

LEVELS OF SOME PRIORITY SUBSTANCES ON ADRIATIC SEA, ALBANIA

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Abstract: *This study evaluated levels for organochlorine pesticides (DDTs, HCHs, Heptachlors, Aldrins and Endosulfanes), their residues, polychlorinated biphenyls (PCB) and poly aromatic hydrocarbons (PAH) in water samples of Adriatic Sea, Albanian part. Water stations were chosen near the main river estuaries of Albania (Vjosa, Semani, Shkumbini, Erzeni, Mati and Buna rivers). These rivers have catchment areas that cover almost all Albania. First, agricultural, industrial and urban waste is transported in these rivers and after that they finished in Adriatic Sea.*

Water samples were analyzed for a five-year period from February 2015 to December 2019. Liquid-liquid extraction was used to isolate chlorinated pollutants and a florisil column was used for clean-up procedure. Analysis of organochlorine pesticides (according to Method EPA 8081B) and 7 PCB markers was realized using GC/ECD and RTX-5 capillary column. The PAHs were isolated by liquid-liquid extraction technique and after sample concentration qualitative and quantitative analyses were performed by the GC/FID technique.

Organochlorine pollutants were detected for all stations of Adriatic Sea because of new arrivals by agricultural and industrial activity in river basins. The highest levels were found near Shkumbini and Semani estuaries due to impact Myzeqeja agricultural area. New arrivals from water irrigation and rainfall influence in found levels. Degradation products of pesticides and volatile PCBs were found at higher levels for all samples analyzed. The levels of some individual organochlorine pesticides were higher than EU and Albanian norms for Semani and Shkumbini rivers. Also, PAHs were found at higher levels for Semani River because of extracting-processing industry in Patos-Marinza area. Monitoring of organic pollutants in water of Adriatic Sea should be continuous because of its importance in fishing, tourism, recreation and Albania economy overall.

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

INTRODUCTION

Albania is a country located in the Balkan Peninsula in Southeast Europe. It is rich in marine and surface waters. It faces the Adriatic Sea and the Ionian Sea that are part of the Mediterranean Sea. The total length of the coastline is approximately 274 km, 178 km of which are covered by sandy beaches and the remaining by different landforms. The main lagoons (Narta, Karavasta and Patoku lagoons) are formed in estuaries of rivers that flow in Adriatic Sea. These water ecosystems are rich in flora and fauna. Fishing, tourism and ship transport activity in marine waters have an important role in Albanian economy. The major

