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EVALUATION OF ORGANOCHLORINE PESTICIDES AND PCB IN SURFACE WATERS OF MYZEQEJA AREA, ALBANIA

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Abstract: Myzeqeja is the main agricultural area in Albania. It is located in South-West of central Albania. Organochlorine pesticides such as DDT, Lindane, Endosulfanes, Aldrines, etc. were used in this area for many years (from 1945 to 1992) firstly for fighting malaria vectors (mosquitos) and after that for agricultural purposes. Also, this area is affected from industrial activity (oil extraction and processing industry) and urban pollution. In this study data about concentrations of organochlorine pesticides and PCBs (polychlorinated biphenyls) in surface waters of Myzeqeja area are presented. Organochlorine pollutants are very stable compounds. They can be found in environment for many years after their application. Water irrigation and rainfall realize the transportation of organic pollutants from soil to underground and surface waters. Myzeqeja water stations were selected for six streams, five channels and Semani River (five stations). Water samples were sampled in December 2017. For isolation of organochlorine pesticides and PCBs liquid-liquid extraction assisted with n-Hexane as extraction solvent was used. The simultaneous analysis of organochlorine pollutants in water samples was performed by gas chromatography technique using electron capture detector (GC/ECD). Rtx-5 capillary column (30 m x 0.33 mm x 0.25 um) was used for separation of 17 organochlorine pesticides according to EPA 8081A and 7 PCB markers. Relatively high concentrations of organochlorine pesticides were detected in water samples of Myzeqeja area. The presence of pesticides shows impact of previous use of pesticides in this area. PCB volatile were found in higher level because of atmospheric deposition. Levels of organochlorine pollutants in surface water samples of Myzeqeja region were higher than reported values for other areas of Albania because elevated agricultural and industrial activity in this area.

INTRODUCTION

In this study one of the most important agricultural areas of Albania was consider. Myzeqeja fields lies in the South-West of central Albania between Shkumbini and Vjosa rivers. It is the main agricultural area of Albania, encopassing 1350 km^2. Its large spaces were used and continue to be widely used for agricultural purposes (Como *et al,* 2013). The fields that lie in these areas are very fertile, especially for cereals 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 their 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 1990s. PCBs 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 of the application site. Generally these compounds are difficult to degrade. In the soil or sediment the speed of 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 exces¬sive 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. Input of these contaminants into the agricultural areas (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). Leaching occurs downward, upward or sideways. 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). These pollutants were reported in many matrices (soil, water, sediment, biota, food) because of their ability to spread out far away from their application places (Stoykova *et al* 2015). Many chromatographic methods were developed in recent years for detecting all possible and known organic pollutants in soil samples. Determination of chlorinated pollutants in surface water samples of Myzeqeja area was realized by using capillary GC/ECD and GC/MS methods.

MATERIAL AND METHODS

Sampling of water samples in Myzeqeja area

Myzeqeja water stations were selected for six streams, five channels and Semani River (five stations). Water samples were sampled in December 2017. The sampling stations are presented in Figure 1. 2 L of water were taken from each station in Teflon bottles. The sampling method was based on UNEP/MED Wg. 128/2, 1997. Water samples were tranported and conserved at +4^{o}C prior to their analyze.

Fig. 1. Sampling stations of water samples in Myzeqeja sampling stations

GC/ECD analyze of organochlorine pesticides and PCB markers in water samples

Liquid-liquid extraction was used for the extraction of organochlorine pesticide residues and polychlorinated biphenyls from water samples in Myzeqeja area. 1 L of water, 10 µl PCB-29 as internal standard and 20 mL n-hexane as extracting solvent were added in a separatory funnel. After extraction the organic phase was dried with 5 g anhidrous Na_2SO_4 for water removing. A Florisil column was used for the sample clean-up. After the concentration to 1 ml, the samples were injected in GC/ECD HP 6890 Series II. Procedural blanks were regularly performed and all results presented are corrected for blank levels. Rtx-5 capillary column (30 m x 0.33 mm x 0.25 µm) was used to isolate and determine simultaneously organochlorine pesticides (based on EPA 8081A method) and 7 PCB markers. EPA 8081A Mixture and 7 PCB markers were used for qualitative and quantitative analysis of chlorinated pollutants. Splitless injection was made for 2 µl sample. Injector temperature was held at 280^{o}C. ECD temperature was held at 300°C. Helium was used as carrier gas with 1 ml/min. Nitrogen was used as make-up gas with 25 ml/min. Quantification of chlorinated pollutants was based on external standards. Five points of calibration were selected for chlorinated pollutants to concentrations 10, 20, 50, 100 and 250 ng/L (EU, 2007; Konstantinou *et al,* 2006; Lekkas *et al,* 2004; Vryzas *et al,* 2009).

