ORGANOCHLORINE POLLUTANTS IN AGRICULTURAL SOIL SAMPLES FROM MYZEQEJA AREA, ALBANIA

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Abstract: *In this paper were presented concentration and distribution of organochlorine pesticides, their residues and polychlorinated biphenyls (PCB) in soil samples from Myzeqeja area. This area is located in South-West central Albania. Myzeqeja field is the main agricultural area in Albania. It is known for elevated agricultural activity after Second War until now. In the past the main parts of Myzeqeja field have been a wetland. Firstly, DDT and other organochlorine pesticides were used in this area against malaria vector and after that for agricultural purposes. In this area use of organochlorine pesticides continued until 90'. PCBs weren't 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 of the application site. Generally these compounds are difficult to degrade. In the soil or sediment the speed of their degradation is lower.*

Fourteen soil samples were selected in agricultural areas that are in use from local farmers. Sampling was realized in March 2018. In the analytical method were combined ultrasonic bath extractions, acid hydrolyze and a Florisil column for samples clean-up. The analysis of the organochlorine pesticides and PCB in soil samples was performed by gas chromatography technique using electron capture detector (GC/ECD). Rtx-5 (30m x 0.33mm x 0.25μm) capillary column was used for simultaneous determination of organochlorine pesticides and PCB. The highest levels of chlorinated pollutants in study areas were found for organochlorine pesticides because of their previous uses for agricultural purposes. Methoxychlor, Endrin Keton and Mirex were the most frequently detected pesticides for all samples. Volatile PCBs were found in higher concentrations because of their atmospheric origin. Found levels were higher / comparable with reported studies for other agricultural areas in Albania.

Keywords: *Myzeqeja, Organoclorined pesticides, PCBs, soil samples, GC/ECD*

Introduction

In this study one of the most important agricultural areas of Albania was considered and analyzed. Myzeqeja area is situated in the South-West of central Albania between Shkumbini and Vjosa rivers. It's the main agricultural area of Albania with 1350 km^2. Its large spaces were used and continue to be widely used for agricultural purposes (Nuro and Marku, 2012). The fields that lie in these areas are very fertile, especially for cereals and greens and the surrounding hills in the east of the area. The main parts of these fields are covered by the Shkumbini, Vjosa and Semani rivers and those branches. It is known for elevated agricultural activity after Second War until now. In the past the main parts of Myzeqeja field have been a wetland. Firstly, DDT and other organochlorine pesticides were used in this area against malaria vector and after that for agricultural purposes. In this area use of organochlorine pesticides continued until 90'. Pesticides, especially organochlorine pesticides, are kinds of

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chemical substances classified as Persistent Organic Pollutants (POP) substances because they are persistent for many years after their application (Shayler et al, 2009). Their degradation is difficult and continuous for many years after their application. Organochlorine pesticides were created mainly to harm the reproduction pathway of the pathogens to the plants. Pesticides were used widely for many years almost for all countries include Albania. Pesticides are very toxic substances and when they enter to the human body through foods then they can seriously damage human health. Many studies have shown that pesticides may be carcinogenic, cause genetic mutations, and impair reproductive abilities. Also, these substances affect the immune system (Hildebrandt et al, 2009; Fernandez et al, 2008). Polychlorinated biphenyls (PCB) are chlorinated 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). PCBs weren't in use in Albania but they were reported in many ecosystems because of atmospheric depositions. 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) (Gaw et al, 2006; Muir and Sverko, 2006).

