O 51. A COMPARISON OF PESTICIDE AND PCB LEVELS BETWEEN SOIL AND FRUIT/VEGETABLE SAMPLES FROM MYZEQEJA AREA, ALBANIA

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ABSTRACT: In this paper are presented concentrations of organochlorinated pesticides and polychlorinated biphenyls (PCB) in soil, fruit and vegetable samples from Myzeqeja area. Previous aplication of pesticides for agricultural purposes or/and atmospheric deposition of PCBs and other volatile/semivolatile compounds, irrigation waters, agromechanics and different acidents are the main ways of organic pollutants presence in soil samples. Myzeqeja field is the main agricultural area in Albania. Soil and plant (fruit/vegetable) samples (in the same area) were selected in 15 different stations of Myzeqeja field. Samples were taken in May 2020. Ultrasonic extraction used for extracting organochlorinated pesticides, their residues and PCBs from soil and fruit/vegetable samples. Clean-up procedure was performed using firstly silicagel with sulfuric acid and a second clean-up procedure in an "open" florisil column. Qualitative and quantitative analysis was realized in Varian 450 gas chromatograph equipped with ECD detector. For simultaneous separation of organochlorinated pesticides and PCB markers was used Rtx-5 capillary column (30m x 0.32mm x 0.25μm). In all studied samples were found organochlorinated pollutants. These facts reflect the presence of these pollutants because their previous use, bioaccumulation processes, slope, soil geology, fruit/vegetable type, irrigation water used, atmospheric deposition, etc. The main origin of organochlorine pesticides could be as result of their previous uses for agricultural purposes because the higher concentrations for their metabolites. Profile PCB marker were as following: PCB 28 > PCB 138 > PCB 153. This fact confirms atmospheric origin of these compounds in Myzeqeja area.

Keywords: *Organoclorined pesticides, PCB, Soil samples, Fruit and Vegetable samples, Gas chromatography*

INTRODUCTION

In this study was determined concentrations of organochlorine pesticides (OCPs) and PCBs in the main and the most important agricultural areas of Albania. Myzeqeja field lies in the South-West Albania between Shkumbini and Vjosa rivers. This area is used and continue to be used for agricultural purposes because is very fertile, especially for cornes, fruits and vegetables. Before, Second World War the main parts of Myzeqeja field have been a wetland. Organochlorine pesticides (DDT, Lindane, HCB, etc) were used intensively form 1946 to 1990s in this area firstly for against mosquitos (malaria vector) and after that for agricultural purposes. Polychlorinated biphenyls (PCB) were not in use in Albania but they were reported in many ecosystems because of atmospheric depositions.
Organochlorine pollutants have high stability, high bioaccumulation capacity and the ability to spread out far away from the application site. OCPs and PCBs are very stable compounds in enviroment. Depending of matrices their degradation process need many years. Their degradation speed in soil or sediments is slower. Soil contamination is one of most important factors influencing the quality of agricultural products. Usage of heavy farm equipment, the land drainage, an excessive application of agrochemicals, emissions, etc, generate a number of undesired substances, which after deposition in soil may influence crop quality (Como et al, 2013; Stancheva et al 2011). Runoff affects the movement of pollutants in water over a sloping surface. The amount of pollutants runoff depends on: the slope, the texture of the soil, the soil moisture content, rainfall, and the type of pesticide used (Gashi et al 2013). The fate of a pesticides to soil depends largely on two of its properties: persistence and adsorption. Once applied to cropland, a pesticide may be taken up by plants, adsorbed to plant surfaces, broken down by sunlight (photdegradation), or ingested by animals, insects, worms or microorganisms in the soil. Factors controlling pesticide adsorption include pesticide charge; soil pH, temperature and water content; the presence of previously adsorbed chemicals that have a stronger bond to soil particles; and the amount

and type of organic matter present. In general, pesticide adsorption relates inversely to pesticide solubility in water. Highly soluble pesticides are weakly adsorbed and pose a greater threat of groundwater contamination (Penttila and Siivinen, 1996).
Organochlorine pesticides and PCBs are classified as Persistent Organic Pollutants (POP) because they are persistent for many years after their application (Shayler et al, 2009). Human exposure to chlorinated organic pollutants primarily occurs through food contamination. Fish, meat, fruit, vegetables and other dairy products are the most important dietary sources of pesticides and their metabolites for humans (Lazaro et al, 1996). Great concern was caused by chlorinated compounds, which proved to be extremely persistent in the environment and accumulative in the food chain (Penttila & Siivinen, 1996; WHO & FAO 1983; Wilhelm et al, 2002).