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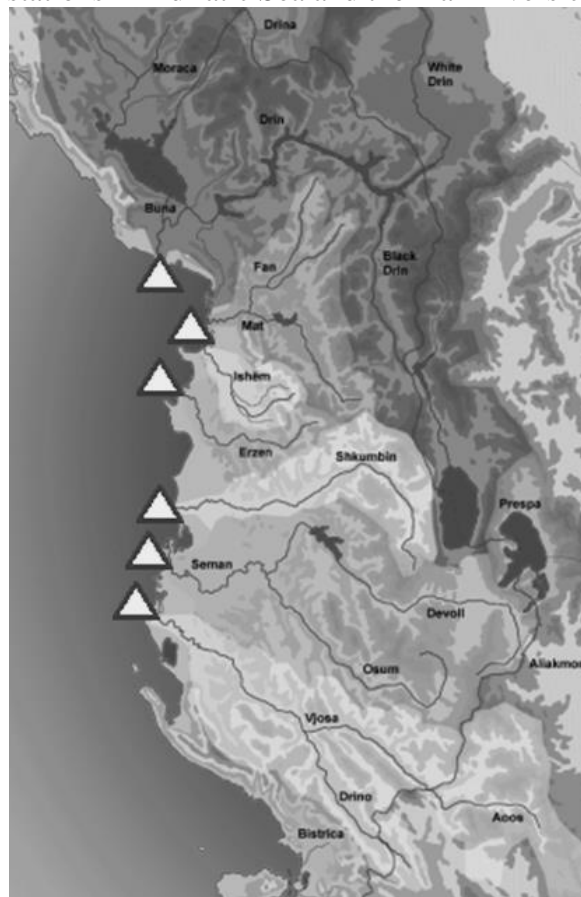
surface water resources are many lakes and rivers. Three main lakes of Albania are Shkodra Lake, Ohrid Lake and Prespa Lake. The most important rivers are Drini, Mati, Ishmi, Erzeni, Shkumbini, Semani, Osumi, Vjosa, Bistrica and Buna (Cullaj et al, 2005). Waters of these rivers are in use mainly for producing electricity by hydropower plants and for water irrigation in agricultural. Note that occasionally waters of rivers are polluted by urban and industrial waste and by remains of agricultural pesticides and veterinary drugs. These pollutants end up in the seawater. The main rivers of Albania flow in Adriatic Sea. Based on this fact, monitoring pollution levels in marine and surface water samples must be continuous, especially recently after rapid growth of tourism in Albania. Marine and surface water resources have a direct impact on people health and present an important contributor to the country's economy too. This is the reason that river waters must have additional attention in assessing their chemical and microbiological parameters by responsible institutions. In this context, this study presents concentrations of organochlorine pesticides, their residues, PCB markers and PAHs in water samples of Adriatic Sea for a five-year period. Sampling stations were selected near the main river estuaries (Vjosa, Semani, Shkumbini, Erzeni, Mati and Buna rivers) that discharge to the sea. These rivers have catchment areas that cover almost all Albania so the arrival of new pollutants is not excluded.

For more than 50 years (after the Second World War to 90') organochlorine pesticides were used widely in Albania against malaria vector and for agricultural purposes. The main agricultural areas are located in the western of the country near Adriatic Sea. These fields are covered mainly by the Vjosa, Semani, Shkumbini, Erzeni, Mati and Buna rivers and their branches. The use of pesticides in Albania after 1990 decreased rapidly due to migration and 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 the early 1990s, but they were reported in many water ecosystems of our country because of atmospheric depositions. PAHs are pollutants generated by automobiles transport, extracting/processing of oil industry, coal mine and other industries. Forest burning and their natural background make them very often in environment. Organochlorine pollutants (OCP and PCB) and PAHs have high stability, high bioaccumulation capacity and the ability to spread out far away from the application site. Generally, these compounds are difficult to degrade and can persist for many years in particular in water ecosystems (Corsi et al, 2010; Nuro et al, 2012).

MATERIALS AND METHODS

Study areas

The study areas were river estuaries of Vjosa, Semani, Shkumbini, Erzeni, Mati and Buna (Adriatic Sea, Albania). Water samples were taken two times per year in a five-year period from February 2015 to December 2019. The sampling stations are presented in Figure 1. 2,5 liters 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 transported and conserved at +4°C before their analysis.

Figure 1. Sampling stations in Adriatic Sea and the main rivers catchments in Albania

Treatment of water samples for pesticide and PCB analyzes

Liquid-liquid extraction was used for extraction of organochlorine pesticide and polychlorinated biphenyls from marine water samples of Adriatic Sea. One liter of water and 30 ml n-hexane as extracting solvent were added in a separatory funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removing. A florisil column was used for the sample clean-up. 20 ml n-hexane/dichloromethane (4/1) was used for elution. After concentration to 1 ml, the samples were injected in GC/ECD (Lekkas et al, 2004; Vryzas et al, 2009; Nuro et al, 2012).

