O 11. EVALUATION OF ORGANOCHLORINE POLLUTANTS IN RIVER ESTUARIES OF VJOSA, SEMANI AND SHKUMBINI (ALBANIAN RIVERS)

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ABSTRACT: Purpose of this study was evaluation of levels for some organochlorine pesticides (DDTs, HCHs, Heptachlors, Aldrins and Endosulfanes) and polychlorinated biphenyls (PCB) in water samples of Vjosa, Semani and Shkumbini rivers. These rivers have a catchment area that collect waters from large agricultural areas includes Myzeqeja Field. Many industrial wastes finished in these rivers because of elevated industrial activity near these rivers. All these rivers flow into Adriatic Sea, so it is important to evaluate the pollutant levels in their estuaries. Water samples were taken two times per year in a three years period from March 2017 to December 2019. Liquid-liquid extraction was used to isolate chlorinated pollutants and a florisil column was used for clean-up procedure. Analysis of organochlorinated pesticides (according to Method EPA 8081) and polychlorinated biphenyls (7 PCB markers) were realized by using gas chromatography technique equipped with electron capture detector and RTX-5 capillary column. Organochlorinated pollutants were detected for all stations, for each sampling periods because of agricultural and industrial impact in water rivers. The highest levels were found in Semani and Shkumbini rivermouths due to higher agricultural areas near these rivers. New arrivals from water irrigation and discharges of industrial wastes influence in found levels. Degradation products of pesticides and volatile PCBs were found in higher levels for all analyzed samples. The levels of organochlorine pollutants were higher than EU and Albanian norms for Semani and Shkumbini rivers.

Keywords: Organochlorine pesticides; PCBs; PAH; Water analyzes; GC/ECD

1. INTRODUCTION

Albania is country rich in marine and surface waters. It is facing the Adriatic Sea and the Ionian Sea. The major water resource is surface water presented by lakes and rivers. Three main lakes of Albania are Shkodra Lake, Ohrid Lake and Prespa Lake. The most important rivers are: Drini, Mati, Ishmi, Erzeni, Shkumbini, Semani, Osumi, Vjosa, Bistrica and Buna (Cullaj et al, 2005). The main rivers of Albania discharge into the Adriatic Sea. In this study were evaluated concentrations of some organochlorine pollutants in water samples of river estuaries for Vjosa, Semani and Shkumbini.

Vjosa River is 270 kilometer long. It lies between Greece (first 80 km) and Albania territory (from Permeti to Vlora). Along its entire course it is untamed and free flowing and characterized by beautiful canyons, braided river sections, islands and meandering stretches. The meandering lower part opens up into a valley with extensive wetlands, providing habitats for spawning fish, migratory birds and others. Finally, it drains into the sea just north of the Narta lagoon – one of the biggest and ecologically richest lagoons of Albanian. The Vjosa is draining a total area of 6,700 km^2 in Albania and Greece and discharges an average of 204 m^3/s into the Adriatic Sea. In the first part, the river lies in a mountainous area that is mainly clean due to the greater slope and faster flow. In the second part because of plain part the river moves more slowly and is more polluted due to the influence of the agricultural areas of the Myzeqeja Field (Nuro et al, 2018).

The Semani River lies in western Albania. It is formed by join together of Osumi and Devolli rivers near Kucova. These rivers begin in South-East Albania (Erseka and Devolli respectively) and pass in Korca, Gramshi, Skrapari and Berati areas. Osumi River is considering a clear river because of mountainous areas where it is lies but Devolli River lies through Korca Field that is second agricultural area in Albania. Semani is 85 km long (281 km including its longest source river Devoll) and its drainage basin is 5,649 km^2 (include two main effluents). It flows in Fieri territory into the Adriatic Sea (near Topoja) with an average discharge of 95.7 m^3/s. Semani River is considered one of the most polluted rivers in Albania because it is directly influenced from extracting and processing oil industry (Patos-Marinza area and refineries of Fieri and Ballshi) and in the same time it is affected from waters that came from Myzeqeja field which is the main agricultural area in Albania. Gjanica River that joins with Semani some kilometers from Fieri brings a considerable pollution from oil industry.

Shkumbini River originates from Valmara Mountains (Pogradeci) in Southeastern Albania. After descending from the Valamara's, it flows in Pogradeci and Librazhdi territories in many deep gorges and canyons. A significant inflow comes from Gur i Kamjës in southwest of Pogradec. Over the course, it flows between the Mokra and Shebenik Mountains in the east and the Polis Mountains in the west. Close to Librazhdi the river joins the Rapun stream. It passes in Elbasani, Peqini and in the end the river cross the Myzeqeja field. Before reaching the Adriatic Sea it forms a small delta in Karavasta Lagoon. It is 181 km long and its drainage basin is 2,444 km^2. Its average discharge is 61.5 m^3/s. Also, Shkumbini River is affected from elevated industrial and agricultural activity especially in its second part where the flow is slower and the activity is higher (Como et al 2013, Murtaj et al 2013).

Before 90' organochlorinated pesticides (OCP) were used widely in Albania for agricultural purposes. The main agricultural areas were in the western of the country but almost every were in the country had been developed different directions of agricultural (fruits, corns, vegetables, etc). This study considers water samples of estuaries for three main rivers that pass throught Myzeqeja Field which is the main agricultural areas of Albania. It lies in the South-West of central Albania. The fields that lie in these areas are very fertile, especially for cereals, fruits and vegetables. 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 (Lindane, HCB, Aldrins, Endosulfanes and Heptachlors) were used in this area against malaria vector and after that for agricultural purposes. The use of pesticides in Albania after the 1990 decreased rapidly due to migration and/or immigration of population. PCBs were not in use in Albania until 90'. They can be found only in some electrical transformers that were used in early 1990 but they were reported in many ecosystems because of atmospheric depositions. Organochlorine pollutants (OCP and PCB) have high stability, high bioaccumulation capacity and the ability to spread out of the application site. Generally these compounds are difficult to degrade. 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 (Corsi et al, 2010; Nuro et al, 2012).