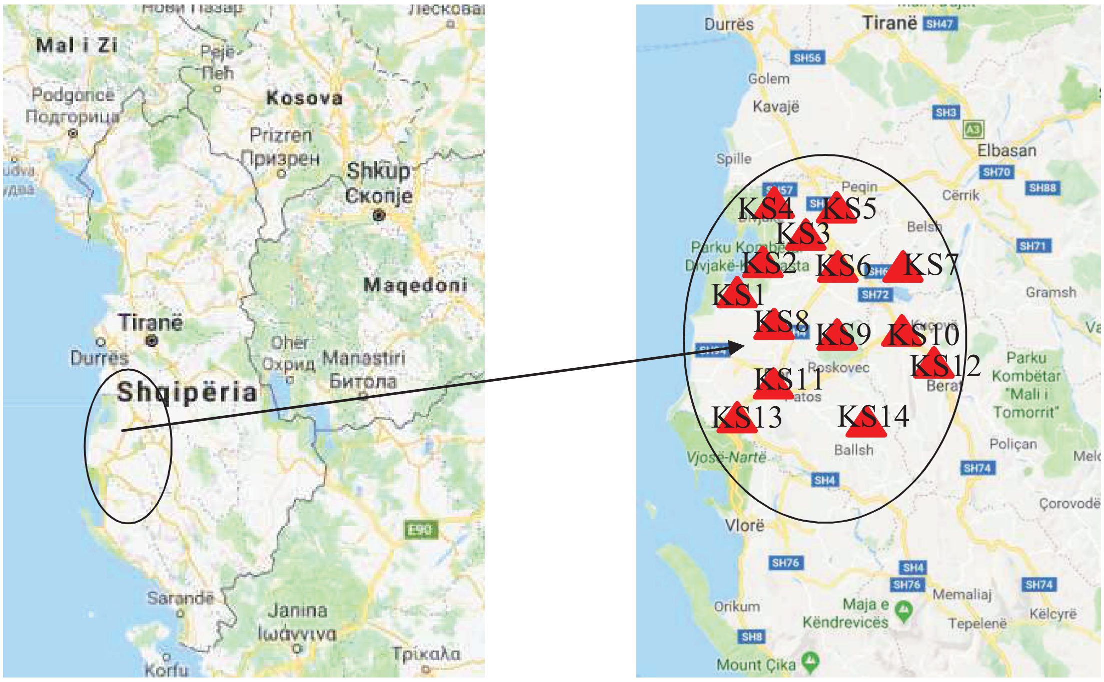
Organochlorine pollutants (organochlorine pesticides, PCB, Dioxin, etc.) have high stability, high bioaccumulation capacity and the ability to spread out of the application site. Generally these compounds are difficult to degrade. In the soil or sediment the speed of their degradation is lower. Soil 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 originating from mining, metallurgical, and chemical and coal power plants and transport, all generate a number of undesired substances (nitric and sulphur oxides, PAHs, heavy metals, pesticides), which after deposition in soil may influence crop quality. Thus, input of these contaminants into the environment should be carefully monitored. Runoff could affect the movement of pesticides in water over a sloping surface. The amount of pesticide runoff depends on: the slope, the texture of the soil, the soil moisture content, rainfall, and the type of pesticide used. Leaching occurs downward, upward, or sideways. Many chromatographic methods were developed last years for detecting traces of organic pollutants in soil samples (Di Muccio, 1996; Erikson, 2001). Determination of halogenated pollutants is based mainly in capillary GC/ECD and GC/MS methods.

2. Materials and methods

2.1. Sampling of soil from Myzeqeja area

Soil sampling stations are given in Figure 1. Sampling was carried out in March 2018 in 14 different stations of Myzeqeja field. Soil samples were taken into agricultural parcels that were used and continue to be used by farmers. Samples were collected by dividing the sampling area in the form of a square with 25 x 25 x 25 cm. The soil samples were transported at + 4^{o}C until analyzed. Soil samples were dry firstly in room temperature and after that for 4 hours in 105^{o}C. This procedure was based on ISO 10382 Method, accepted as Albanian standard.

Figure 1. Map of soil sampling from the Myzeqeja area



2.2. Treatment of soil samples for analysis of pesticides and PCBs

An amount of 10 g dry soil samples was taken to determine the organochlorine pesticides and PCBs in the Myzeqeja areas. The sampled amount is placed in the erlermayer and a volume of 50 ml of Hekzan / Dichloromethane extract to the 3: 1 ratio in volume / volume mixture is added. Extraction of organochlorine compounds was performed in ultrasonic bath for 30 minutes at 30ºC. By the filtration process, the extract is separated into a glass to which is added 5 g of silica gel with 45% sulfuric acid to enable the hydrolysis of the macromolecules. The final excretion was carried out by passing the respective extracts for the flourisil columns, which were activated in advance with a volume of 10 ml n-Hekzan. The 20 ml volume of n-hexane/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 using Kuderna-Danish and then injected the respective eluate into the HP 6890 Series II gas chromatography apparatus equipped with ECD Detector (Nuro and Marku, 2012).