Gas chromatography analysis of pesticides and PCBs

Organochlorine pesticides and PCBs were analyzed simultaneously using capillary column model Rtx-5 (30 m long x 0.25 mm i.d. x 0.25 μm film thicknesses) on a gas chromatograph HP 6890 Series Plus with μECD detector. Helium was used as carrier gas (1 ml/min) while nitrogen as make-up gas (24 ml/min). The manual injection was done in split mode (1:50) at 280°C. The organochlorine pesticides detected were DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), HCHs (α -, β -, γ - and δ -isomers), Heptachlor's (Heptachlor and Heptachlorepoxyde); Aldrin's (Aldrine, Dieldrine and Endrin) and Endosulfanes (Endosulfan alfa, Endosulfan beta and Endosulfan sulfat). Analysis of PCBs was based on the determination of the seven PCB markers (IUPAC Nr. 28, 52, 101, 118, 138, 153 and 180). Quantification of OCPs and PCBs were based on external standard method (Vryzas et al, 2009; Lekkas et al, 2004; Nuro et al, 2014).

Treatment of water samples for PAH analyzes

Liquid-liquid extraction was used for extracting PAHs from marine water samples. One liter of water and 30 ml dichloromethane as extracting solvent were added in a separator funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removing. Extracts were concentrated to 1 ml using Kuderna-Danish and then were injected in GC/FID for PAHs their quantification (Nuro et al, 2014; Gustafson and Dickhut, 1997).

Determination of PAH in water samples

Gas chromatographic analyses of PAH in water samples were realized with a Varian 450 GC instrument equipped with a flame ionization detector and PTV detector. VF-1 ms capillary column (30 m x 0.33 mm x 0.25 μm) was used to isolate and determine 13 most toxic PAHs according to Albanian and EU norms. Helium was used as carrier gas with 1 ml/min. FID temperature was held at 280°C. Nitrogen was used as the make-up gas (25 ml/min). Hydrogen and air were flame detector gases with 30 ml/min and 300 ml/min, respectively. EPA 525 Mixture was used for qualitative and quantitative of PAH analyze. Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Pyrene, Benzo [a] anthracene, Chrysene, Perilene, Benzo [b] fluoranthene, Benzo [k] fluoranthene, Indeo [1,2,3-cd] pyrene, Dibenzo [a, b] anthracene and Benzo [g, h, i] perylene were determined in seawater samples. Quantification of PAH was based on external standard method (Nuro et al, 2014; Gustafson and Dickhut, 1997).

RESULTS AND DISCUSSION

Marine water samples from Adriatic Sea (Albanian part) were selected near the six main river estuaries that flow on it (from South to North: Vjosa, Semani, Shkumbini, Erzeni, Mati and Buna rivers). The average data of a five-year period (2015–2019) are shown in this study to understand their pollution impact on seawater. These rivers cover a large catchment area including the main agricultural areas and the main cities as well as industrial areas of Albania. Organochlorine pesticides, their degradation products and PCB markers were analyzed using GC/ECD and GC/FID techniques.

