



ORIGINAL SCIENTIFIC PAPER

Analysis of organic pollutants in water samples of White Drin, Black Drin and Fierza Reservoir

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Abstract

This study presented data about concentrations of some organic pollutants in Albanian part of Black Drin (BD), White Drin (WD) and Fierza Reservoir (FR). Thirteen stations were analyzed in this study. Sampling of water was realized in May 2017. Drin River presents important aquatic area in Albania. For all water samples were analyzed organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), benzene, toluene, ethylbenzene and o-, m-, p-xylenes (BTEX) and polyromantic hydrocarbons (PAH). Organochlorinated pesticides and PCBs were found in higher level for Fierza Reservoir stations. Their concentrations for Black and White Drin samples were 5-10 times lower.

1. INTRODUCTION

The Drin River is the longest river in Albania with a total length of 335 km of which 285 km flows in Albania. It has two distributaries, one going directly into the Adriatic Sea, the other one into the Bojana River. The Drin starts at the confluence of its two headwaters. The Black Drin flows out from the Lake Ohrid in Struga and runs through the Republic of Macedonia and Albania. The White Drin originates from the Zhleb Mountain, in the Dukagjin region of Kosovo, and runs from there through to Albania. From Kukës, the Drin flows through northern Albania, first flowing through the Hasi area to the north, passing through the towns of Spas, Msi and Fierze. At Vau Dejes it enters the low Shkodra Field and splits into two arms. One empties into the Bay of Drin into the Adriatic Sea southwest of the city of Lezha. The other empties into the Bojana River. Even though being a shorter branch by 15 km, the section that reaches the Bojana is called Great Drin. The Great Drin is very wide and brings a huge amount of water (320 m³/s), but being short, some maps indicate it as a lake. After Vau i Dejës, the longer branch continues to the south, passing through Bushat, Gjader, Lezhë and Medes. In the south of Lezha it enters the low and flooded littoral area and flowing through the marshes it finally reaches the Adriatic. The Drin and its surrounding mountainous areas have a great variety of flora and fauna. Recently many fish species have been introduced such as the zander (pike-perch) of northern Europe which is a predator of the native fish population. The Drin is extremely important for the Albanian economy, especially for its electrical production. Four hydropower facilities produce most of Albania's electricity. The artificial Lake Fierza created by the dam at Fierzë is the largest artificial lake in Albania with its surface of 73 km². The

second largest artificial lake, Koman, is also built on this river [1].

Organic pollutants, in particularly hydrocarbons and chlorinated pollutants, such as; BTEX, PAH, organochlorine pesticides, PCBs, Dioxins, etc, have been reported in many ecosystems. Before years 90' organochlorine pesticides were widely used in Albania for agricultural purposes. Organochlorine pesticides as: DDT, Lindane, HCB, Aldrins and Heptachlors were widely used. After years 90' the scale of pesticides used in agriculture has decreased, due to the change of land use. The expired pesticides by the former, has generated. These pesticides have been damaged due to the inappropriate conditions of conservation and storage. Commercial PCB mixtures were used after 90' in Albania, mainly, either as dielectric fluids in capacitors and transformers or as heat exchange fluids. The same properties which make PCBs interesting for industrial use cause adverse effects on reproduction, development, and endocrine function [2]. Volatile PCB levels were reported in many studies realized in different Albanian ecosystems [3]. Probably, atmospheric deposition is considered to be the main factor of PCB pollution in Albania. Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) are also major constituents of gasoline. Exhaust emissions from vehicles, as well as evaporative losses from gasoline stations and vehicles, are major sources of BTEX [4] that are released in the atmosphere. Because of their ability to persist in the atmosphere from days to weeks, and because they will, in part, dissolve into water, BTEX are expected to be present in air, waters, soil and sediments. The volatilization of BTEX occurs slowly from ponds and lakes, as well as from slow-moving and deep streams and rivers. These compounds are released into

the environment during manufacture, transportation, usage, and disposal, leakage in underground storage tanks and pipelines in gasoline industry, and through leachate from landfills. Polyaromatic hydrocarbons are a large group of compounds with a molecular structure that includes two or more fused aromatic rings. They are widely distributed in the environment as a result of the incomplete combustion of organic materials, both of natural (e.g. forest fires) and anthropogenic sources (e.g. motor vehicles, industrial processes,). The spillage of fossil fuel can be a significant source of contamination, as well as the leaching from pipes [5,6].