RESULTS AND DISCUSSION

Analyze of organochlorine pesticides, their residues and PCB was realized in surface water samples of Myzeqeja area. Pesticides were used in this area for many years for fighting malaria vectors and for agricultural purposes. Organochlorine pollutants are very stable compounds while can be found in environment for many years after their application.

Figure 2 shows the total of organochlorine pesticides in water samples of Myzeqeja area. The higher concentration was for Channel 3 in Patos with 97.3 ng/L. For the 60% of the study stations organochlorine pesticides levels were lower than 5 ng/L. The average level of organochlorine pesticides and their residues was 19.89 ng/L. The found level could be mostly because of previous use of pesticides in this area. The distribution of organochlorine pesticides (**Figure 2**) in water samples 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**) were: Endosulfanes > Aldrines > DDTs > HCHs > Mirex. Profile of pesticides was connected with individual levels in different sampling stations. HCHs were found in low level almost for all samples. Average of HCHs was 2.4 ng/L. This could be because of their previous use and HCH stability. Lindane was found in 35% of water samples in low level. Profiles of HCHs were: beta-HCH Lindane > alfa-HCH > delta-HCH. Total of HCHs were lower than permitted level (20 ng/L) for surface waters conform Directive 2008/105/EC. Levels of Heptachlor and Heptachlorepoxide were in range 0.05 ng/L (LOD) to 7.1 ng/L. The higher levels were found for its degradation products (heptachlor epoxides). Total of Heptachlors were lower than permitted level (10 ng/L) for surface waters conform Directive 2008/105/EC. Aldrines levels were from 0.05 (LOD) ng/L to 26.8 ng/L. Aldrin was found in low level almost for all samples. Profile of Aldrines was: Dieldrin > Endrin keton > Endrin > Aldrin. Total of Aldrins were lower than permitted level (10 ng/L) for surface waters conform Directive 2008/105/EC except Marinza 1, Channel 3 Patos and Semani 2. DDT levels were from 0.05 ng/L (LOD) to 16.4 ng/L. Higher levels were found for DDT in three stations. DDT was found in 40% of water samples. DDT could be found because of their previous use in agricultural areas or because a punctual source. Profile of DDTs was: DDT > DDD > DDE. Total of DDTs were lower than permitted level (25 ng/L); DDT concentration was lower than permited level (10 ng/L) for surface waters conform Directive 2008/105/EC. Endosulfanes levels were found from 0.05 ng/L (LOD) to 39.5 ng/L. Endosulfanes were detected for 42% of analyzed samples. Endosulfan alfa was found higher than Endosulfan sulfat. Total of Endosulfanes were lower than permitted level (5 ng/L) for surface waters conform Directive 2008/105/EC except Marinza 1, Patos 3 and Roskovec 1 samples. Mirex was found only in 2 samples. Concentration of Mirex was higher in Patosi 3 channel. This fact could be because of new arrivals from water irrigation or a punctual source. Organochlorine pesticides are not used anymore right after the 90' in Albania. These data shown the presence for pesticide residues in water samples because of their previous use. The found levels for organochlorinated pesticides in surface waters of Myzeqeja area were comparable/higher than reported levels for other ecosystems in Albania.

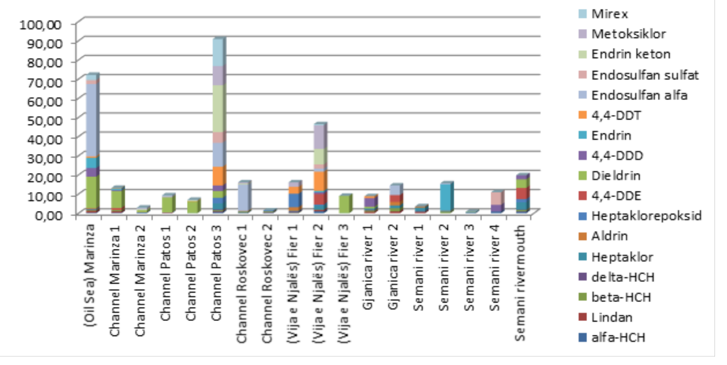

Fig. 2. Total of organochlorine pesticides in surface water samples of Myzeqeja area