MATERIAL AND METHODS

Sampling of vegetable, fruits and soil samples

For this study were sampled in the same stations (14 station in total) soil and fruit/vegetable samples. Stations were selected in agricultural areas that are used and continus to be in use as well as to be more representative of Myzeqeja field. Soil samples were taken until 30 cm depth and transported in plastic bags (+4°C). In the laborator they were dried in open air. Onion (S1 – North of Myzeqeja field), potato (S2 and S5), lettuce (S3 and S12), spinach (S4), carrot (S6 and S11), tomato (S7, S10 and S13), peper (S8), cucumber (S9), strawberry (S14 – South of Myzeqeja field). Fruit/vegetable samples were transported in plastic bags in +4°C prior to their analyze. Soil and fruit/vegetable samples were taken in May 2020.

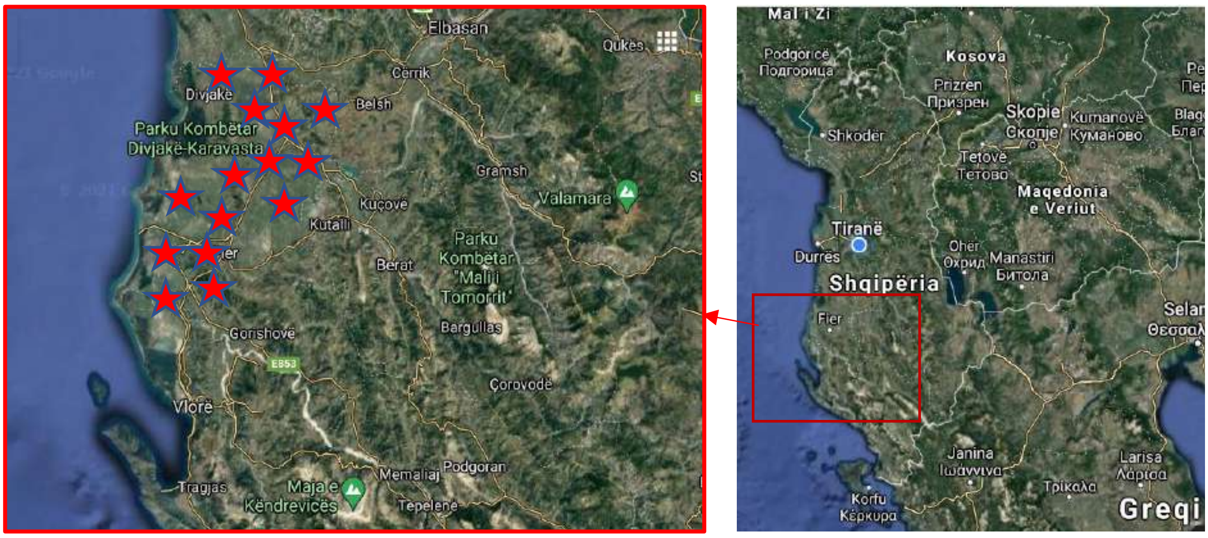

Figure 1. Sampling station in Myzeqeja field, May 2020

Treatment of fruit and vegetable samples for GC analyze

The vegetable and fruit samples were homogenized with anhydrous sodium sulphate (1:10) and were extracted by ultrasonic bath (10g fresh weight of biota) assisted by 50 ml hexane:dichloromethane 3:1, (v:v). The extract was purified firstly by shaking with 15g silica gel, impregnated previously with 45% sulfuric acid for the macromolecules hydrolize. A further clean-up was performed in an open glass column with Florisil, deactivated with 5% water. The organochlorine compounds were eluted with 7 ml of hexane:dichloromethane 4:1(v:v). The extract was concentrated to 2 ml and analyzed by GC-ECD (Nuro et al, 2014).

Treatment of soil samples for GC analyze

Soil samples were dry firstly in open air and after that were sived for selecting 63 micron fraction. A sub-sample from 10 g of soil samples were extracted by ultrasonic bath assisted by 50 ml hexane/dichloromethane 3:1, (v:v). The extract was purified by shaking with 5 gr sodium sulphate and 5g silica gel, impregnated previously with 45% sulfuric acid. A further clean-up of this extract was performed in a open glass column packed with Florisil, deactivated with 5% water. The organochlorine compounds were eluted with 7 ml of hexane:dichloromethane 4:1(v:v). The extract was concentrated to 2 ml and after that analyzed by GC-ECD (Nuro et al, 2014).

Gas chromatography analyzes of pesticides and PCBs

Organochlorine pesticides and PCBs were analyzed simultaneously using HP 6890 Series Plus with μECD detector and a capillary column Rtx-5, 30m long x 0.25mm i.d. x 0.25 μm film thicknesses. Helium was used as carrier gas and nitrogen as make-up gas. Manual injection was done in split mode (1:50) in 280^{0}C. The organochlorine pesticides detected were according EPA 8081 standard: HCHs (a-, b-, γ- and d-isomers), DDT's-related chemicals (p,p-DDE, p,p-DDD, p,p-DDT), Heptachlors (Heptachlor and Heptachlor epoxide), Aldrine's (Aldrine, Dieldrin, Endrin and related compounds), Endosulfane's (I, II and Endosulfane sulphate isomer's), Methoxychlor and Mirex. Analysis of PCBs was based on the determination of the seven PCB markers (IUPAC Nr. 28, 52, 101, 118, 138, 153 and 180). Quality assurance procedures included determination of LOD, LOQ, precision, reproducibility and accuracy of the method. Five calibration points with concentrations of 5, 10, 25, 50, 100 ng/ul were selected for both, pesticides and PCB's. Qualitative analyze was based on external standard method (Vryzas et al, 2009; Lekkas et al, 2004; Nuro et al, 2014).