2. MATERIALS AND METHOD

2.1. Sampling of water samples in Black Drin, White Drin and Fierza Reservoir

Thirteen stations were analyzed in this study. Sampling of water was realized in May 2017. Four water samples were taken in different stations of Black Drin, four samples in White Drin and five water samples in Fierza Reservoir. The sampling sites for water samples in BD, WD and FR are presented in Figure 1. 1.5 L of water were taken from each station in teflon bottles. Water samples were transported and conserved in +4°C prior analysis.

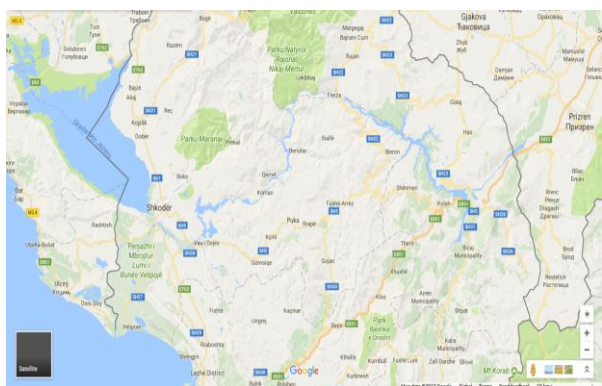


Figure 1. The map of sampling of water samples in Black Drin, White Drin and Fierza Reservoir

2.2. Preparation of water samples for OCP and PCB analyzes

Chlorinated pesticides and PCBs in water samples were extracted using liquid-liquid extraction (LLE) assisted with Hexane solvent. 1 L of water and 20 ml Hexane as extract solvent was added in a separatory funnel. After shaking organic phase was collected in a beaker when was added 5 g Na_2SO_4 anhydrous for removing water. After concentration in 1 ml Hexane, the samples were injected directly to GC/ECD for simultaneous of chlorinated pesticides and PCBs [7,8].

2.3. Preparation of samples for BTEX analyzes

Headspace solid phase micro extraction (HS-SPME) technique was used to trace BTEX in sediment and water samples. 5.0 mL of water sample was placed in a 10 mL headspace vial (5 replicate vials for each sample) to adsorb BTEX. The vials were placed in a heating block for 45 min at 50°C. Extraction of volatile compounds was done using a 100 μm Polydimethylsiloxane fibre in a SPME manual holder [9,10]. Direct injection in HS mode was performed in 280°C in a PTV injector.

2.4. Preparation of water samples for PAH analyzes

PAH in water samples were extracted using liquid-liquid extraction (LLE) assisted with Dichloromethane solvent. 1 L of water and 20 ml Dichloromethane as extract solvent was added in a separatory funnel. After shaking organic phase was collected in a beaker when was added 5 g Na_2SO_4 anhydrous for removing water. After concentration in 1 ml Dichloromethane, the samples were injected directly to GC/FID [5].

2.5. Apparatus and chromatography

Gas chromatographic analyses were realized with a Varian 450 GC instrument equipped with two PTV injectors and a flame ionization detector and with a 63Ni electron-capture detector. The column used for isolation of chlorinated pesticides and PCBs (simultaneously) was Rtx-5 (30mx x 0.33mm x 0.25 μm) capillary column. The injector and detector temperatures were set at 280°C and 320°C, respectively. Carrier gas was He at 1 ml/min and make-up gas was nitrogen 25 ml/min. The initial oven temperature was kept at 60°C for 4min, which was increased, to 200°C at 20°C/min, held for 7 min, and then increased to 280°C at 40°C/min for 20min. The temperature was finally increased to 300°C, at 100°C/min, held for 7min. Injection volume was 2 μl , when splitless injections were made [7,8,11]. VF-1ms capillary column (30 m x 0.33 mm x 0.25 μm) was used to isolate and determine BTEX and PAH compounds in separately injections. A temperature for FID was held at 280°C. Nitrogen was used as carrier and make-up gas for both analyses. Hydrogen and air were flame detector gases with 30 ml/min and 300 ml/min, respectively. Injections of BTEX were done in injector PTV directly by using Head-Space mode (280°C for 20 seconds) of Polydimethyl Siloxane fiber. 1 μl extract in Dichloromethane (extracting solvent) were injected for PAH analyses. Quantification of BTEX and PAH was based on external standards [6,9,10].