2. MATERIALS AND METHOD

Chemicals

Hexane and Dichloromethane for pesticide residue grade were purchased from Sigma Aldrich. Anhydrous sodium sulfate (Na_2SO_4), Florisil (≥ 400 Mesh ASTM) and silica gel (60-100 Mesh ASTM) were purchased also from Sigma Aldrich. H_2SO_4 with 95-97% purity for GC analyses was purchased by Merck. The sodium sulfate, florisil and silica gel were pre-extracted and rinsed with Hexane/Dichloromethane (4/1) just before utilization. EPA 8081 pesticide (17 compounds of organochlorine pesticides) and 7 PCB markers mix standard were purchased from Sigma Aldrich. Standard solutions for all pollutants were prepared by dissolving their stock solutions in Hexane in different concentrations and storing them in refrigerator. All glassware was rigorously cleaned with detergent followed by pyrolysis at 220°C. Procedural of blanks were regularly performed and all results presented are corrected for blank levels.

Study areas

The study areas were river estuaries of Vjosa, Semani and Shkumbini (Adriatic Sea, Albania). Water samples were taken two times per year in a three years period from March 2017 to December 2019. 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°C prior to their analyze.

Treatment of water samples for organochlorine pesticides and PCBs analyze

1 L of water and 40 mL n-Hexane (extracting solvent) were added in a separatory funnel. Liquid-liquid extraction was used for the simultaneously extraction of 15 organochlorine pesticide and PCB markers from water samples. The organic phase after separation was dried with 5 g Na_2SO_4 anhydrous, for water removing. A Florisil column was used for the sample clean-up. After the concentration to 1 ml using a thermal block, the samples were injected in GC/ECD (Nuro et al, 2012; Kostandinou et al, 2006; Wells and Hess, 2000).

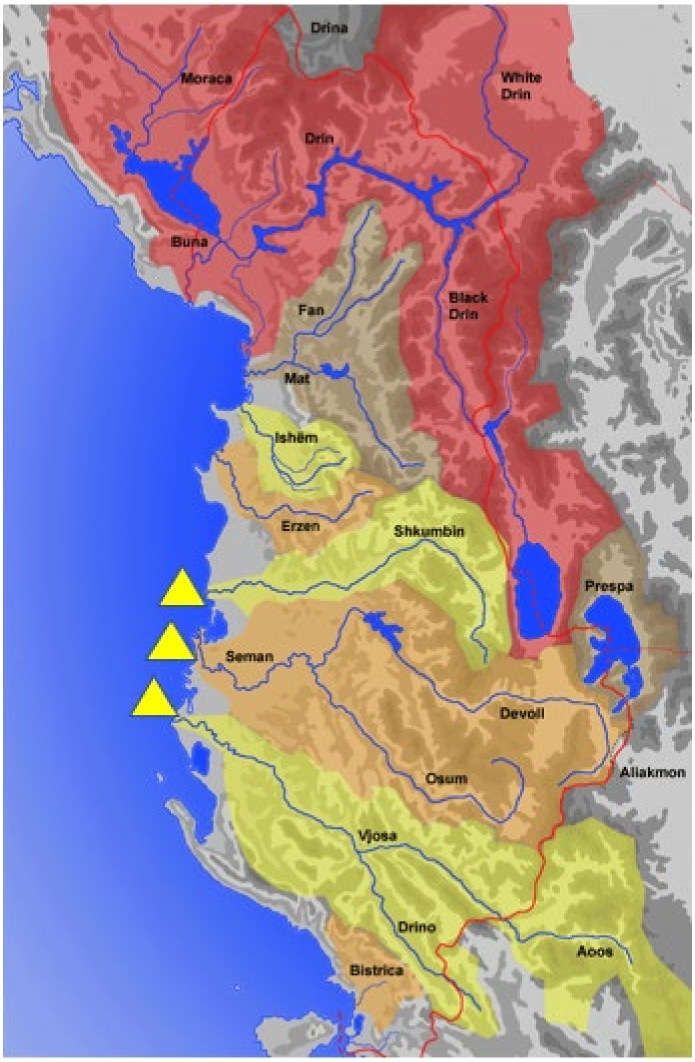

Figure 1. Sampling stations of water samples in river estuaries of Vjosa, Semani and Shkumbini

Apparatus and chromatography

Chromatographic analyse were realized in a Varian GC 450 model. GC was equipped with split/splitless injector, Rtx-5 capillary column (30 m x 0.33 mm x 0.25 μm) and electron capture detector. Nitrogen was used as carrier gas (1 ml/min) and make-up gas (25 ml/min). Injector and ECD temperature was hold respectively 280ºC and 300°C. Quantification of organochlorine pesticides and their residues was performed in external standard. Five concentrations of pesticides and PCB mixture (5, 10, 25, 50 and 100 ng/ml) were used for calibration (Lekkas et al, 2004; Vryzas et al, 2009; Nuro et al, 2012). Organochlorine pesticides were: Lindane and its isomers (alfa-HCH, beta-HCH, gama-HCH or Lindane and delta-HCH); Heptachlor's (Heptachlor and Heptachlorepoxide); Aldrin's (Aldrine, Dieldrine and Endrin); DDTs (4,4-DDE; 4,4-DDD and 4,4-DDT) and Endosulfanes (Endosulfan alfa, Endosulfan beta and Endosulfan sulfat) while PCB markers were (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138 and PCB 180).