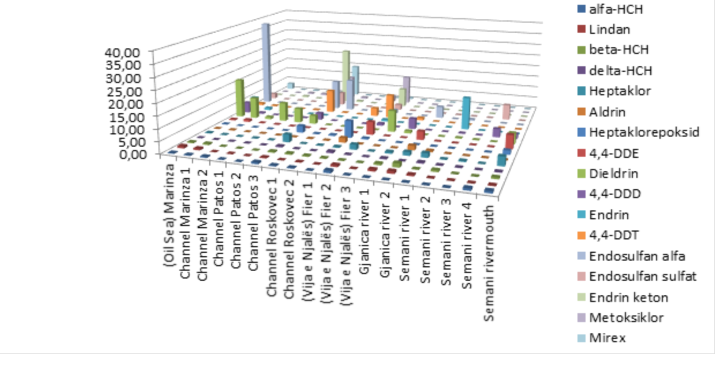

Fig. 3. Distribution of organochlorine pesticides in surface water samples of Myzeqeja area

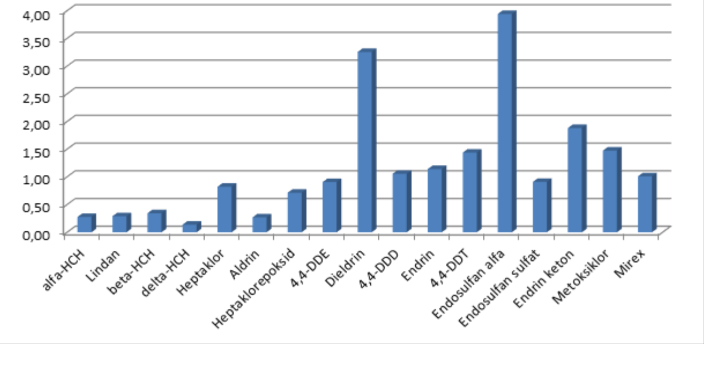

Fig. 4. Profile of organochlorine pesticides in surface water samples of Myzeqeja area