3. RESULTS AND DISCUSSION

Analysis of organic pollutants in water samples and the Black Drin, White Drin and Fierza Reservoir was realized in May 2017. Chlorinated organic pollutants (chlorinated pesticides, their residues and PCB) were studied using capillary GC/ECD. BTEX and PAH qualitative and quantitative analyze was conducted with capillary column with GC/FID technique. OCPs, PCBs and PAH were extracted using liquid-liquid extraction. Extraction and injection of BTEX were performed using Head Space mode. Figure 2 shows the total of organochlorine pesticides in water samples of Black Drin, White Drin and Fierza Reservoir, May 2017. The organochlorine pesticides detected were HCB, HCHs (alpha-, beta-, gama- and delta-isomers) and the DDT-related chemicals (p,p-DDE, p,p-DDD, p,p-DDT), Aldrines (Aldrine, Dieldrine, Endrine) and Heptachlors. The highest level was for FR2 station with 50.3ng/L. The lower levels were for BD1, BD2, BD4, WD1 and FR5 samples. Their concentrations were lower than 2 ng/L. The average levels of organochlorine pesticides for all stations were: BD with 0.7 ng/L; WD with 10.24 ng/L and FR with 20.01 ng/L. Found levels were lower than reported levels for other rivers of Albania [3]. This is due to mountainous terrain that favors the rapid movement of water and small agricultural areas that lie in the basins of these rivers. Higher levels in FR were because of concentration factor for the pollutants in this area. The distribution of organochlorine pesticide levels in BD, WD and FR water samples are shown in Figure 3. The found levels were almost the same for all studied stations. This is connected with the same origin of pollution for BD, WD and FR. In some stations were shown higher levels for individual pesticides. These higher concentrations could be

because of punctual pollution for example by accidental, new arrivals from estuaries or rainfall of agricultural areas near the rivers. Figure 3 shows the profile of organochlorine pesticides in water samples of the BD, WD and FR. Σ Endosulfanes > Mirex > Σ Aldrin > Σ DDT > Σ HCH was the found profile of pesticides in studied water samples. Note that found profile was associated with individual levels for studied pesticides. Endosulfan I was found in higher levels in FR2, BD4 and BD2. This could be because of recent use for this pesticide in areas near the sampling stations or in BD basin. Mirex was found in higher levels in one samples of White Drin and two samples of Fierza Reservoir. This could be because of recent use for this pesticide in agricultural areas near White Drin River. These pesticides can be in use under false commercial names. For other pesticides was shown in higher level their metabolites such as Heptachlor epoxides, DDT metabolites, Lindane isomers and Oxcychlordane. DDT was found in 8% of water samples. Profiles of DDTs were: DDD > DDE > DDT. Lindane wasn't the most found HCH. HCHs profiles were: Alfa-HCH > Lindan > beta-HCH > delta-HCH. This could be because of previous uses of these compounds for agricultural purposes but also with the chemistry of each individual studied pollutant (mainly with the stability and solubility of pesticides and their residues in water samples).

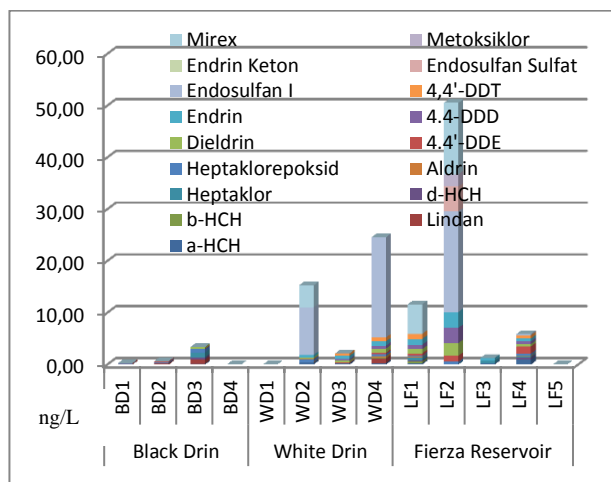


Figure 1. Total of organochlorine pesticides in water samples of BD, WD and FR – May 2017