3. RESULTS AND DISCUSSION

Water samples from river estuaries of Vjosa, Semani and Shkumbini were analyzed for two times per year in a three years period (2017-2019). These rivers flow in Adriatic Sea, in West (central) Albania. These rivers cover a large catchment area and pass throught Myzeqeja Field which is the main agricultural areas of Albania. DDT, Lindane, HCB, Aldrins, Endosulfanes and Heptachlors were used in this area for against malaria vector and for agricultural purposes. Also, industrial activities and atmospheric deposition of pollutants can influence water of Vjosa, Semani and Shkumbini rivers. All these rivers flow in Adriatic Sea and this was the reason that we though to analyze water samples in their estuaries to see also their impact in the sea. Organochlorine pesticides, their degradation products and PCB markers were analyzed in a total of 27 water samples. Average data on organochlorine pesticides and their classes was shown in Table 1.

Figure 2 shows total of organochlorine pesticides (average concentrations) found in water samples of river estuaries for Vjosa, Semani and Shkumbini. Higher level of organochlorine pesticides were found for Semani River (146.0 ng/l) and Shkumbini River (131.7 ng/l). The main factor of higher concentrations of OCPs in these two water rivers can be their previous uses for agricultural purposes. Rivers furnished continuously with new inputs from rainfall and water irrigation. Punctual sources or recent use of pesticides can impact on differences between rivers. The lower level was found in water samples of Vjosa River (23.8 ng/l).

Figure 3 shown distributions of organochlorine pesticides in three river estuaries. There are noted similarities in all samples because the same pollution origin. For Semani and Shkumbini rivers were noted the presence of individual pesticides in higher levels than others. This could be connected with punctual sources or a momentum value.

Total for the pesticide groups of HCHs, Heptachlors, Aldrins, DDTs and Endosulfanes was shown in Figure 4. Endosulfanes were found in higher concentrations for three rivers. May be, this pesticide could be in use recent years near Myzeqeja area. After that, Aldrins and Heptachlors were found in Vjosa River; HCHs, Aldrins, Heptachlors and DDTs in Semani River and Heptachlors, Aldrins, DDTs and HCHs in Shkumbini River. These differences could be because of punctual sources near these rivers and chemical-physical characteristics of individual pesticides. Pesticide concentrations for each classes in water samples of Vjosa, Semani and Shkumbini rivers were in the same levels with reported data on previous studies for the same stations (Murtaj et al 2014; Como et al 2013, Nuro et al 2017).

Concentrations of Lindane and its isomers (alpha-, beta-, gama- and delta-hexachlorocyclohexanes-HCHs) were shown in Figure 5. Their total was respectively: Semani River (26.4 ng/l) > Shkumbini River (12.5 ng/l) > Vjosa River 1.8 (ng/l). It was noted that Lindane concentration wasn't the higher than other HCHs. It was found only in 60% of all analyzed samples. beta-HCH were found the primary isomer for all three rivers. Its origin could be because of their presence as impurity in Lindane formulations or because of Lindane chemistry. This is valid for all Lindane isomers. HCHs could be also products of degradation of other pesticides or because of impact of urban waste especially in rivers water. For all stations, total of HCHs were lower than permitted level of 0.04 ug/l conform EU Directive 2013/39 and Albanian norms for surface waters.

Heptachlors were found in higher concentration in water samples of Shkumbini with 23.2 ng/l (Figure 6). Levels of Heptachlors in Semani and Vjosa rivers were respectively with 12.0 ng/l and 4.6 ng/l. The higher levels in three rivers were found for Heptachlorepoxide, its degradation products. This fact is connected with previous use of Heptachlor. Levels of Heptachlors in some stations of Shkumbini and Semani rivers were higher than EU Directive 2013/39 or Albanian norms.

Concentrations and profiles of Aldrines were shown in Figure 7. The higher levels of Aldrines were for Shkumbini River with 21.5 ng/l and for Semani River with 20.2 ng/l. In fact the higher level of Aldrine in Semani River was connected with higher concentration of Dieldrin while in Shkumbini River in higher concentration was Endrin. This is connected with time of use for Aldrine in the agricultural areas near these rivers. Aldrines were found 2 times higher than EU directive 2013/39 and Albanian norms for Semani and Shkumbini river.

Concentrations of DDTs for Vjosa, Semani and Shkumbini rivers were shown in Figure 8. The higher level of DDTs was found in Shkumbini River with 13.9 ng/l and after that in Semani River with 11.4 ng/l. Total of DDTs in Vjosa River was 0.5 ng/l. DDT was found on 25% of samples only for Semani and Shkumbini rivers. DDT was not detected in water samples of Vjosa River. Its degradation products (DDE and DDD) were found in high concentration for all samples because of previous use of DDTs in the agricultural areas of Myzeqeja. DDT levels were lower than 1 ng/l for all stations except two samples in Semani rivermoth station (2017). 4,4'-DDT were lower than permited level of 0.01 ug/L for Vjosa and Shkumbini rivers.