2.3. Apparatus and chromatography

Gas chromatographic analyses were performed with HP 6890 Series II gas chromatograph apparatus equipped with a ^{63}Ni 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 24ml/min. The initial oven temperature was kept at 60^{0}C for 4 min, which was increased, to 200^{0}C at 20^{0}C/min, held for 7 min, and then increased to 280^{0}C at 4^{0}C/min for 20 min. The temperature was finally increased to 300^{0}C, at 10^{0}C/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 2012). The following organchlorine pesticides: hexachlorocyclohexane (HCH) isomers (alfa-, beta/, gamma-, delta- and epsilon-HCH), Aldrines (Aldrin, Dieldrine, Endrine, Isodin), Heptachlors (Heptachlor and cis-, trans-Heptachlorepoxides), Chlordanes (cis-, trans- and Oxychlordane), Endosulphanes (alfa, beta and Endosulphan sulphate), DDT-related chemicals (*o,p*-DDE, *p,p*-DDE, *p,p*-DDD, *p,p*-DDT) Methoxychlor and Mirex were detected. PCB markers (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138 and PCB 180) were studied simultaneous with above pesticides in soil samples.

RESULTS AND DISCUSSIONS

The focus of this study has been one of the most important agricultural areas of Albania. Myzeqeja area is located in the South-West of central Albania. It consists of the large surfaces that were used and continue to be widely used for agricultural purposes. Total of organochlorine pesticides found in analyzed soil samples of Myzeqeja area was given in Figure 2. Organochlorine pesticides were found in all soil samples. The average level of detected pesticides was 143.2 ug/kg. Maximum level of organochlorine pesticides was for KS3 sample with 283.4 µg/kg, while the minimum level of pesticides was for KS10 with 11.2 ug/kg. Presence of chlororganic pesticides found in the soil samples was due to previous uses of the compounds in these areas for agricultural purposes. Their absorption process on lands is relatively strong and consequently they will continue to be there for a long time. It was noted that lands near Shkumbini rivermouth (KS3), Semani rivermouth (KS6) and Vjosa rivermouth (KS 13) were most polluted stations. Pesticide use in these areas has been more frequent. Water of these rivers was used random for water irrigation. This fact affect on new arrival of pesticides from other areas and their concentration on these lands. Figure 2 shows the distribution of organochlorine pesticides, which is the same distribution of pesticides for all sampling stations, due to the same origin of pesticides in these samples. Distribution of organochlorine pesticides was built by higher levels of some individual pesticides. Higher levels were found for Methoxcychlor and Endrin keton because of previous uses for these pesticides in agricultural areas (Figure 3). For some soil samples were detected DDTs, Endosulphan alfa, Mirex and Dieldrin. Total of Lindane and its isomers were higher in the KS12 and KS13 soil samples with 1.9 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 processes. The profile of HCHs for all analyzed samples was: alpha-HCH > Lindan > beta-HCH > delta-HCH, which is mainly related to the physico-chemical properties of HCH isomers. HCH levels for all samples were lower than the allowed values in the soil based on Albanian and EU norms (Anonymous 1994, 1998, 2009; ISO 2002). Maximum of Heptachlors were found in KS13 soil sample with 6.0 ug/kg. Heptachlors were not detected or were detected in LOD levels for 65% of soil samples. Heptachlor could be used earlier in these areas. Heptachlors were below than permitted levels in all analyzed soil samples. Aldrines were found in 83% of soil samples taken from Myzeqeja area. Total of Aldrines in the soil samples was displayed at maximum value for KS6 area with 139.5 µg/kg. Aldrines distribution was the same for all samples due to their same origin. Endrin keton was found at the highest level for all samples followed by Dieldrin and Endrin. They are degradation product of Aldrine. Aldrine was not detected in all samples. Aldine could be used earlier in these areas. Aldrines were lower than permitted levels in soil samples for all studied areas except KS3, KS6 and KS7. DDTs were detected in 40% of soil samples taken in analysis. Total of DDTs was higher for KS6 sample with 113.2 ug/kg. DDT was the main compound followed by DDD and DDE. This profile could be connected with new arrivals of DDT for KS5, KS6 and KS7 stations. DDT's found concentrations were lower than permitted level for all analyzed soil samples except KS6 station. Endosulfanes were detected for 50% of soil samples. The higher concentrations of Endosulfanes were for KS13 soil sample with 129.6 ug/kg. Higher levels belong to the endosulfan alpha. Their levels were below permitted level for all samples. Methoxcychlor was found in higher concentrations for KS1