RESULTS AND DISCUSSION

Analyze of organochlorine pesticides, their residues and PCB was realized in soil and fruit/vegetable samples from Myzeqeja field. Pesticides were used intensively in this area from 1946 to 1992 for against malaria vectors (mosquitos) and for agricultural purposes. Organochlorine pollutants are very stable compounds while they can be found in environment for many years after their application. Soil and fruit/vegetable samples were taken in the same stations in order to evaluate their acumulation process from soil to plants.
Figure 2 shows the total of OCPs in soil and fruit/vegetable samples from Myzeqeja field. Organochlorine pesticides were found in all soil and fruit/vegetable samples. OCPs concentrations were found 20 – 50 times higher in soil samples. Their range was in soil samples 70.5 – 345.7 ng/g (155.3 ng/g mean value) and in fruit/vegetable samples were 0.1 – 13.5 ng/g (4.7 ng/g mean value). S8 soil sample and potato sample were the most polluted samples. The found level could be mostly because of previous use of pesticides in this area. The distribution of organochlorine pesticides in all analyzed samples (soil and fruit/vegetable) was almost the same for all stations because the origin of pollution is the same. It was noted that some pesticides were in higher levels for some stations. This could be because of punctual sources or new arrivals from different effluents and drainage channels of agricultural areas. Profile of organochlorine pesticides (Figure 3) in soil samples were: Endosulfan sulfat > Endosulfan alfa > Endrin keton > Dieldrin > Metoxychlor. Almost the same profile was found in fruit/vegetable samples where Endosulfanes and Adlrins were found in higher concentrations compare to other groups of pesticides. Their presence in fruit/vegetable could be because of bioaccumulation process not because of their recent use. Note that profile of pesticides could be connected with the period in which these pesticides were applied in different sampling stations. Also, individual properties (physico-chemical properties) of each pesticide and their residues could be affect their profile.
Figure 4 shows the profile of Lindane and its isomers in soil and fruit/vegetable samples from Myzeqeja field. Lindane and its isomers were found in all soil samples and in 76% of fruit/vegetable samples. Their mean concentration was 1.3 ng/g in soil samples while in fruit/vegetable were 0.72 ng/g. Their total were 2-5 times higher in soil samples. Alfa-HCH was found in higher level in soil samples while beta-HCH was identify as main HCHs in fruit/vegetable samples. This profile could be because of HCHs

stability and their bio-affinity to pass from soil to plants. Total of HCHs were lower than permitted level for soil and fruit/vegetable samples conform Albanian and EU legistation.

Heptachlores in soil and fruit/vegetable samples from Myzeqeja field was shown in Figure 5. Heptachlor and Heptachlor epoxide were found in all soil samples and in 83% of fruit/vegetable samples. Their mean concentration was 2.9 ng/g in soil samples while in fruit/vegetable were 0.4 ng/g. Their total was found 2-12 times higher in soil samples. Heptachlor epoxide (degradation product of Heptachlor) was identified in higher concentrations in all samples because of Heptachlor previous use. Total of Heptachlors were lower than permitted level for soil and fruit/vegetable samples conform Albanian and EU legistation.

Figure 6 shows profile of Aldrines in soil and fruit/vegetable samples from Myzeqeja field. Aldrines were found in all soil and fruit/vegetable samples. Their mean concentration was 31.8 ng/g in soil samples and 1.4 ng/g in fruit/vegetable. Their total was found 2-100 times higher in soil samples. Degradation products of Aldrine was identify in higher concentrations in all analyzed samples because of its previous use. Profile of Aldrines in soil samples was: Endrin keton > Dieldrin > Endrin > Aldrin. Dieldrin was found in higher concentration in fruit/vegetable samples. Total of Aldrins were lower than permitted level for soil and fruit/vegetable samples conform Albanian and EU legistation.

Figure 7 shows profile of DDT and its degradation products (DDD and DDE) in soil and fruit/vegetable samples from Myzeqeja field. DDTs were found in 87% soil samples and in 66% of fruit/vegetable samples. Their mean concentration was 7.2 ng/g in soil samples and 0.6 ng/g in fruit/vegetable. Their total was found 2-10 times higher in soil samples. DDD and DDE were found in higher concentrations in all samples because of DDT previous use. Higher levels of DDTs were found in three soil samples (S6, S8, S11) of Myzeqeja field. Profile of DDTs in soil samples was: DDD > DDE > DDT. DDE was found in higher concentration in fruit/vegetable samples. This difference betwen soil and fruit/vegetable samples could be conected mostly with the higher bioaffinity of DDE. Total of DDTs were lower than permitted level for soil and fruit/vegetable samples conform Albanian and EU legistation.