Endosulfans concentrations in three rivers were presents in Figure 9. Total of Endosulfans were higher in Semani River (76 ng/l) and Shkumbini River (60.6 ng/l). Note that Endosulfans were found in higher level only for two samples in Semani River (2017 and 2018) and for one sample in Shkumbini River (2018). This fact suggests punctual source of Endosulfan's in these ecosystems. It's not excluded the recent use of Endosulfan in water basins of Semani and Shkumbini rivers. Endosulfans could be in use in these areas under false trade name. Endosulfanes concentrations for water samples of Semani and Shkumbini rivers were more than 10 times higher than permitted level based on EU Directive 2013/39. Presence of Endosulfane in surface water samples must be lower than N.D.5 ug/l.

Table 1. Average levels (ng/l) of individual organochlorine pesticides in water samples

	Vjosa Rivermouth	Semani Rivermouth	Shkumbini Rivermouth
a-HCH	0.28	1.34	2.37
b-HCH	1.13	12.79	6.90
Lindane	0.35	8.02	2.99
d-HCH	N.D.	4.25	0.20
Heptachlor	1.43	2.17	10.40
Aldrine	1.53	3.54	4.90
Heptachlorepoxide	3.21	9.81	12.76
Endosulfan alfa	0.76	6.84	11.16
Dieldrin	2.61	11.31	4.87
4.4'-DDE	0.06	5.26	9.54
Endrin	1.17	5.33	11.73
Endosulfan beta	6.32	14.18	17.30
4.4-DDD	0.42	4.61	3.52
Endosulfan sulfat	4.57	54.96	32.17
4,4'-DDT	N.D.	1.54	0.87
∑ OCP	**23.84**	**145.95**	**131.68**
∑ HCH	1.76	26.40	12.46
∑ Heptachlors	4.64	11.98	23.16
∑ Aldrins	5.31	20.18	21.50
∑ DDTs	0.48	11.41	13.93
∑ Endosulfans	11.65	75.98	60.63

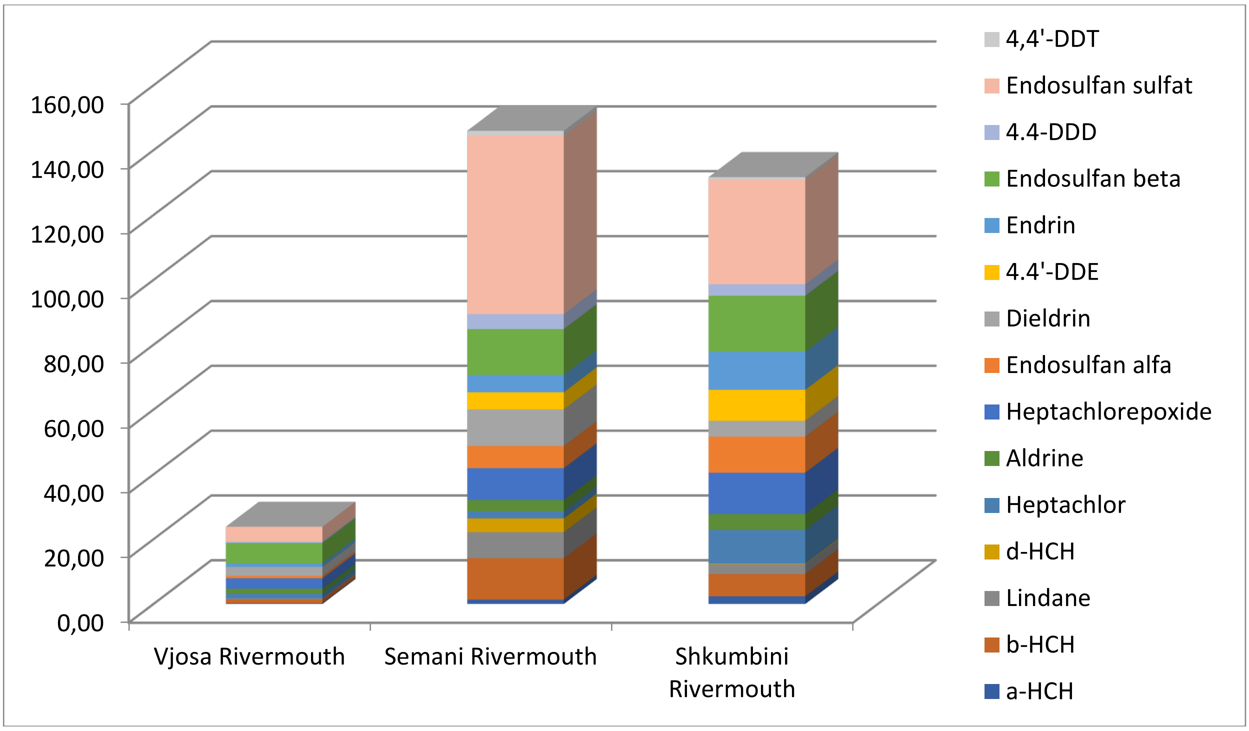

Figure 2. Total of organochlorine pesticides in water samples of Vjosa, Semani and Shkumbini river estuaries