(183.4 ug/kg), KS2 (174.3 ug/kg), KS3 (158.4 ug/kg), KS5 (107.4 ug/kg) and KS4 (71.2 ug/kg). It wasn't detected for 40% of analyzed soil samples. Methoxcychlor may be still in use in these areas under a falsificated trade-mark. Its level was below permitted level for all samples except KS1, KS2, KS3 and KS5 samples. Mirex was detected for 60% of soil samples from Myzeqeja area. Its average was 9.7 ug/kg, the maximum was for KS3 sample with 25.1 ug/kg and the minimum for KS9, KS14, KS10 where Mirex wasn't detected. Its level was below permitted level for all samples.

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

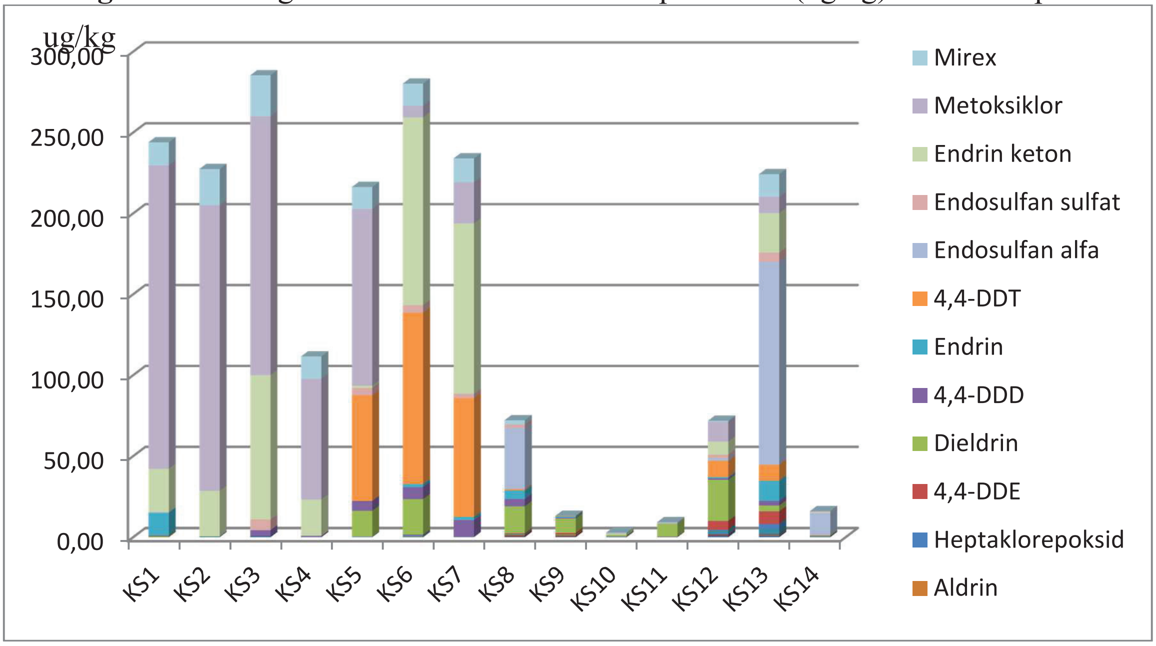


Figure 3. Distribution of chlorinated pesticides (ug/kg) in soil samples

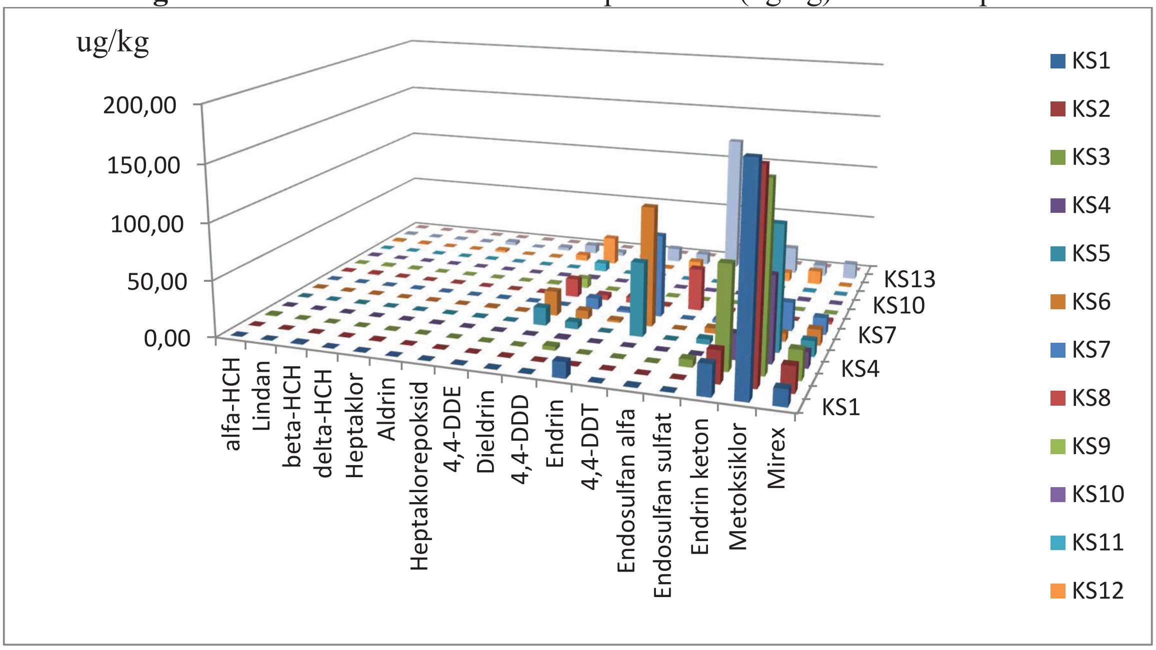
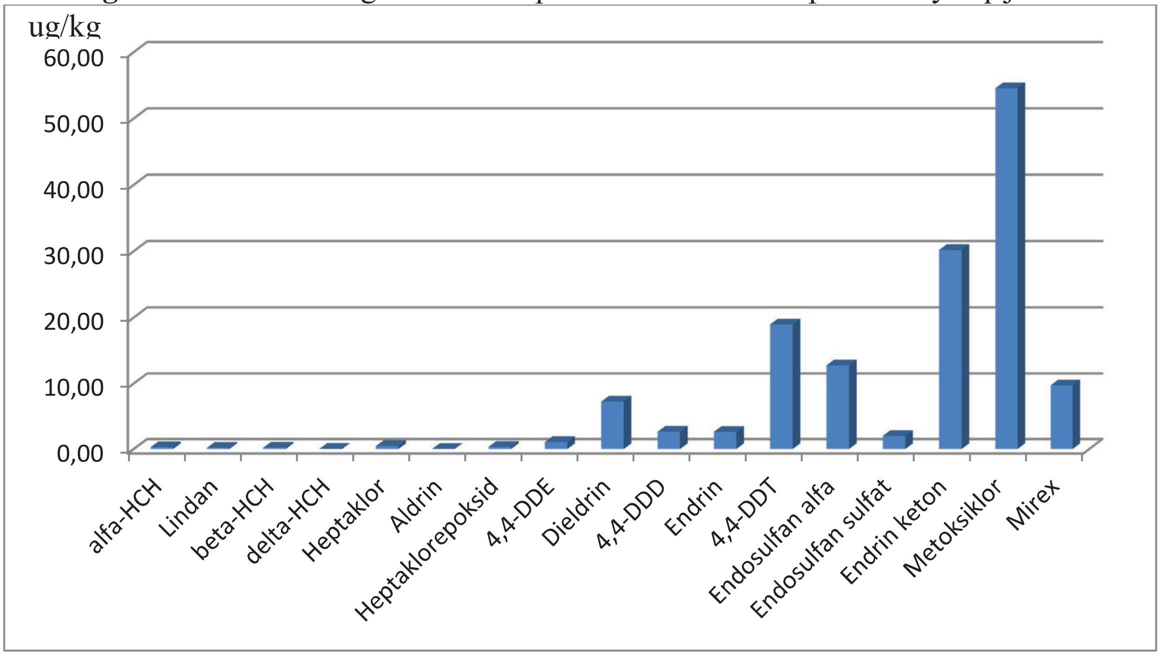