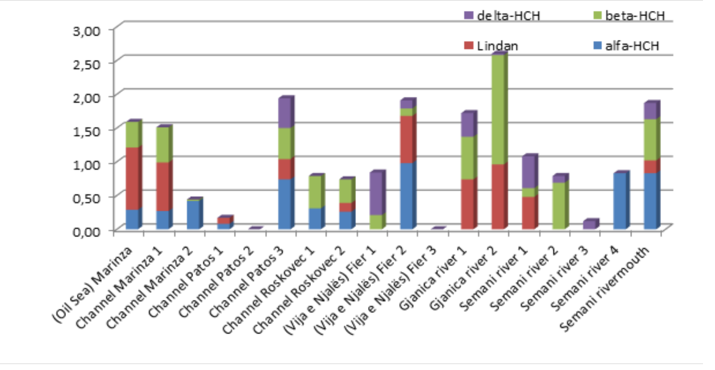

Fig. 5. HCHs in surface water samples of Myzeqeja area

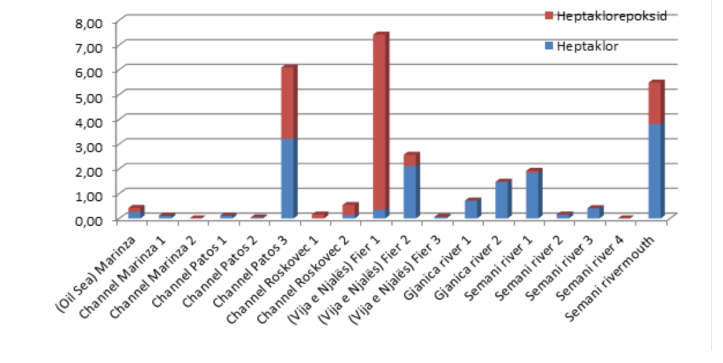

Fig. 6. Heptachlors in surface water samples of Myzeqeja area

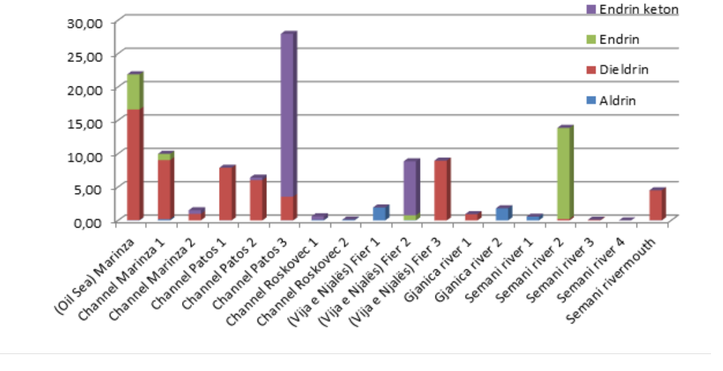

Fig. 7. Aldrins in surface water samples of Myzeqeja area

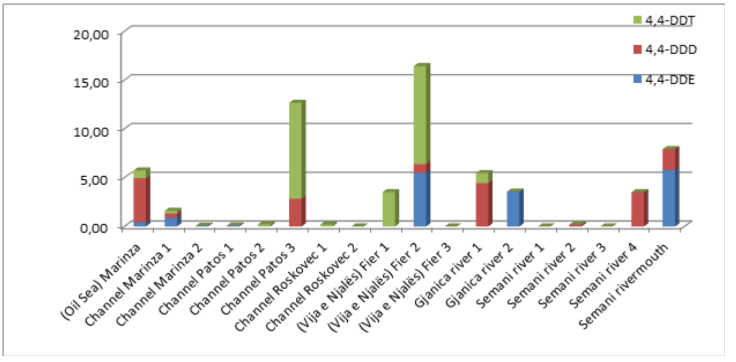

Fig. 8. DDTs in surface water samples of Myzeqeja area

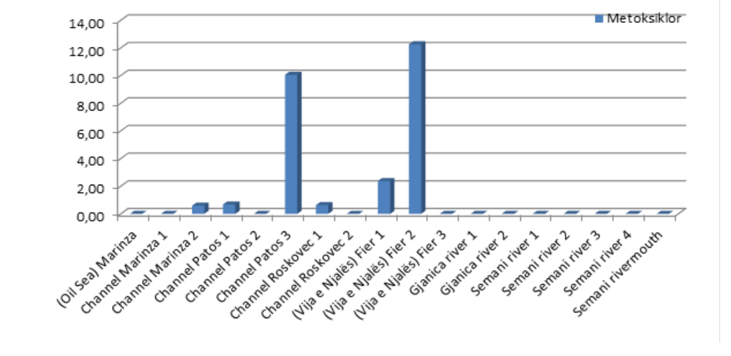

Fig. 9. .Methoxychlor in surface water samples of Myzeqeja area

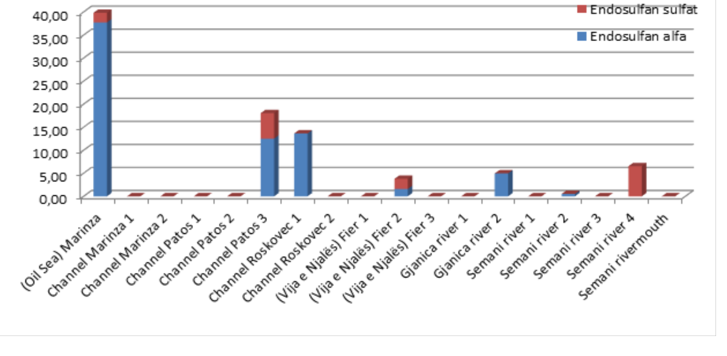

Fig. 10. Endosulfanes in surface water samples of Myzeqeja area

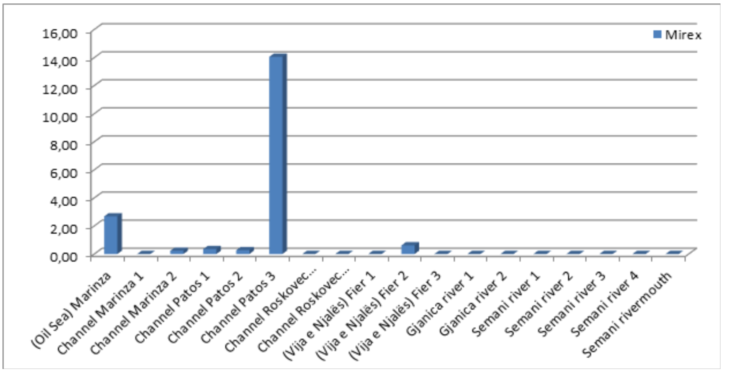

Fig. 11. Mirex in surface water samples of Myzeqeja area

Figure 5 shows the total of PCB markers in water samples of Myzeqeja area. PCB markers were found for all analyzed samples. Their average was 17.74 ng/L. The higher level was for Channel 3 Patos station with 44.9 ng/L. Distributions of PCBs (**Figure 6**) was almost the same for all samples. This could be because of the same origin of pollution for PCBs in water of Myzeqeja area. PCB 28 was found in higher level almost for all samples. Its origin could be because of atmospheric deposition (Nuro et al, 2014). PCB 138 was found in higher level for three stations of Semani River. PCB 138 can be classified as heavy congeners of PCBs. Its origin could be terrestrial. Profiles of PCBs (**Figure 7**) were: PCB 28 > PCB 138 > PCB 180 > PCB 118 > PCB 101. The levels of PCBs in waters of Myzeqeja area were comparable than reported levels for other water ecosystems in Albania (Como *et al,* 2010; Neziri *et al,* 2013; Nuro *et al,* 2014) Discharging of wastes from industries and mechanical businesses could affect the found level and their profile.