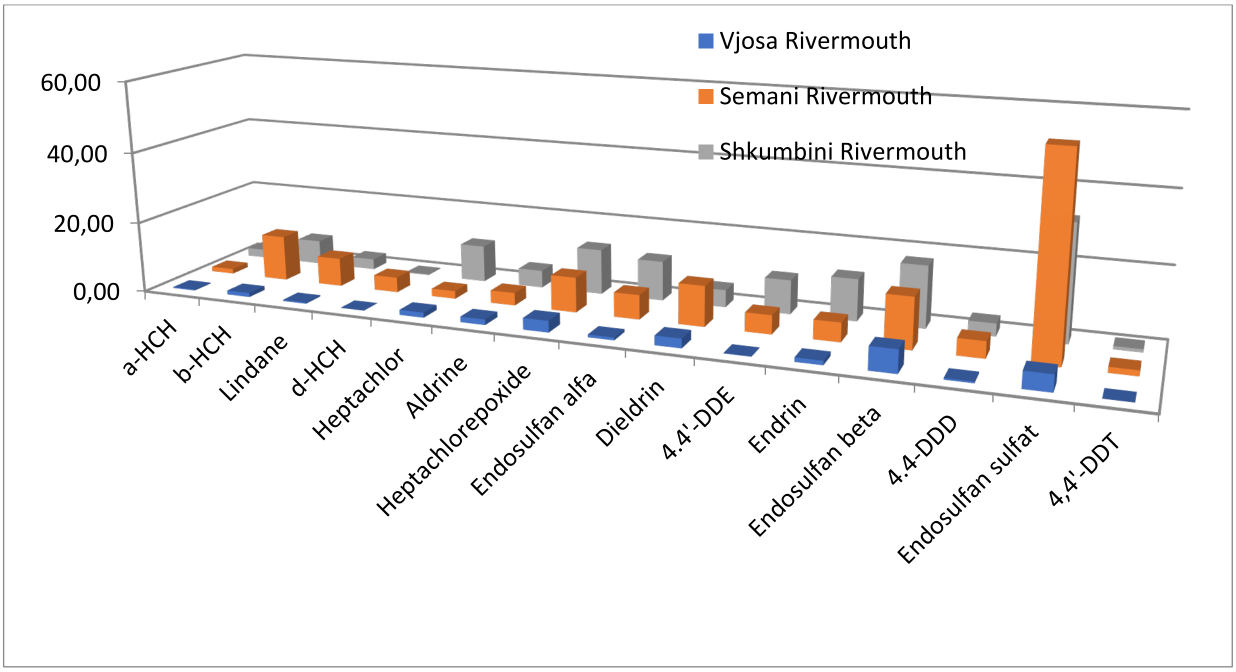

Figure 3. Distribution of organochlorine pesticides in water samples of river estuaries

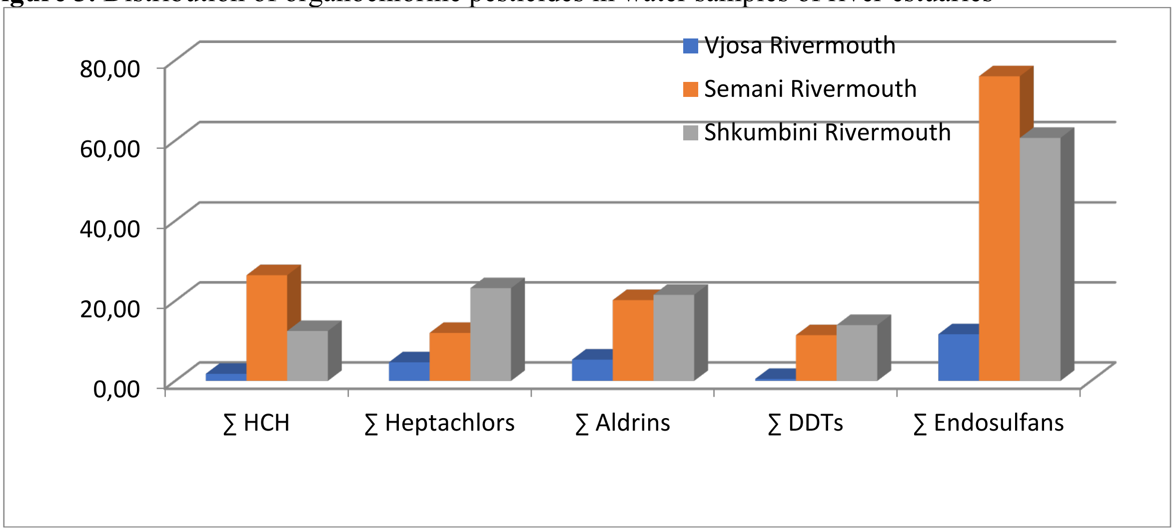

Figure 4. Distribution of organochlorine pesticides based on their classes

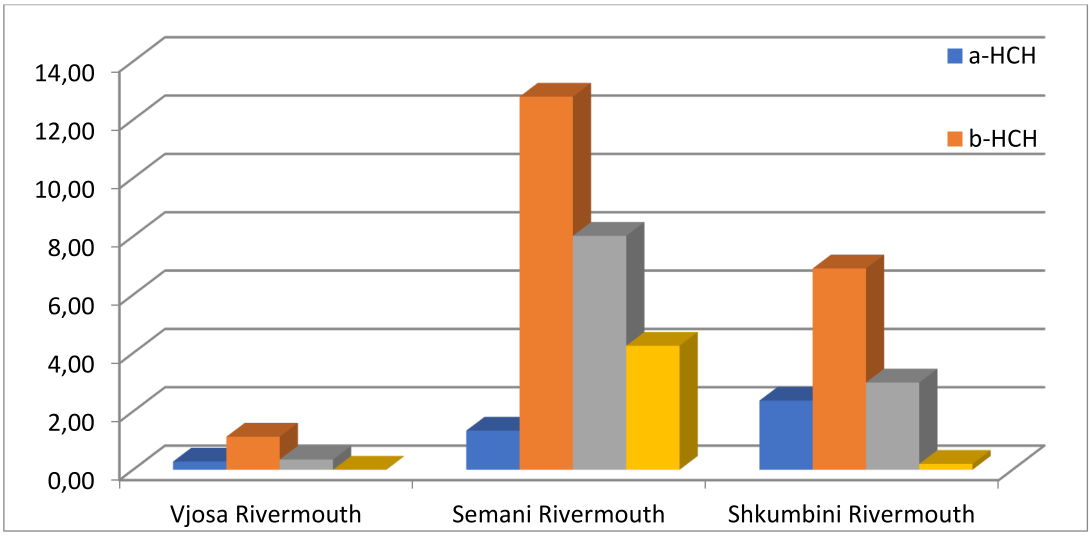

Figure 5. Lindane and its isomers in water samples of Vjosa, Semani and Shkumbini river estuaries