Figure 8 shows profile of Endosulfanes in soil and fruit/vegetable samples from Myzeqeja fiel. Endosulfane's were found as primary pollutants in all soil samples and fruit/vegetable samples. Their mean concentration was 102.6 ng/g in soil samples while in fruit/vegetable were 4.4 ng/g. Their total was found 2-50 times higher in soil samples. Endosulfan sulphate was identify in higher concentrations in all soil and fruit/vegetable samples. Endosulfanes could have been used in this area recent years under a false trademark. Total of Endosulfanes were lower than permitted level for soil and fruit/vegetable samples conform Albanian and EU legistation. except S3, S6, S8, and S13 samples.

Mirex was found only in 2 soil samples in low level (0.3 ng/g). It was not found in fruit/vegetable samples. Mirex is not used in Albania but their presence coud be because of atmospheric deposition or water irrigation.

Methoxychlor was found in 71% soil samples and in 29% of fruit/vegetable samples. Mean concentration of Methoxychlor in soil samples was 10.7 ng/g while in fruit/vegetable was 0.4 ng/g ng/g. Its total was found 5-50 times higher in soil samples. Its presence could be because of its previous use. Methoxychlor concentration was lower than permitted level for soil and fruit/vegetable samples conform Albanian and EU legistation.

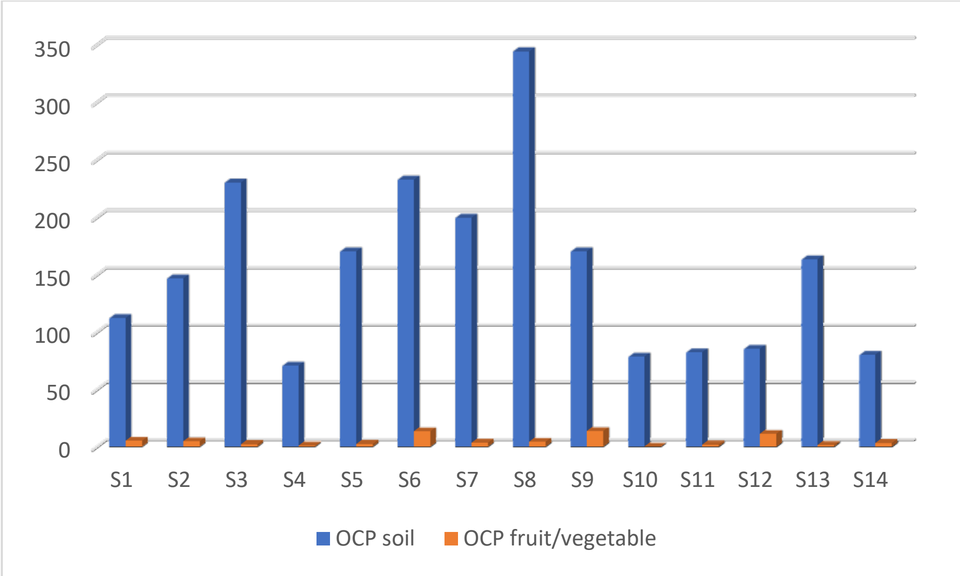

Figure 2. Total of OCPs in soil and fruit/vegetable samples from Myzeqeja field

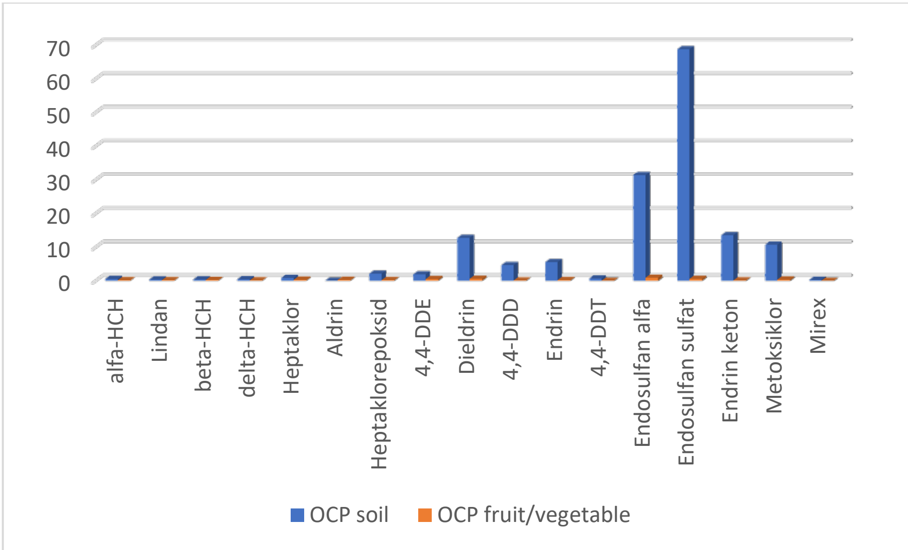

Figure 3. Profile of OCPs in soil and fruit/vegetable samples from Myzeqeja field

