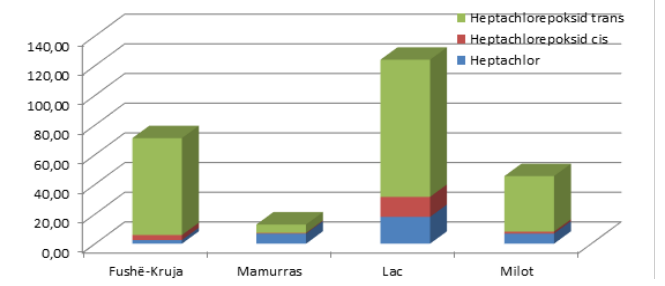

Fig. 5. Heptachlors (µg/kg) in soil samples

Figure 6 shows the total values of the Aldrines found in soil samples taken from the Laç - Mamurras - Fushe - Krujë - Milot areas. The average level of these compounds in the soil samples was displayed at maximum value for Fushe-Kruja area with 29.5 µg/kg. Aldrines distribution was the same for all samples due to their same origin. Endrine was found at the highest level for all samples. It is a degradation product of Aldrine. Aldrine could has been used earlier in these areas. Aldrines were lower than permited levels in soil samples for all studied areas.

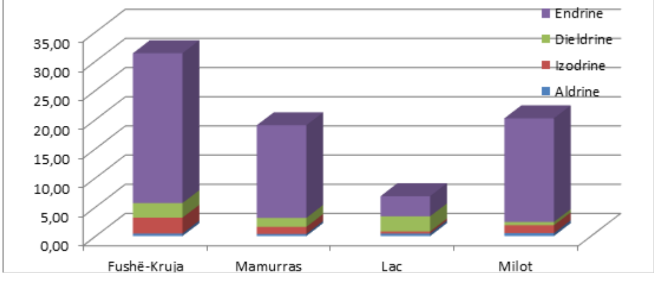

Fig. 6. Aldrines (µg/kg) in soil samples

Figure 7 shows the total values of the Clordanes found in soil samples taken from the Laç - Mamurras - Fushe - Krujë - Milot areas. The average level of these compounds in the soil samples was displayed at maximum value for the Laç region with 8.7 µg/kg. Chlordanes distribution was the same for all samples except Laci samples where Chlordane trans was found at the highest level. Chlordane cis was found higher on other samples. Chlordanes could have been used earlier in these areas. Chlordanes were lower than permited levels in soil samples for all areas.

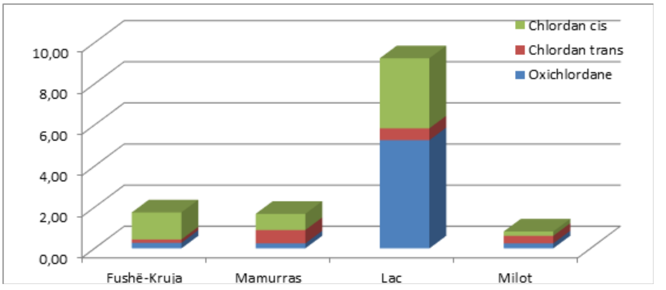

Fig. 7. Chlordanes (µg/kg) in soil samples from the Fushe-Kruja, Lac, Mamurras and Miloti areas

DDT was detected in all soil samples taken in analysis and the total value of DDTs was given in Figure 8, from which it was noticed that the maximum value was obtained in soil samples taken in the Mamurras region with a value of 26.2 ug/kg. While all DDTs apply the same distribution for all samples. It should be noted that for Fushe-Kruja and Mamurrasl soil samples, high levels of Methoxychlor were detected, which is a compound that replaces DDT. DDD was found in higher level for Miloti samples, while 2,4-DDT itself was detected at high levels in Laci areas. It was evident that its metabolites DDE and DDD were found in soil samples in higher level as result of DDT degradation. DDTs profile appear in the following incremental scale: Methoxychlor > DDD > DDE > DDT, which is related to previous uses of DDT and its physico-chemical properties and its metabolites. DDT's found concentrations were lower than permited level for all analyzed soil samples.

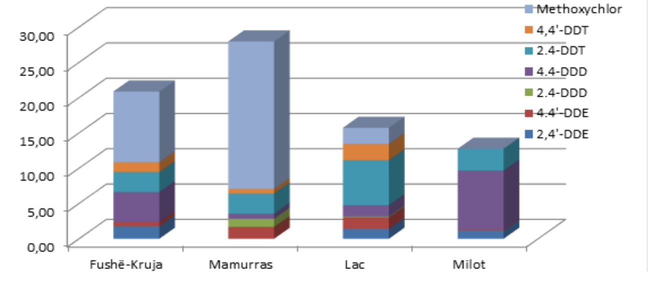

Fig. 8. DDT concentrations (µg/kg) to soil samples

The amount of endosulfan was in higher concentrations in soil samples taken from the Laci and Fushe-Kruja regions, as shown in Figure 9. Their distribution appears to be the same for all samples due to the same origin. Higher levels belong to the endosulfan alpha compound in soil samples from the Laci area, Endosulfan beta was in higher level for soil samples taken from the Fushe-Kruja region and

Endosulfan sulphate were higher in soil samples of Miloti and Mamurras areas. Endosulfanes may be still in use in these area under a falcificated trade-mark. Their levels were below permitted level for all samples.