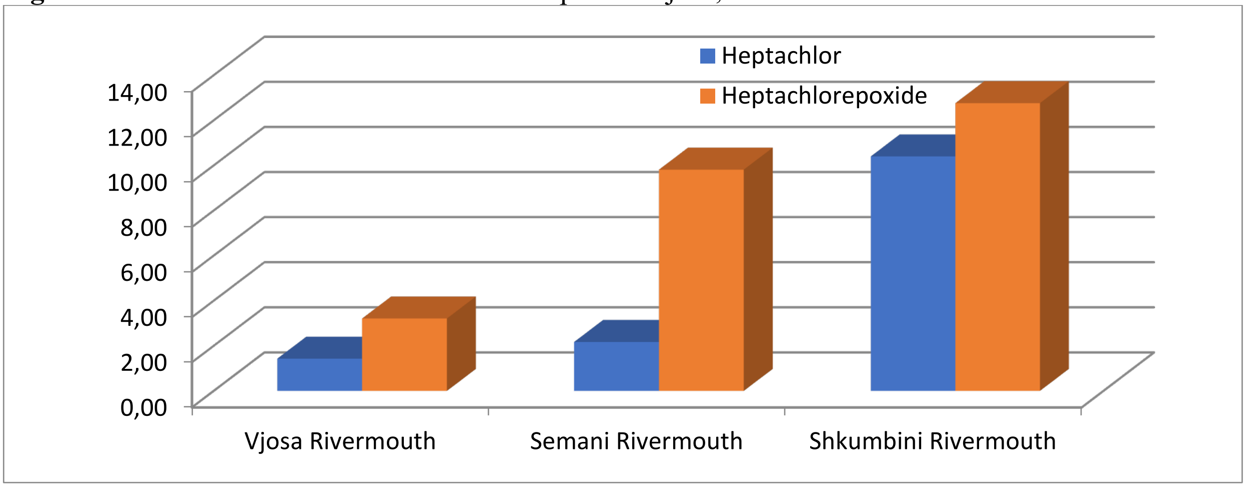

Figure 6. Heptachlors in water samples of river estuaries

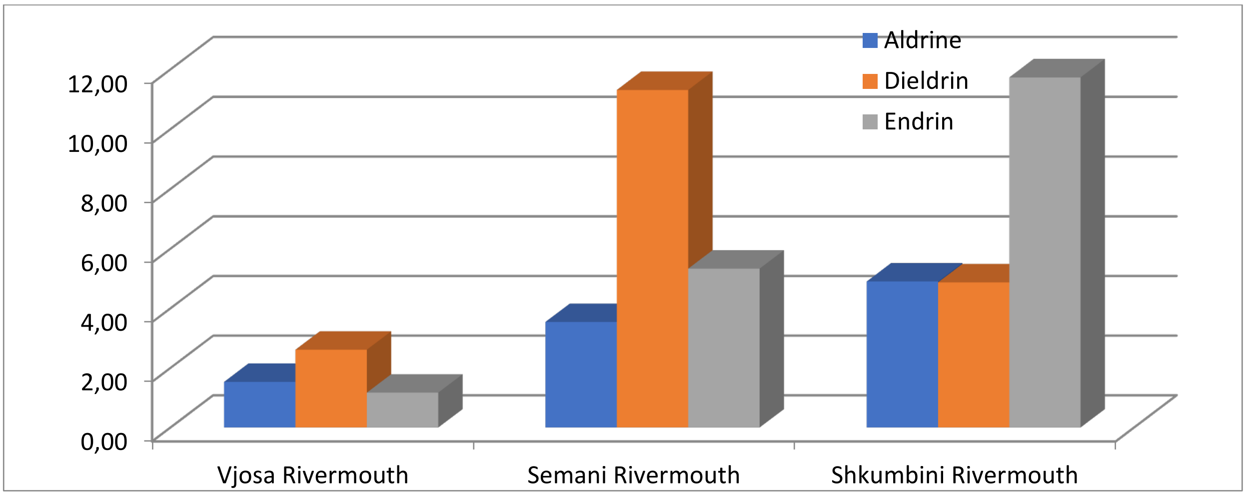

Figure 7. Aldrines in water samples of river estuaries

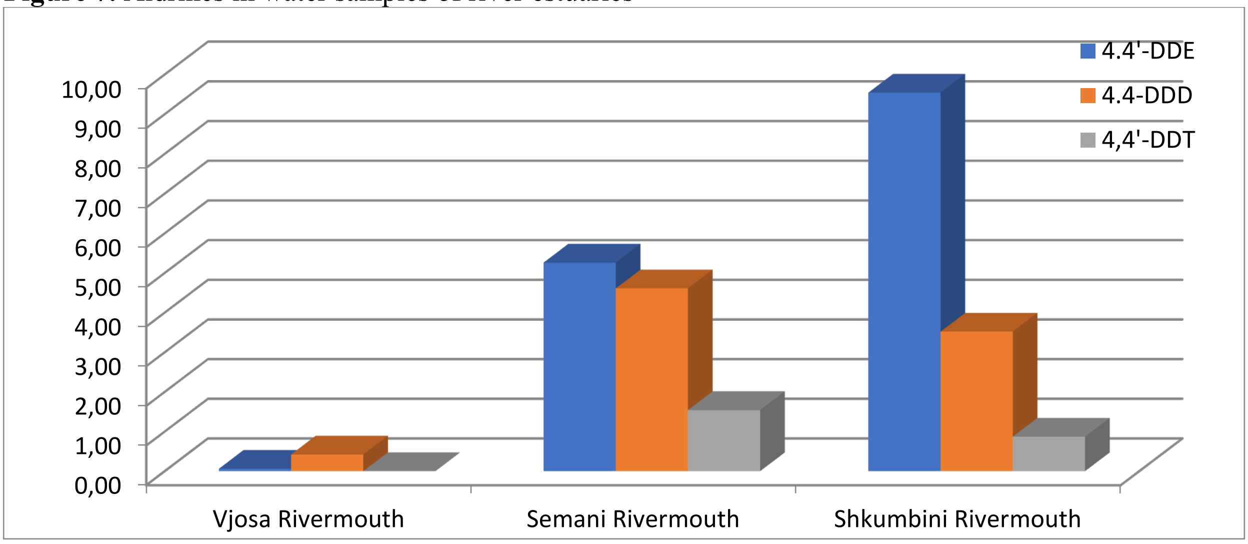

Figure 8. DDTs in water samples of three river estuaries

Average data on 7 PCB markers was shown in Table 2. Figure 10 shows total of PCB markers in water samples of river estuaries for Vjosa, Semani and Shkumbini. Also, higher level of PCBs were found in Semani River (69.7 ng/l) and Shkumbini River (60.8 ng/l). The main factor for higher concentrations of PCBs in these two water rivers can be elevated industrial activity in their water basins. Again, Vjosa River was the most "clean" with PCBs (18.3 ng/l).

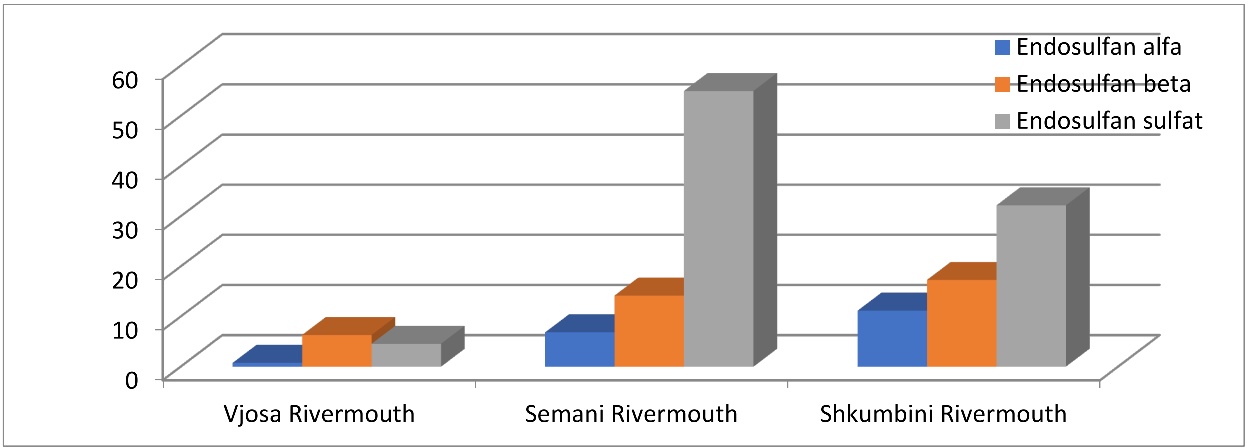

Figure 9. Endosulfanes in water samples Total of Vjosa, Semani and Shkumbini river estuaries

Figure 11 shown distributions of PCB markers in three river estuaries. There are not similarities between samples because differences in pollution origin. For Semani and Shkumbini rivers were noted the presence of heavy PCB congeners (PCB 180) that is connected with punctual sources for PCBs in these ecosystems while in Vjosa River in higher levels were detected volatile congeniers (PCB 28 and PCB 52) that is connected with atmospheric deposition. These differences could be because of impact that came from elevated industrial activity in Semani and Shkumbini rivers. Note that some of industries that can influence more are extraction and processing of oil industry (Semani Rivers) and metallurgical complex near Elbasani (Shkumbini River). PCB concentrations for water samples of Vjosa, Semani and Shkumbini rivers were in comparable levels than reported data on previous studies for the same stations (Murtaj et al 2014; Como et al 2013, Nuro et al 2017).

Table 2. PCB data (average) in water samples of Vjosa, Semani and Shkumbini river estuaries

	Vjosa Rivermouth	**Semani Rivermouth**	**Shkumbini Rivermouth**
PCB 28	7.34	13.26	15.33
PCB 52	5.28	9.37	11.62
PCB 101	0.63	3.72	5.82
PCB 118	2.83	7.22	11.82
PCB 153	N.D.	5.62	2.91
PCB 138	0.63	17.81	1.52
PCB 180	1.63	12.73	11.82
∑ PCB	**18.34**	**69.73**	**60.84**