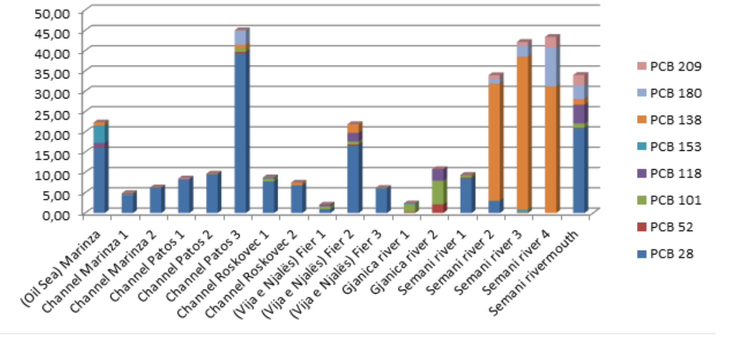

Fig. 12. PCB markers in surface water samples of Myzeqeja area

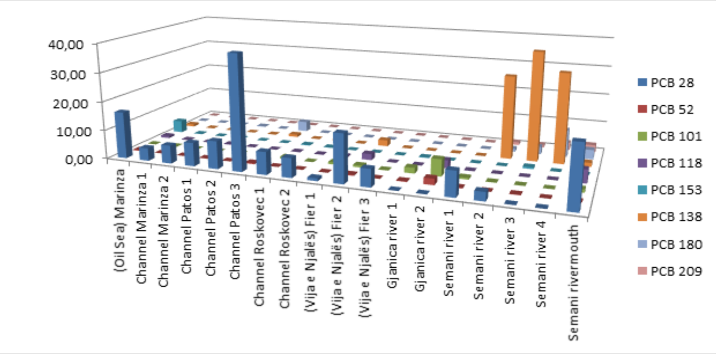

Fig. 13. Distribution of PCB markers in surface water samples of Myzeqeja ar*ea*

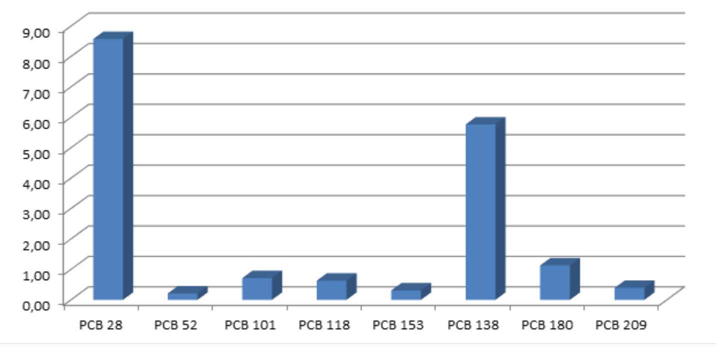

Fig. 14. Profile of PCB markers in surface water samples of Myzeqeja area

CONCLUSIONS

This study presents first data on organochlorine pesticides, their residues and polychlorinated biphenyls in surface water samples of Myzeqeja area. Myzeqeja water stations were selected for six streams, five channels and Semani River (five stations). Water samples were sampled in December 2017. Determination of organochlorine pollutants in water samples was performed by GC/ECD technique suggested by literature. Organochlorinated pesticides and PCB markers were detected for all analyzed samples. This could be because of punctual sources or new arrivals from different effluents and drainage canals of agricultural areas. Profile of organochlorine pesticides was: Endosulfanes > Aldrines > DDTs > HCHs > Mirex. Profile of pesticides was connected with individual levels in different sampling stations. These data shows presence for pesticide residues in water samples because of their previous use. PCB 28 was found in higher level almost for all samples. Its origin could be because of atmospheric deposition. PCB 138 was found in higher level for three stations of Semani River. Its origin could be terrestrial. Individual pollutants were found in lower than permitted level for surface waters conform Directive 2008/105/EC except some samples for some individual pesticides. This fact could be because of new arrivals from water irrigation or a punctual source. The found levels for organochlorinated pesticides and PCBs in surface waters of Myzeqeja area were comparable/higher than reported levels for other ecosystems in Albania.

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 (A.N.) and all the other authors (E.M. and B.M.) contributed equally to the discussions of the text.

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