Figure 2. DDTs in water samples of Adriatic Sea

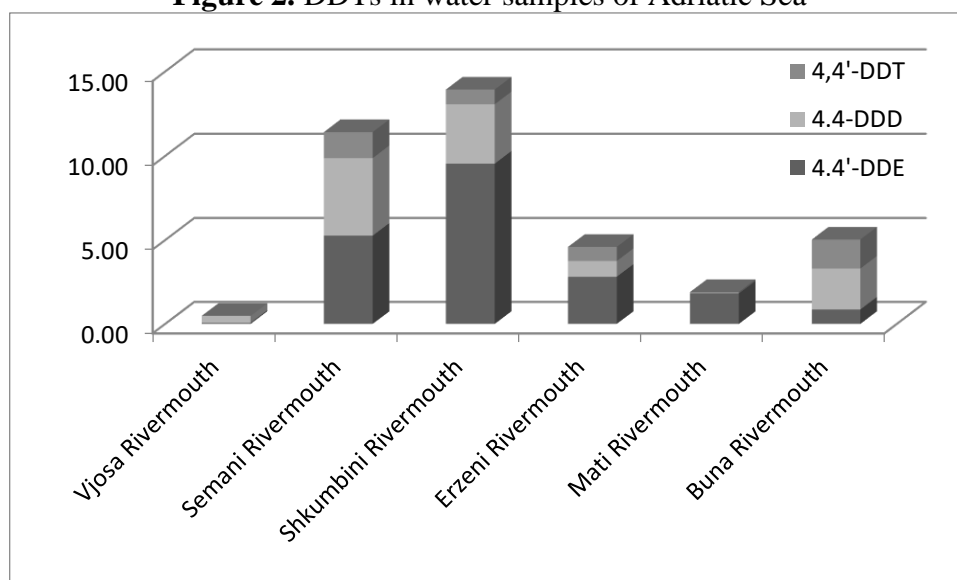
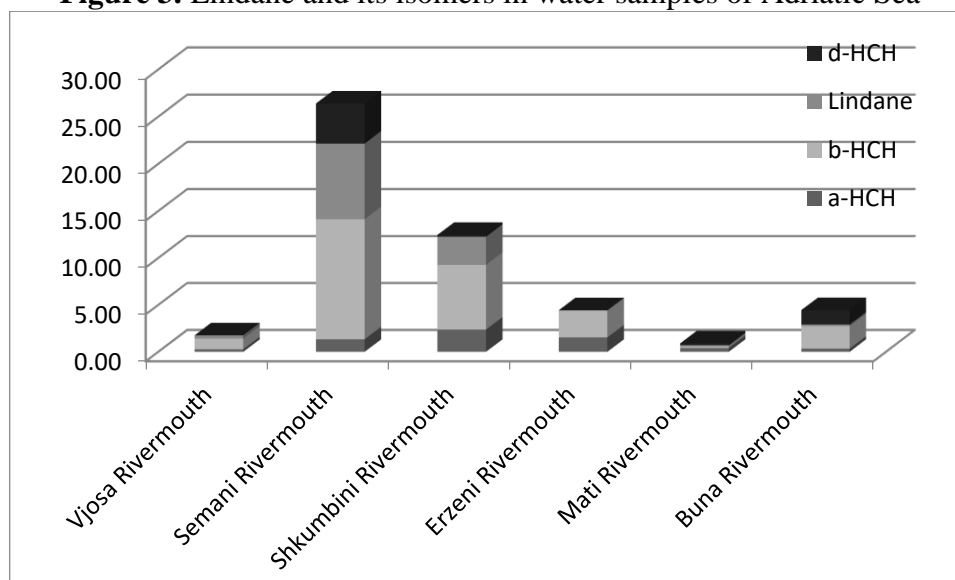


Figure 2 shows DDTs (4,4'-DDT, 4,4'-DDD and 4,4'-DDE) in marine water samples of Adriatic Sea located near river estuaries for Vjosa, Semani, Shkumbini, Erzeni, Mati and Buna rivers. The higher DDT levels were found in Shkumbini river mouth water samples (13.7 ng/l) and after that in Semani River (10.9 ng/l) because of new arrivals by Myzeqeja field that lie near these rivers. Total of DDTs near Vjosa river mouth was lower (0.5 ng/l) compared with other stations on Adriatic Sea. DDT pesticide was found partially on samples of Semani, Shkumbini, Erzeni and Buna rivers. DDT was not detected in water samples of Vjosa and Mati rivers. DDT degradation products (DDE and DDD) were found in high concentration for all samples because of DDT previous use for malaria vector and agricultural purposes. DDT levels were lower than 1 ng/l for all stations except for two samples in Semani rivermouth station (2017) and three samples in Buna rivermouth station (2016, 2017 and 2018). For other stations 4,4'-DDT was lower than permitted level (0.01 ug/L) based on Albanian and EU norms.