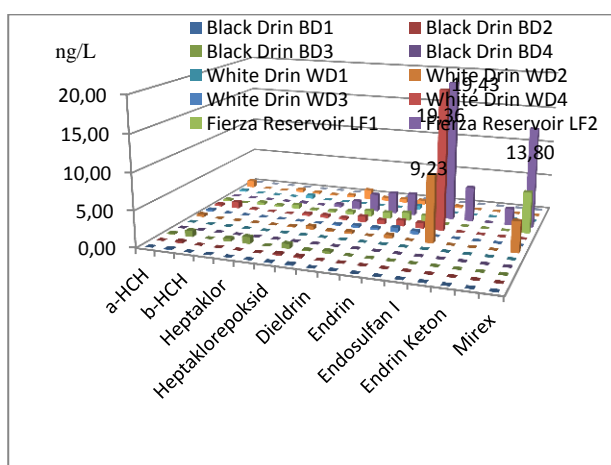


Figure 3. Total of organochlorine pesticides in analyzed water samples

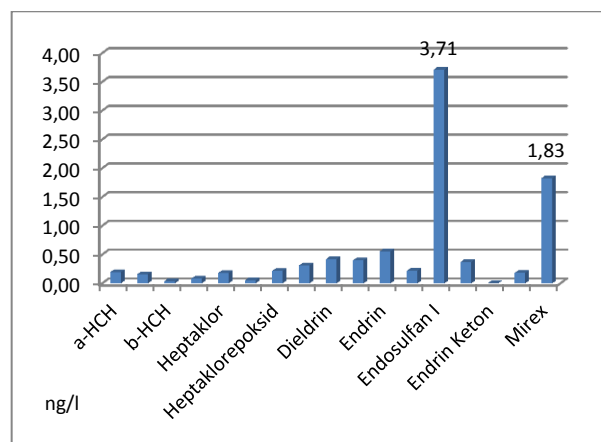


Figure 4. Profile of organochlorine pesticides in water samples

Figure 5 shows the total of PCBs in water samples of Black Drin, White Drin and Fierza Reservoir analyzed in May 2017. Analyzes of PCBs was based on the determination of the seven PCB markers (IUPAC Nr. 28, 52, 101, 118, 138, 153 and 180). The highest levels were found for BD station with 25.9 ng/L. PCBs weren't detected in BD1, BD2, BD4, WD1, FR3 and FR5 stations. Total of PCBs were in the same range with total of organochlorinated pesticides because their common in chemical and physical properties. The average levels of PCBs for BD stations were 1.15 ng/L; for WD stations were 9.46 ng/L and for FR stations were 8.23 ng/L Figure 6 shown distribution of PCBs in BD, WD and FR stations. PCBs distributions were the same for all stations because of their same origin. Exception was shown for some stations (WD3, WD4, FR2 and FR4) where individual of PCBs were in higher levels. Figure 7 shows the profile of PCBs in water samples of the BD, WD and FR. Volatile PCBs (PCB 28) were found more than other PCB markers in all stations. The origin of PCBs in these ecosystems is mainly because of atmospheric deposition in rivers basin. PCB 209 and 153 were also found in higher levels compare with other congeners. This is mainly associated with the direct discharges of waste waters in BD, WD and FR by many mechanical businesses.