Figure 4. Profile of organochlorine pesticides in soil samples of Myzeqeja area



PCB markers in soil samples

Total of PCBmarkers on soil samples from the Myzeqeja area was given in Figure 5. PCBs were detected for all analyzed samples. Average of PCBs for all analyzed samples was 33.1 ug/kg. PCBs were found in higher level for soil samples taken in KS6 station with 84.7 µg/kg. Distribution of PCBs markers in soil samples from Myzeqeja field was the same because of their same origin (Figure 6). For around 50% of samples were detected presence of volatile PCBs and for other 50% of samples presence of heavy PCBs. Presence of heavy PCBs on these areas could be as result of accidental spillage from electrical transformer or others equipment, agricultural mechanic, mechanical businesses, etc. Volatile PCBs presence could be because of atmospheric deposition. Profile of PCB markers (Figure 7) was: PCB 138 > PCB 28 > PCB 153 > PCB 180 > PCB 118. PCB markers levels were below permitted level for all studied soil samples.

Figure 5. Total concentrations of PCBs in Myzeqeja soil samples

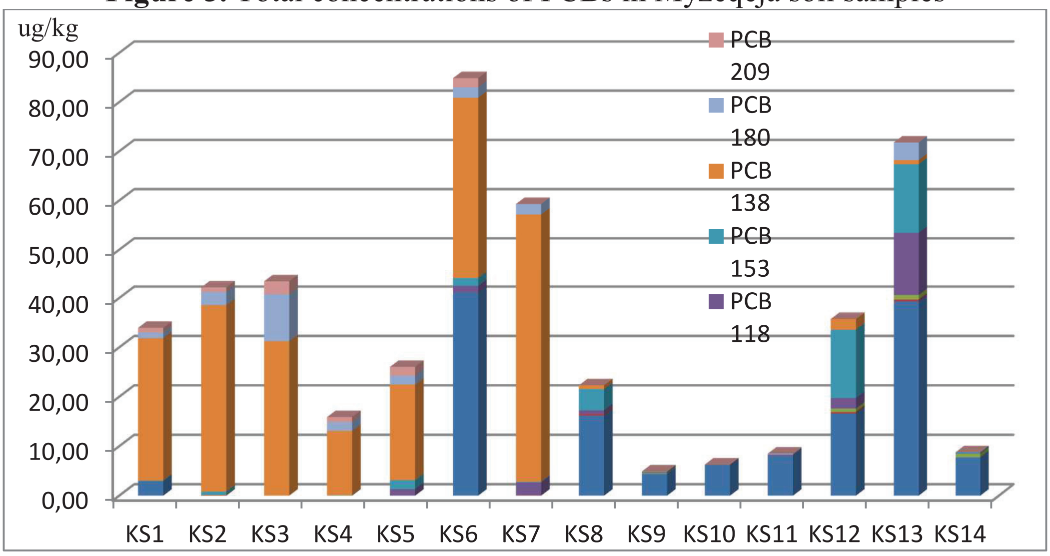


Figure 6. Distribution of PCBs in soil samples of Myzeqeja area

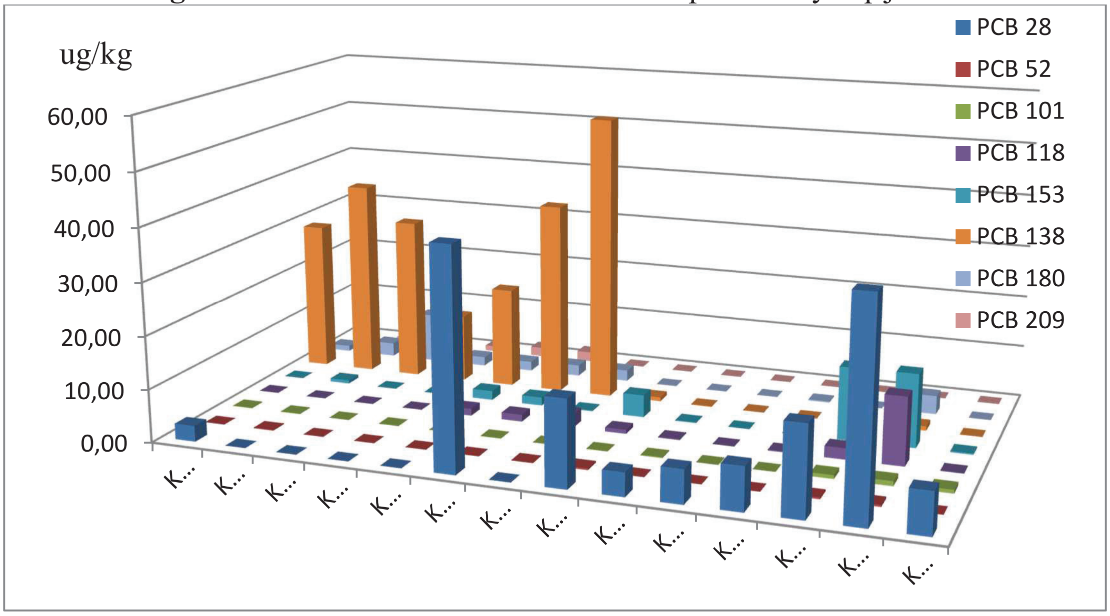
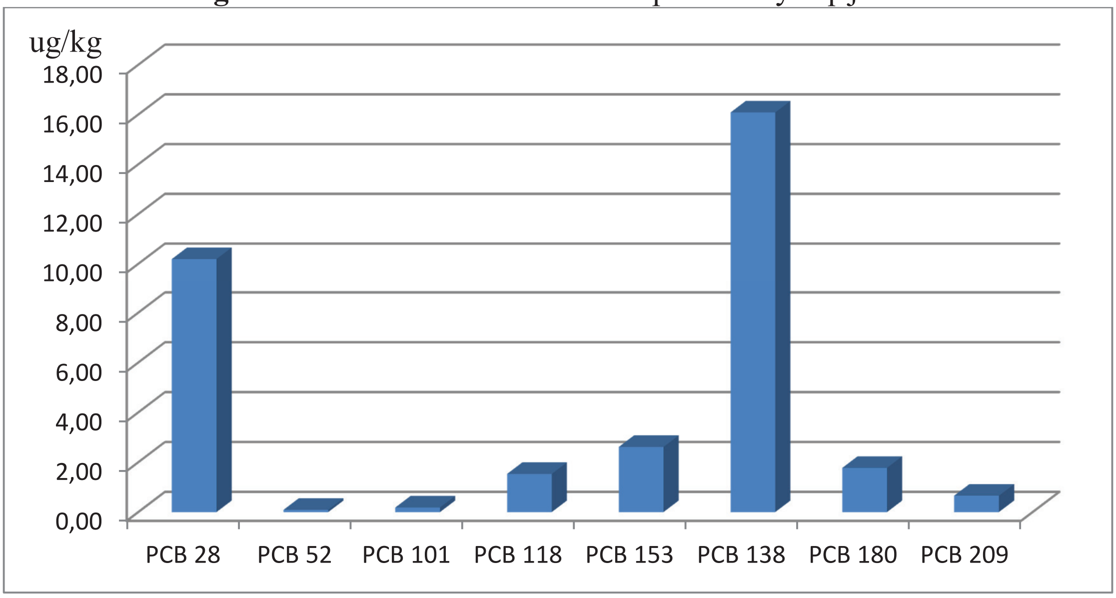


Figure 7. Profile of PCB in soil samples of Myzeqeja area



CONCLUSION

The objective of this study was evidence of organochlorine pesticides, their residues and PCB markers on soil samples from the Myzeqeja area. It is the large surface used and continues to be widely used for agricultural purposes. For extraction of organochlorine pesticides and PCBs in soil samples were used ultrasonic extraction technique assisted by n-hexane/dichloromethane as extracting solvents. The extracts were further purified by passing through a florisil column. Qualitative and quantitative determination was accomplished by the GC/ECD technique. This technique was suggested by literature. Organochlorine pesticides and their residues were found in all soil samples taken from Myzeqeja area. Their total was higher for the soil samples taken in Shkumbini, Semani and Vjosa rivermouths. Presence of chlororganic pesticides found in the soil samples was due to previous uses of the compounds in these areas for agricultural purposes. Their absorption process on lands is relatively strong and consequently they will continue to be there for a long time. Higher levels were found for Endrin keton and Methoxychlor 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 norms. Exception was for Methoxcychlor in some soil samples. It may be still in use in these areas under a falsificated trade-mark. PCB markers were found for all analyzed soil samples. Distribution of PCBs markers was built by volatile PCBs and heavy PCBs. PCB 138 was found in higher level in all analyzed soil samples. Presence of heavy PCBs on these areas could be a result of accidental spillage from electrical transformer or others equipment, agricultural mechanic, mechanical businesses, etc. Volatile PCBs presence could be because of atmospheric deposition. PCB markers levels were below permitted level for all soil samples.

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