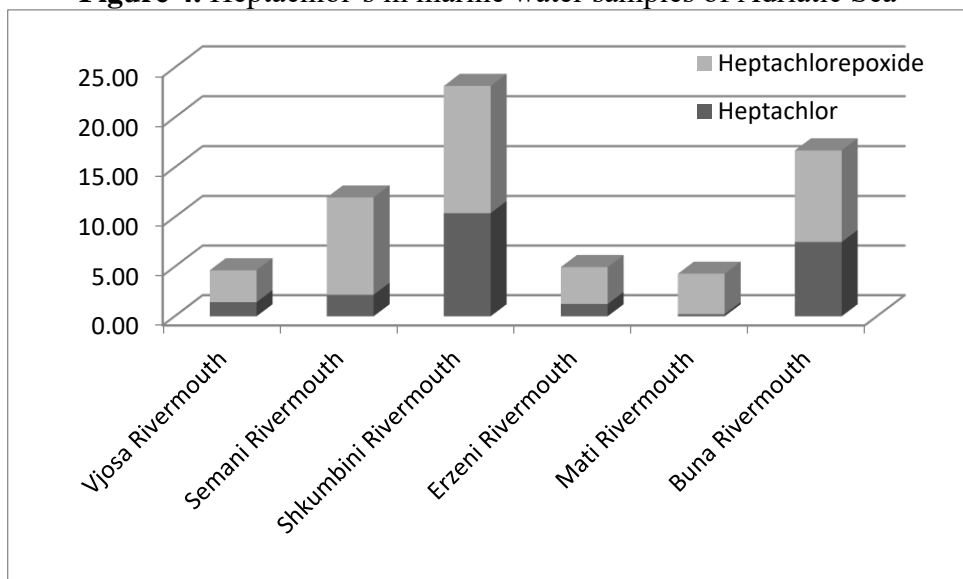
Concentrations of Lindane and its isomers (alpha-, beta-, and delta-hexachlorocyclohexanes-HCHs) are shown in Figure 3. Also, HCHs were found in higher concentrations in water samples near Semani and Shkumbini river mouths (25.4 and 12.5 ng/l) while samples near Mati and Vjosa estuaries were at lower concentrations (0.8 and 1.1 ng/l). Note that Lindane was found only in 25% of all analyzed samples. beta-HCH was found to be the primary isomer for all seawater samples. Its origin could be because of beta-HCH presence as an impurity in Lindane formulations or because it's physical – chemistry properties. HCH isomers could be found because of Lindane previous use in agricultural or due to degradation of other pesticides. HCH's arrival by urban waste it's not excluded. For all stations, total of HCHs was lower than permitted level of 0.04 ug/l conform to EU Directive 2013/39 and Albanian norms for surface waters.

Figure 3. Lindane and its isomers in water samples of Adriatic Sea



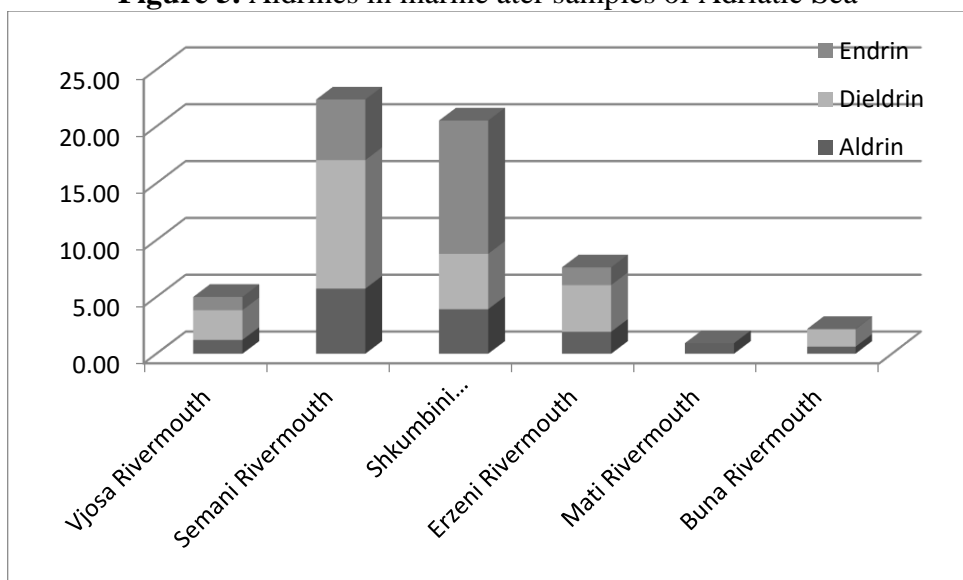
Average concentrations of Heptachlors in seawater were shown in Figure 4. Heptachlors were found in higher concentrations in water samples of Adriatic Sea near Shkumbini estuary (23.2 ng/l) and after that near Buna (12.0 ng/l) and Semani samples (4.6 ng/l). In the higher levels in all analyzed samples were found Heptachlorepoxyde, its degradation products. This fact is connected with the previous use of Heptachlor. Levels of Heptachlors in some samples taken near Shkumbini and Semani rivers were higher than EU Directive 2013/39 or Albanian norms.