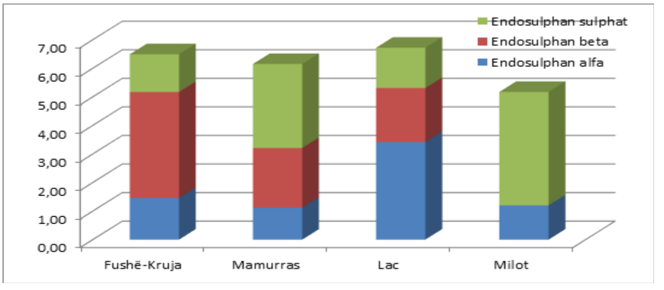

Fig. 9. Endosulfane concentrations (μg/kg) to soil samples

Polychlorinated Biphenyls markers in soil samples

PCB data in soil samples from the Laç, Mamurras, Fushe - Krujë and Milot areas are given in Figure 10. Average for the total of PCBs were found in higher level for soil samples taken in Mamurrasi area with 119.7 μg/kg. Distribution of PCBs markers in soil samples from the Laç - Mamurras - Fushe - Krujë - Milot was the same for all analyzed samples (**Figure 11**). The data reveal higher levels of PCB 153 and PCB 180 in soil samples from the Mamurrasi area. PCB 180 were in higher level for Fushe-Kruja soil samples. Presence of heavy PCBs on these areas coul be as result of accidental spillage from electrical transformer or others equipment, agricultural mechanic, mechanical buisneses, etc. Volatile PCBs (PCB 28 and PCB 52) were found in higher level for Laci areas. Their presence could be because of atmospheric deposition. PCB markers levels were below permited level for soil samples except Mamurrasi sample.

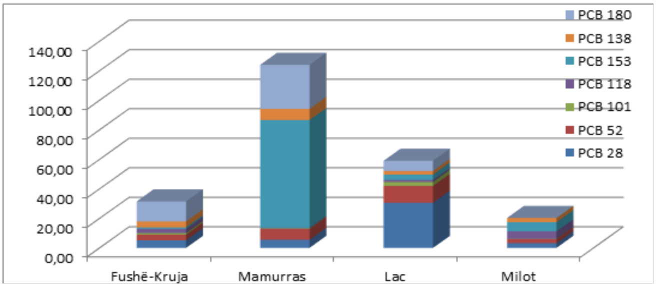

Fig. 10. The total concentrations of PCBs (μg/kg) in soil samples

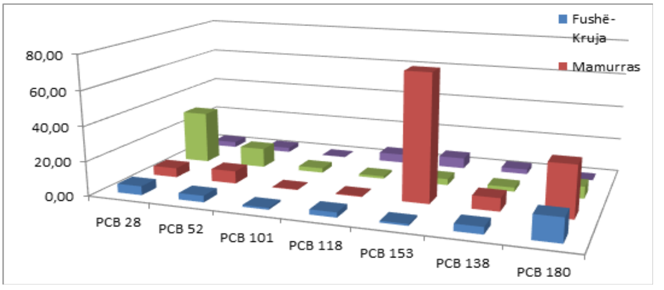

Fig. 11. Distribution of PCBs (µg/kg) in soil samples

CONCLUSION

The objective of this study was to evaluate the concentrations of organochlorine pesticides, their residues and PCB markers on soil samples from the Fushe–Kruja, Laci, Mamurrasi and Miloti areas. These large surfaces are using for agricultural purposes. For determination of chloro-organic pollutants that usually found at trace levels capillary gas chromatography equipped with electron capture detector was used. For extraction of pesticides and PCBs in soil samples ultrasonic extraction technique was used, followed by clean-up procedure in a florisil column. Chlororganic pesticides and their residues were found in all analyzed soil samples. Their total was higher for the soil samples taken in the Laci area while the minimum was found for Miloti soil samples. Presence of chlororganic pesticides in the soil samples were due to previous uses of the compounds in these areas for agricultural purposes. Their absorbtion process on lands is relatively strong and consequently they will continue to be there for a long time. Higher levels were found for Heptachloropoxide > Endrin > Dieldrin > Methoxychlor > HCHs because of previous uses for these pesticides in agricultural areas. Individual levels of pesticides for all samples were lower than the allowed values in the soil based on Albanian and EU norme. Exception was for Heptachlorepoxide in soil samples from Laci area. Endosulfanes may be still in use in these area under a falcificated trade-mark. PCB markers were found for all soil samples from the Laç - Mamurras - Fushe - Krujë - Milot areas. Average for the total of PCBs were found in higher level for soil samples taken in Mamurrasi area. Distribution of PCBs markers was build by individual PCBs. PCB 153 and PCB 180 were found in higher level in soil samples from the Mamurrasi and Fushe-Kruja areas. Presence of heavy PCBs on these areas coul be as result of accidental spillage from electrical transformer or others equipment, agricultural mechanic, mechanical buisneses, etc. Volatile PCBs were found in higher level for Laci areas. Their presence could be because of atmospheric deposition. PCB markers levels were below permited level for soil samples except Mamurrasi sample.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this article. It was written after the proposal of the first author (B.M.) and all the other authors (A.N. and E.M.) contributed equally to the discussions of the text.

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