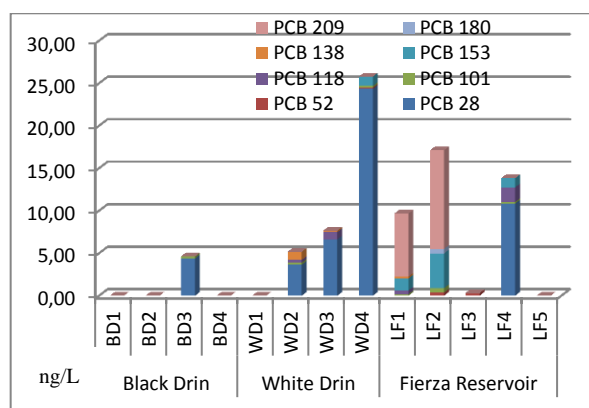


Figure 5. Total of PCB in water samples of BD, WD and FR – May 2017

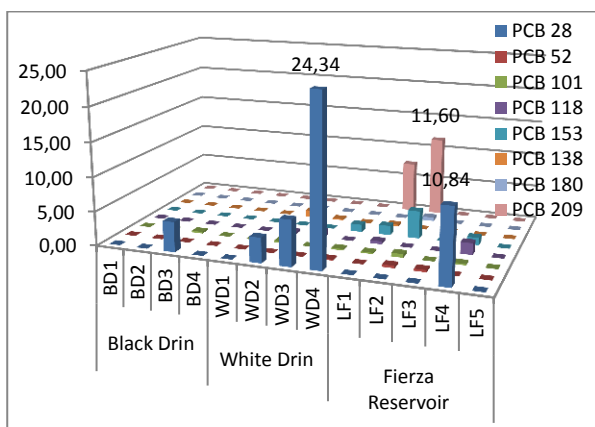


Figure 6. Total of PCBs in water samples

Benzene, Toluene, o-Xylene, m-Xylene, p-Xylene and Ethylbenzene (BTEX) were studied with HS-SPME followed by GC/FID in water samples. Total of BTEX in water samples for each of studied stations of Black Drin, White Drin and Fierza Reservoir was given in Figure 8. BD1 and BD2 stations have the maximum level with 50.63 ug/L and the minimum was for the 60% of stations where BTEX weren't detected. Average levels of BTEX in BD stations were 28.25 ug/L; in WD stations were 1.54 ug/L and in FR the average levels were 6.24 ug/L. Figure 9 shows the distribution of BTEX in BD, WD and FR samples. Distributions of BTEX were the same for all stations except BD1, BD2 and BD3 where Benzene and Toluene were found in higher levels. Figure 10 shows the profile of BTEX in water samples of the BD, WD and FR in May 2017. Benzene was found higher than other BTEX. After that were Toluene, Xylenes and the last was Ethylbenzene. The origin of BTEX in these ecosystems is mainly because of automobilist transport and oil pumps near the rivers. Discharges of the waste water in both rivers by many mechanical businesses could be other factor.