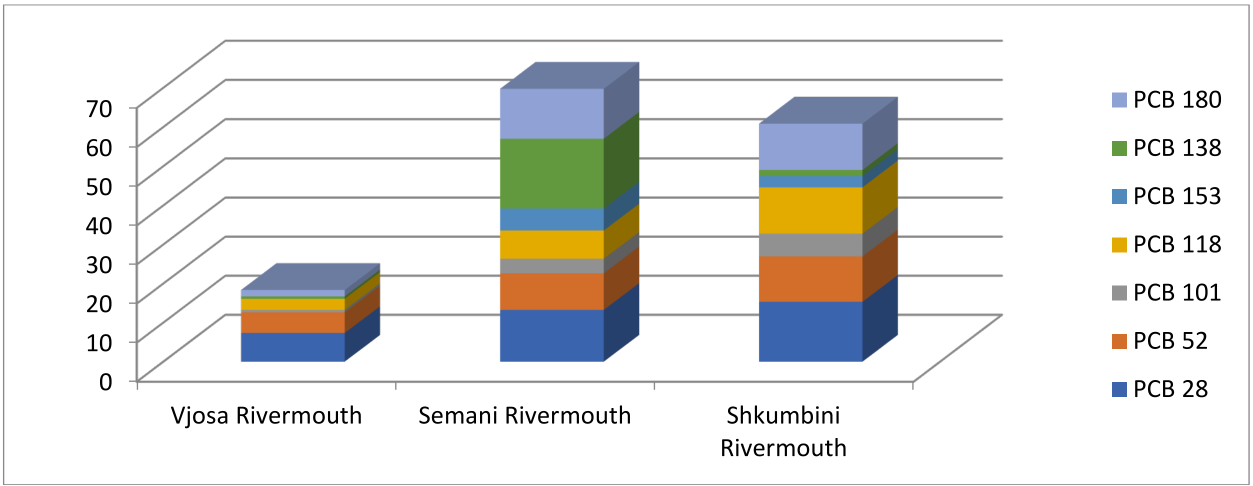

Figure 10. Total of PCBs in water samples of Vjosa, Semani and Shkumbini river estuaries

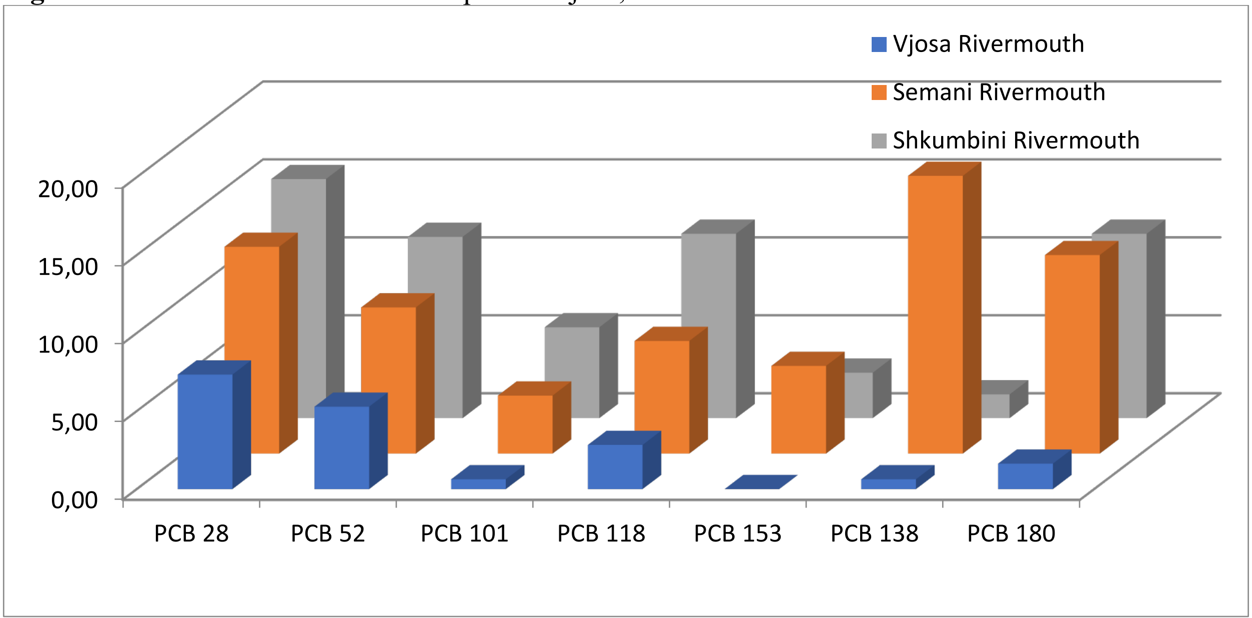

Figure 11. Distribution of PCBs in water samples of three river estuaries

4. CONCLUSIONS

The highest level of contamination with organochlorine pesticides and PCBs were found in Semani and Shkumbini rivers because of new arrivals from waters that are collected by channels of Myzeqeja Field. For some stations of these two rivers were noted the presence of individual pesticides in higher levels than others. In waters samples of Shkumbini and Semani rivers were found in high level heavy PCB. This could be connected with punctual sources of pesticides and PCBs in these stations or a momentum value. It was noted presence of degradation products of pesticides in higher level. This fact is connected with previous use of pesticides in Albania. Endosulfanes were shown to be primary pollutants in all samples. This pesticide could be in use in agricultural areas near these rivers under false trade name. Presence of PCBs could be because of industrial activity or atmospheric deposition. Concentrations of organochlorine pesticides in all water samples of Vjosa River were lower than permitted levels for surface waters according EU Directive 2013/39 while some samples of Semani and Shkumbini rivers were above these norms. Concentrations of organochlorine pesticides and PCBs were found to be in comparable levels than reported data on previous studies for the same stations (Murtaj et al 2014; Como et al 2013, Nuro et al 2017).

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