Figure 4. Heptachlor's in marine water samples of Adriatic Sea



Concentrations and profiles of Aldrines were shown in Figure 5. The higher levels of Aldrines were for Semani River with 22.2 ng/l and for Shkumbini River with 19.9 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 the time of use for Aldrine in the agricultural areas near these rivers. Aldrins were found in lower levels in water samples of Mati, Buna and Vjosa river mouths. Aldrines were found 2 times higher than EU directive 2013/39 and Albanian norms for 44% of seawater samples near Semani and Shkumbini rivers.

Figure 5. Aldrines in marine water samples of Adriatic Sea



Averages of concentrations for Endosulfan in estuaries of rivers (Adriatic Sea) are presented in Figure 6. Total of Endosulfan alpha, Endosulfan beta and Endosulfan sulfate were higher in Buna (79.8 ng/l), Semani (75.6 ng/l), Shkumbini (59.6 ng/l) and Erzeni (51.3 ng/l) river mouths. Note that Endosulfans were found at higher levels for some individual samples near Buna (2015, 2017, 2018), Semani (2017 and 2018) and in Shkumbini river mouths (2018). These data could be the result of Endosulfan's punctual source in agricultural areas near these

ecosystems. It's not excluded the recent use of Endosulfan in water basins of Buna, Semani, Shkumbini and Erzeni rivers. Endosulfan could be in use in these areas under false trade name. Endosulfan concentrations for water samples of Buna, Semani, Shkumbini and Erzeni rivers were 5 to 10 times higher than permitted level based on EU Directive 2013/39. The presence of Endosulfane in surface water samples must be lower than 0.005 ug/l.