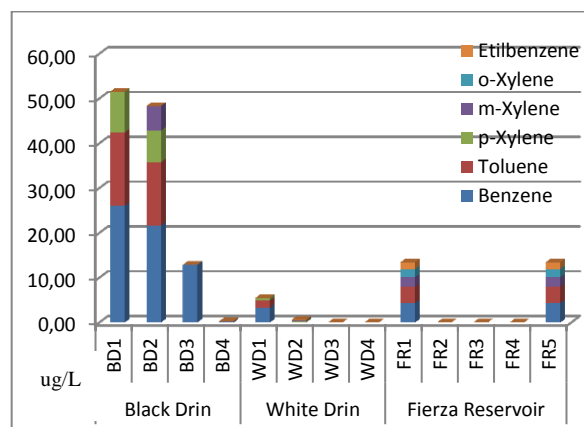


Figure 8. Total of BTEX in water samples

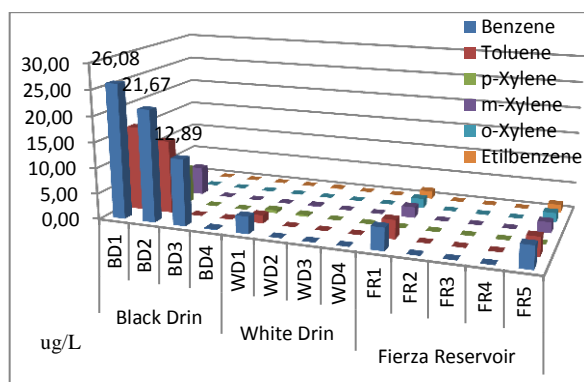


Figure 9. Total of BTEX in water samples of BD, WD and FR – May 2017

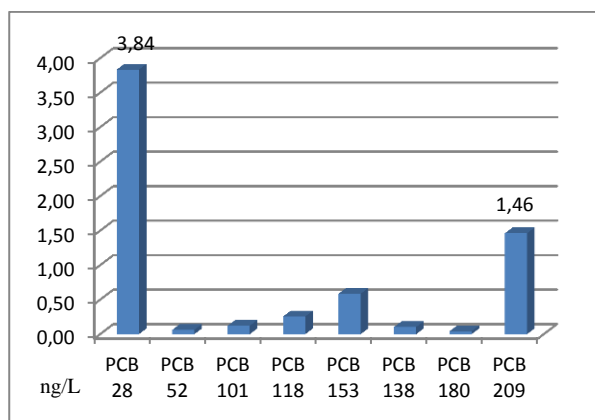


Figure 7. Profile of PCBs in analyzed water samples

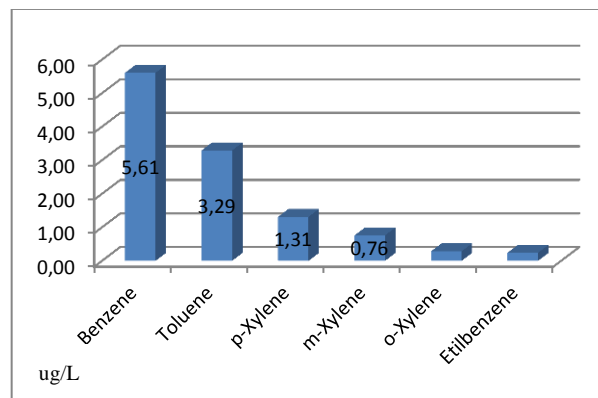


Figure 10. Profile of BTEX in water samples of BD, WD and FR – May 2017

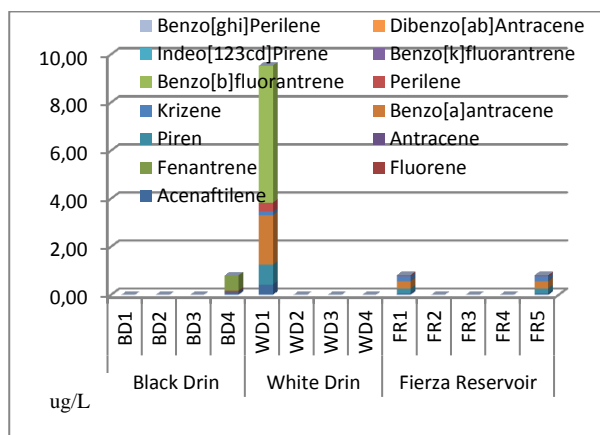


Figure 11. Total of PAHs in water samples

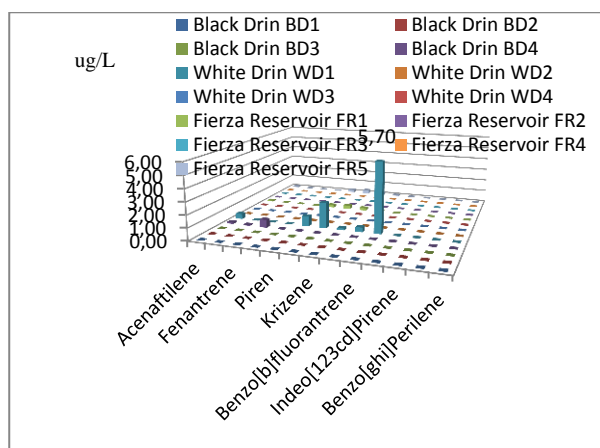


Figure 12. Total of PAHs in water samples

Acenaphtalene, Fluorene, Phenanthrene, Anthracene, Pyrene, Benzo[a]Anthracene, Cryzene, Benzo[b]Fluoranthrene, Benzo[k] Fluoranthrene, Benzo[a]Pyrene, Dibenzo[a,h] Anthracene, Indeo[1,2,3,-cd]Pyrene and Benzo[g,h,i]Perilene were PAH analyzed by using GC/FID technique. Total of PAHs in water samples of Black Drin, White Drin and Fierza Reservoir was shown in Figure 11. Stations WD1 has the maximum level with 9.4 ug/L while the minimum was for 75% of stations where PAHs weren't detected. For all samples were observed presence of these pollutants almost in the limit of detection level except Benzo[b]Fluoranthrene in WD1 station. Profile of PAHs in water samples of BD, WD and FR were shown in Figure 13. Profile of PAHs in BD, WD and FR were: Benzo[b]fluorantren > Benzo[a]anthracene > Pyrene > Acenaphtalene > Phenanthrene > Cryzene > Anthracene. Other PAHs for both rivers were not detected or were less than the limit of detection of GC/FID technique. Levels and profile of PAHs in BD, WD and FR is associated with direct discharging of pumps oil near this area, car servicing, urban waters and automobile transport.