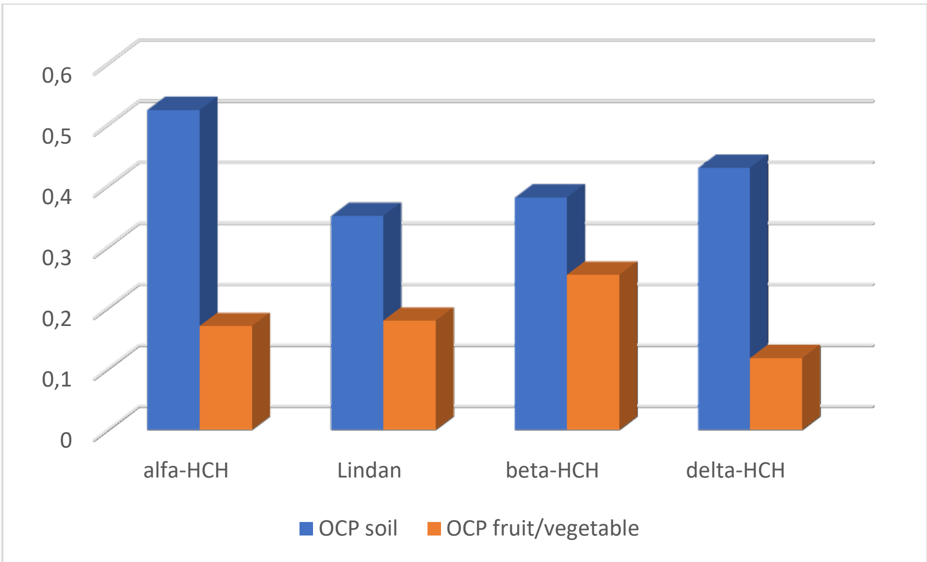

Figure 4. Lindane and its isomers in soil and fruit/vegetable samples from Myzeqeja field