Figure 6. Endosulfanes in water samples of Adriatic Sea

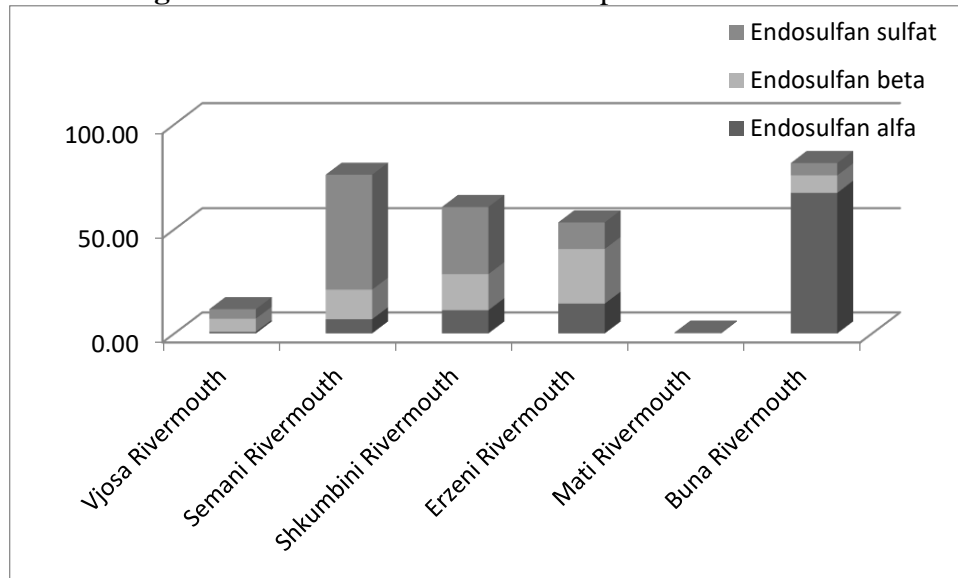


Figure 7. PCB markers in marine water samples of Adriatic Sea

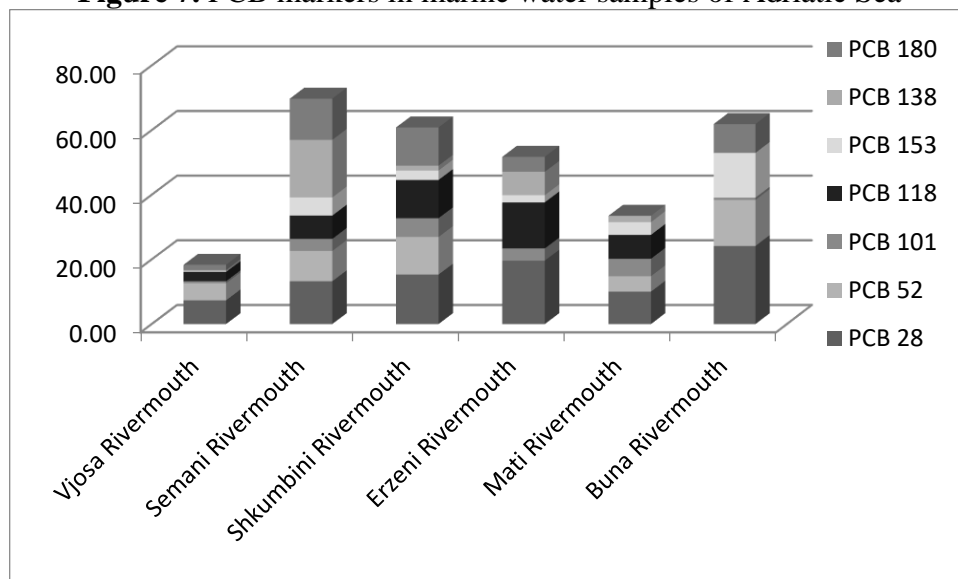
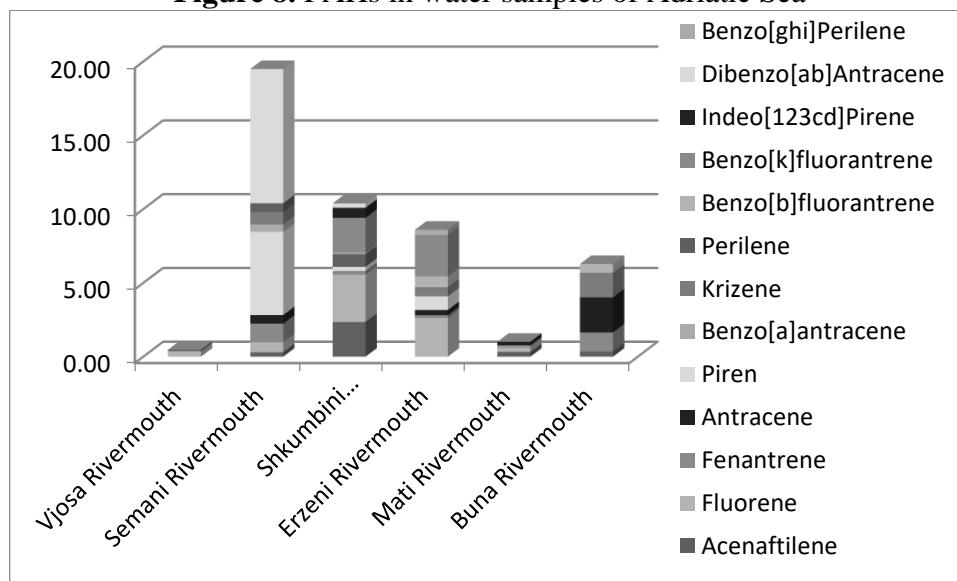