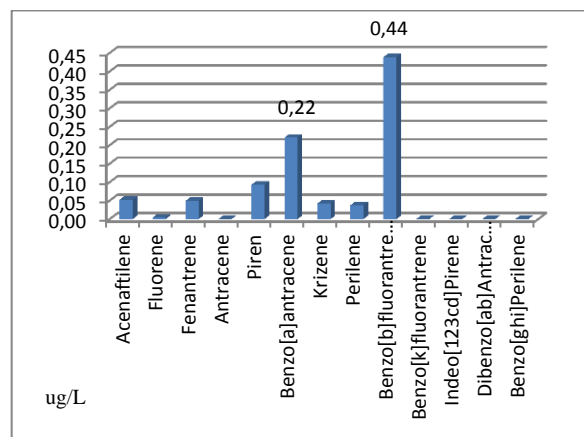


Figure 13. Profile of PAHs in water samples of BD, WD and FR – May 2017

4. CONCLUSIONS

Analysis of organic pollutants in water samples and the Black Drin, White Drin and Fierza Reservoir was realized in May 2017. Chlorinated organic pollutants (chlorinated pesticides, their residues and PCB) were studied using capillary GC/ECD. BTEX and PAH qualitative and quantitative analyze was conducted with capillary column with GC/FID technique. OCPs, PCBs and PAH were extracted using liquid-liquid extraction. Extraction and injection of BTEX were performed using Head Space mode. Total of organochlorine pesticides were found in higher level for Fierza Reservoir stations. Their concentrations for Black and White Drin samples were 5-10 times lower than FR samples. This is due to mountainous terrain that favors the rapid movement of water and small agricultural areas that lie in the basins of these rivers. Higher levels in FR were because of concentration factor for the pollutants in this area. The distributions of organochlorine pesticides were almost the same for all studied stations because of the same origin. Found levels were lower than reported levels for other rivers of Albania [3]. This is connected with the same origin of pollution for BD, WD and FR. In some stations were shown higher levels for individual pesticides. These higher concentrations could be because of punctual pollution for example by accidental, new arrivals from estuaries or rainfall of agricultural areas near the rivers. Profile of organochlorine pesticides in water samples of the BD, WD and FR were: Σ Endosulfanes > Mirex > Σ Aldrin > Σ DDT > Σ HCH. Endosulfan I and Mirex were found in higher levels in some stations. This could be because of recent use for these pesticides under false commercial names. For other pesticides was shown in higher level their metabolites such as Heptachlor epoxides, DDT metabolites, Lindane isomers and Oxychlordane (because of their previous use). Total of PCBs were found in the same range with total of organochlorined pesticides because their common in chemical and physical properties. PCBs weren't detected in 60% of studied stations. In some stations individual of PCBs were in higher levels. PCB 28 were found more than other PCB markers in all stations. The origin of PCBs in these ecosystems is mainly because of atmospheric deposition in rivers basin. PCB 209 and 153 were found in higher levels compare with other congeners. This is mainly associated with the direct discharges of waste waters in BD, WD and FR by many mechanical businesses. BTEX were found in higher level in BD1 and BD2 stations. BTEX weren't detected in 60% of studied samples. Benzene and Toluene were found in

higher levels for some stations because of punctual pollution. BTEX profile in water samples of the BD, WD and FR was: Benzene > Toluene > Ethylbenzene. PAHs (Benzo[b]Fluoranthrene) were found in higher level in WD1 station while the minimum was for 75% of stations where PAHs weren't detected. Profile of PAHs in BD, WD and FR were: Benzo[b]fluorantren > Benzo[a]anthracene > Pyrene > Acenaphtalene > Phenanthrene > Cryzene > Anthracene. Other PAHs for both rivers were not detected or were less than the limit of detection of GC/FID technique. Levels and profile of BTEX and PAHs in BD, WD and FR is associated with direct discharging of pumps oil near this area, car servicing, urban waters and automobile transport.

and sediments of the Ebro River (Spain).
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