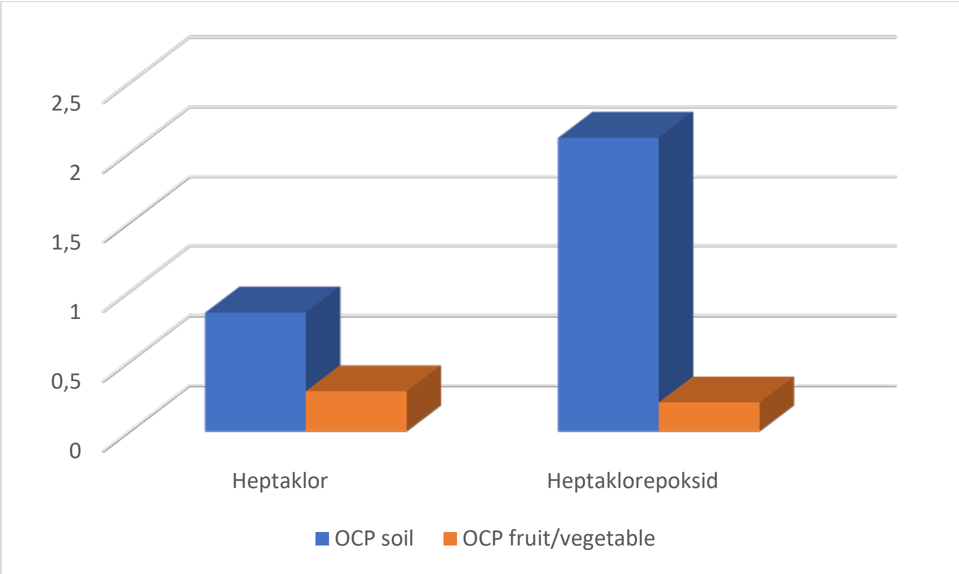

Figure 5. Heptachlores in soil and fruit/vegetable samples from Myzeqeja field

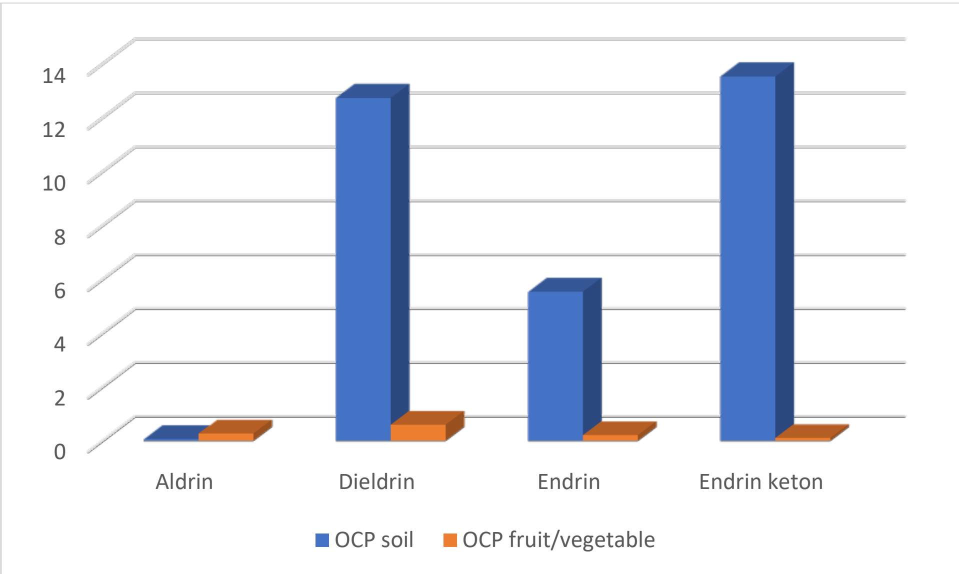

Figure 6. Aldrines in soil and fruit/vegetable samples from Myzeqeja field

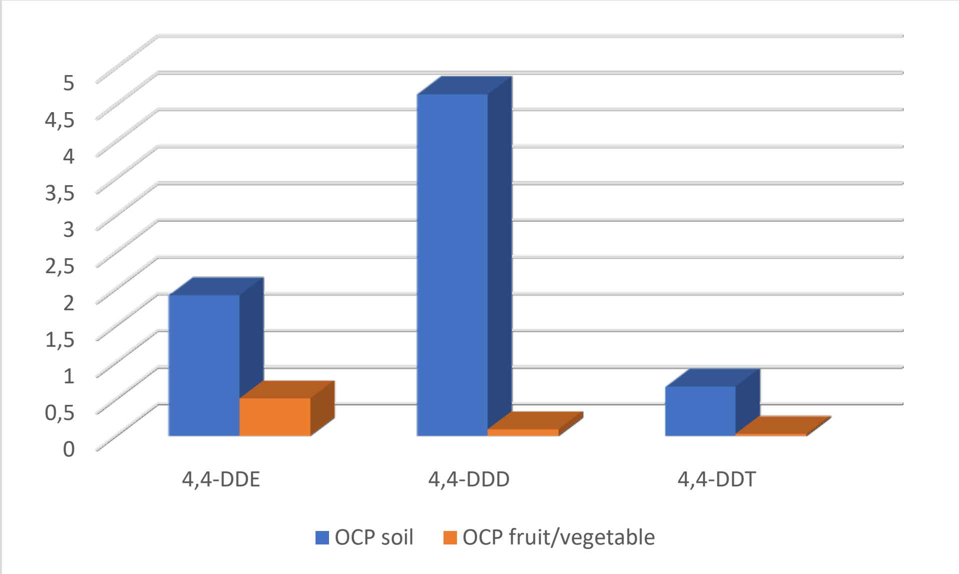

Figure 7. DDTs in soil and fruit/vegetable samples from Myzeqeja field

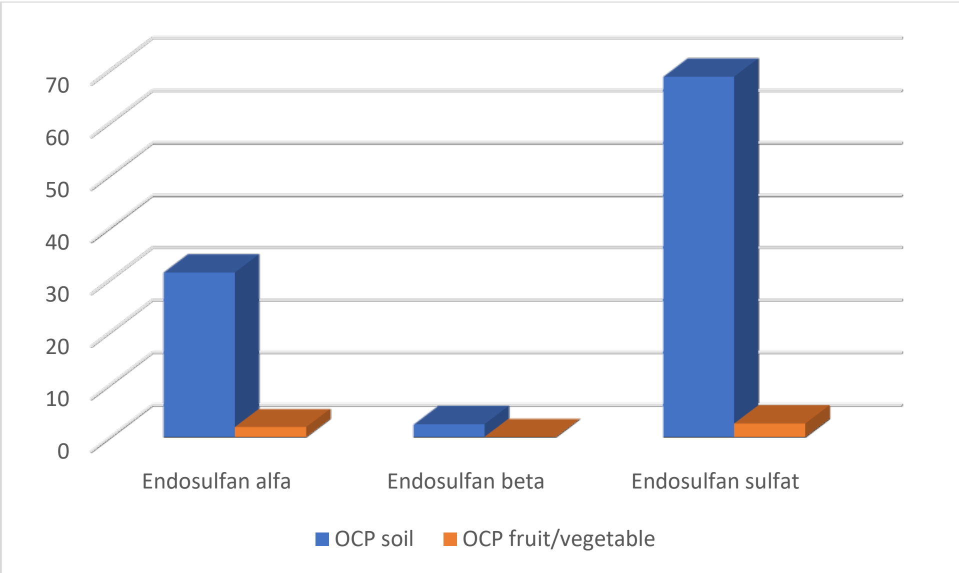

Figure 8. Endosulfanes in soil and fruit/vegetable samples from Myzeqeja field

Figure 9 shows the total of PCB markers in soil and fruit/vegetable samples from Myzeqeja field. PCBs were found in all soil samples and fruit/vegetable samples. Their mean concentration was 27.6 ng/g in soil samples and 2.6 ng/g in fruit/vegetable. Their total was found 3-20 times higher in soil samples. Their range in soil samples was from 8.2 to 80.7 ng/g (27.6 ng/g mean value) and in fruit/vegetable samples was between 0.2 and 7.5 ng/g (2.7 ng/g mean value). S13 soil sample and lettuce sample (S12) were the most polluted samples with PCBs. Distribution