Figure 7 shows the total PCB markers in water samples of Adriatic Sea near six river estuaries for 2015–2019 periods. PCBs were found in all analyzed samples. They were found in this rate: Semani (69.4 ng/l) > Buna (60.7 ng/l) > Shkumbini (60.2 ng/l) > Erzeni (50.5 ng/l) > Mati (31.1 ng/l) > Vjosa (16.7 ng/l). The higher concentrations of PCBs in Semani, Shkumbini dhe Buna rivers can be related to the elevated industrial activity in their water basins. For all water samples, volatile congeners (PCB 28 and PCB 52) were found at higher level. This fact is connected with the atmospheric deposition. For Semani, Shkumbini, Buna, and Erzeni rivers were detected relatively high level of heavy PCB congeners (PCB 180) that is connected with punctual sources of these pollutants. Some industries that can influence PCB levels 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 comparable levels than the reported data on previous studies on the same stations (Murtaç et al. 2014; Como et al. 2013, Nuro et al. 2017).

Figure 8 shows totals of 13 PAHs according to EPA 525 Method in water samples of Adriatic Sea measured by the GC/FID technique. PAHs were detected for all samples under study. They were found in higher concentration for station near Semani River with 19.2 ug/l. Their presence could be because of extracting-processing oil industry in Patos-Marinza area that is part of its basin. Ship transport could be another source of PAH pollution in marine water samples of Adriatic Sea. Dibenzo [ab] anthracene and Chrysene were the most abundant peaks for water samples near Semani River. Average levels of PAHs were relatively high near Shkumbini (10.1 ug/l), Erzeni (8.4 ug/l) and Buna (6.0 ug/l) while in Mati and Vjosa their levels were in LOD (limit of detection) for the GC/FID technique. The presence of some individual PAHs in higher level was noted. Also, this could be a momentum value of PAHs depended on sampling periods. PAH levels in seawater samples near Semani were higher than the reported levels for other ecosystems of Albania (Nuro et al., 2014). The presence of some individual PAHs was higher than permitted level according to Albanian and EU norms.

Figure 8. PAHs in water samples of Adriatic Sea



CONCLUSION

Organochlorine pesticides, their residues, PCBs and PAHs were found in all water samples of Adriatic Sea. The higher level was found near Semani and Shkumbini river mouths because of new arrivals from waters from channels of Myzeqeja field (the main field on Albania). It was noted presence of degradation products of pesticides in higher levels. This fact is connected with the previous use of pesticides in Albania and their degradation process. Endosulfan was shown to be in high level in all samples. This pesticide could be in use in agricultural areas near these rivers under false trade name. PCBs volatile were found at high levels for all seawater samples. Their presence could be because of their atmospheric deposition. In marine water samples near Shkumbini, Buna and Semani river mouths were found heavy PCB. This could be connected with punctual sources of PCBs in these stations or a momentum value. Also, PAHs were found at higher levels for Semani River because of extracting-processing

industry in Patos-Marinza area. Concentrations of some individual organochlorine pesticides and PAHs were found in higher concentrations than permitted levels for surface waters according to EU Directive 2013/39 and Albanian norms. Monitoring of organic pollutants in water of Adriatic Sea should be continuous because of its importance in fishing, tourism, recreation and Albania economy overall.

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