of PCBs was almost the same for all soil and fruit/vegetable samples because of the same origin of pollution. Figure 10 shows profile of PCBs in soil and fruit/vegetable samples from Myzeqeja field. Profile of PCBs in soil samples was: PCB 28> PCB 138 > PCB 153 > PCB 180 > PCB 118. PCB 28 was found in higher level almost for all samples. Its origin could be because of atmospheric deposition. Almost the same profile was found in fruit/vegetable samples. Their presence in fruit/vegetable could be because of atmospheric deposition and bioaccumulation process. Presence of some heavy congeners of PCBs (PCB 180 and PCB 209) could be terrestrial origin. Discharging of wastewaters from industries and mechanical businesses could affect the found level and their profile.

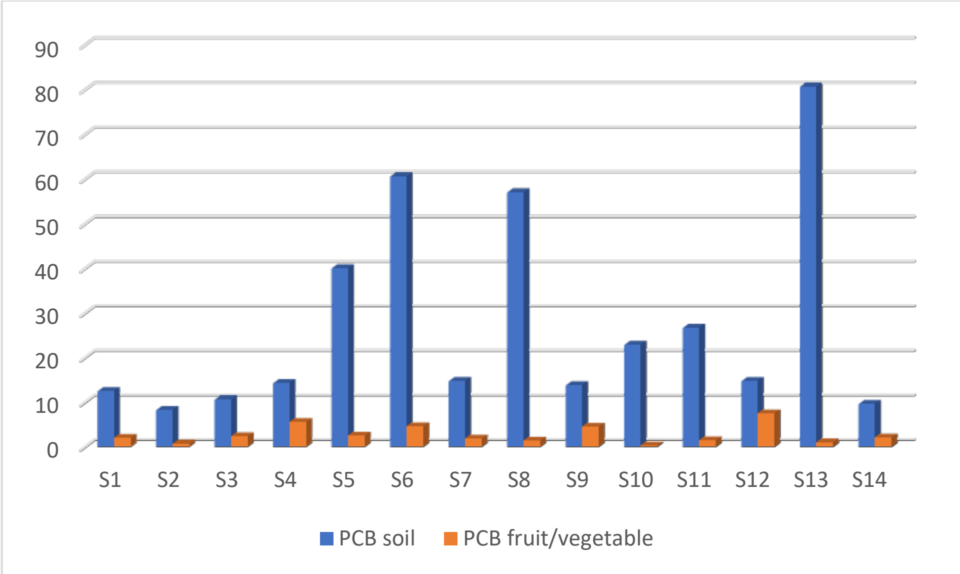

Figure 9. Total of PCBs in soil and fruit/vegetable samples from Myzeqeja field

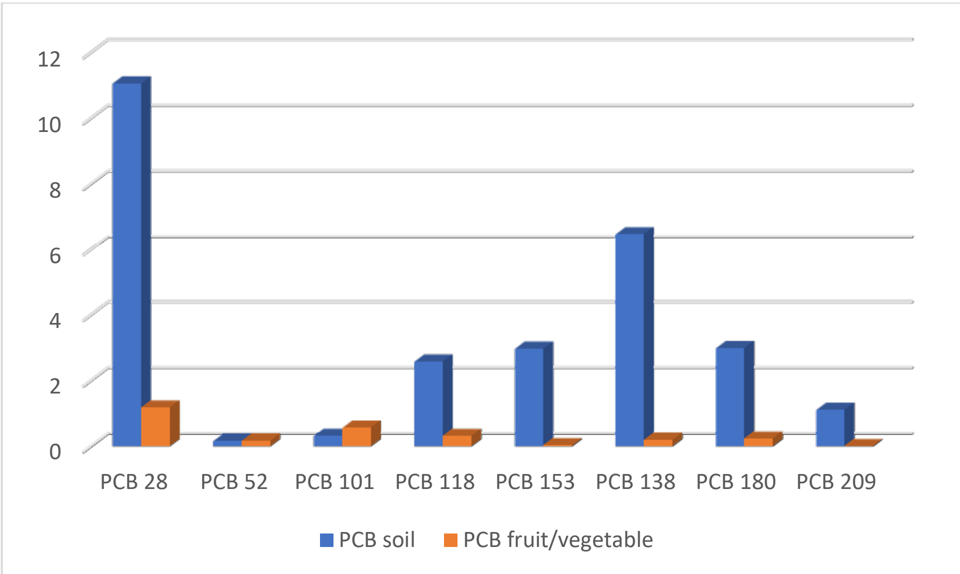

Figure 10. Profile of PCBs in soil and fruit/vegetable samples from Myzeqeja field

CONCLUSIONS

The objective of this study was evidence of organochlorine pesticides, their residues and PCB markers on soil and fruit/vegetable samples from the Myzeqeja field. It is the main agricultural area in Albania. Determinations of organochlorinated pesticides and PCBs in soiland fruit/vegetable samples were realized based in EU protocols for soil and non-fatty food samples. Organochlorine pesticides and their residues were found in all soil samples taken from 14 stations of Myzeqeja area. Organochlorine pesticides are not used in Albania after the 90'. These data shown the presence for pesticide residues in water samples because of their previous use. Their total was found 2-100 times higher for the soil samples due to previous uses of the compounds in this areas for agricultural purposes. Pesticide 323egislatio process on lands is relatively strong and consequently they will continue to be there for a long time. Their profile in all analyzed samples was: Endosulfanes > Aldrins > Methoxychlor > DDTs > Heptachlors > HCHs. Their concentrations and profile could be connected with their previous uses in agricultural and because their individual physical-chemical properties. Individual levels of pesticides for all samples were lower than the allowed values in the soil and fruit/vegetable samples based on Albanian and EU 323egislation. Exception was for endosulfanes in soil samples which could have been used recent years in these area under a falce trade-marks. PCB markers were found for all soil and fruit/vegetable samples from Myzeqeja field. Average for the total of PCBs were found 2-20 times higher in soil samples. Volatile PCBs were found in higher level in all analyzed samples because of their atmospheric deposition origin. Presence of heavy PCBs on these areas coul be as result of terresatial sources by agricultural mechanic, mechanical buisneses, etc. Presence of organochlorine pesticides and PCBs in soil and fruit/vegetable samples from Myzeqeja field should encourage the institutions responsible for ongoing analysis in this area.

REFERENCES

Lazaro R., Herrera A., Arino A., Pilar Conchello M., Bayrri S. (1996) Organochlorine pesticide residues in total diet samples from Aragon (Northeastern Spain). J.Agric.Food Chem. Vol. 44. P. 2742-2747.

Nuro A., Koci K., Marku E. (2007) Occurrence of Persistent Chlorinated Contaminants using Butter as an Integrative Matrix., Journal of Environmental Protection and Ecology 8,No 3, 544-555.

Penttila P.L., Siivinen K.,. (1996) Control and intake of pesticide residues during 1981-1993 in Finland Food Additives & Contaminants: Part A, Volume 13, Issue 6, pages 609 – 621

Rogan W.J., Chen A. (2005) Health risks and benefits of bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT). Lancet. Vol. 366. P. 763-773.

Skibniewska K., Smoczynski S. (2000) Modern looks on the residues chloroorganic insecticide in food. Żyw. Czlow. Metab. Vol. 27 (supl). P. 279-281.

Wilhelm M., Schrey P., Wittsiepe J., Heinzow B. (2002) Dietary intake of persistent organic pollutants (POPs) by German children using duplicate portion sampling. Int. J. Hyg. Environ. Health. Vol. 204. P. 359-362.

Gashi V., Nuro A., Pulaj B., "Study of Organochlorinated Pesticide Residues and Polychlorinated Biphenyls in Soil Samples". Iliria International Review, ISSN 2192-7081, 2013/2, pp. 399-409

Lekkas Th., Kolokythas G., Nikolaou A., Kostopoulou M., Kotrikla A., Gatidou G., Thomaidis N.S., Golfinopoulos S., Makri C. (2004) Evaluation of the pollution of the surface waters of Greece from the priority compounds of List II, 76/464/EEC Directive, and other toxic compounds, Environment International, Volume 30, Issue 8, Pp. 995–1007

Shayler H., McBride M., Harrison E. (2009) "Sources and Impacts of Contaminants in the Soil", Cornell Waste Managemant Institue, Ithaca.

Stancheva M., Makedonski L., Georgieva S. (2011) Organochlorine Pesticides in Fish from Bulgarian Region of Black Sea, Archives of the Balkan Medical Union 46(4):209

Stoykova I., Yankovska-Stefenova T., Yotova L., Danalev D.– THE Impact of Different Solvent Ratios on the Recovery of Lindane in Egg, Annuaire de l'Université de Sofia "St. Kliment Ohridski" Faculte de Biologie 2015, volume 100, livre 4, pp. 96-99