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Research Article

ORGANIC POLLUTANTS IN THE WATER AND SEDIMENT SAMPLES OF THE ALBANIAN IONIAN SEA, SARANDA PORT

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Abstract – The findings reported here belong levels of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAH) in water and sediment samples of Albanian Ionian Sea. Stations from the port of Saranda were selected for this study. The activity in the ports areas is the main reasons for water pollution by chemical substances. Water currents can influence their levels. Some of these substances that present high risks (because of the high toxicity) are classified as priority substances.

Water and sediment samples were taken in February 2023 for 8 stations of Saranda's port. Organochlorine compounds (pesticides and PCB markers) were extracted simultaneously by water samples by using liquid-liquid technique and n-Hexane as extracting solvent. Their extraction in sediment samples was realized by using ultrasonic technique assisted by n-Hexane/$MeCl_2$ mixture (extracting solvent). PAHs were extracted in water samples by using two steps liquid-liquid technique. Firstly by using $MeCl_2$ and after that n-Hexane as extracting solvent. PAH extraction in sediment samples was realized by using ultrasonic technique assisted by using n-Hexane/Acetone as extracting solvent. Analyzes of priority substances was performed using agas chromatograph (Varian 450 GC) equiped with ECD and FID detectors.

Organochlorine pollutants (pesticides, their degradation products and PCB) were detected in all water and sediment samples because of their previous use and/or atmospheric deposition. New arrivals from water current can influence their levels. PAHs were found in more than 50% of water and sediment samples. Their presence could be because of ship transport in port area, automobilist transport and spillages of gasoil stations or mechanical businesses. The found levels for these priority substances in water and sediment samples of Saranda port were lower than reported levels of them from other ports of Albania.

Keywords – Saranda Port, Organochlorine Pesticides, Pcbs, PAH, Water Analyze, GC/ECD/FID

I. INTRODUCTION

In this study, the concentrations of some priority substances in water and sediment samples for Saranda Port were determined. This port is located in the Ionian Sea, in southern Albania. This port is mainly used for passenger transport, for tourist boats, and for fishing boats. This is the largest port in the Ionian Sea, and there is a plan for its further expansion since Saranda is a very popular destination for tourists, especially during the summer months. The Ionian Sea is one of the two seas that wet the shores of Albania. The coast is high and rocky, with many natural beauties. The Ionian Sea is well known to boaters for its calm winds. It is up to 5121 meters deep. The rivers of Pavlla, Kalasa, Bistrica, Kalama, etc. flow into the Ionian Sea. The negative impact of these rivers that bring new arrivals of pollutants (pesticides, hydrocarbons, detergents, etc.) as well as the internal and external water currents are not excluded as factors that affect the pollution of the Ionian Sea, especially in the Saranda area. This area is affected by this pollution, which is added to by ships, automobile transport, and commercial import and export that operate on it.

Organochlorine pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and benzene are classified as persistent organic pollutants (POP) because they are persistent for many years after their application (Shayler et al., 2009). Great concern was caused by chlorinated compounds, which proved to be extremely persistent in the environment and then in the food chain (Penttila & Siivinen, 1996; WHO & FAO, 1983; Wilhelm et al., 2002). For more than 50 years (after the Second World War to 1990), organochlorine pesticides were widely used in Albania for agricultural purposes. The main agricultural areas are located in the western part of the country, near the Adriatic Sea. The use of pesticides in Albania after 1990 decreased rapidly due to migration and immigration. PCBs were not in use in Albania until the 1990s. 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 their atmospheric depositions. PAHs and BTEX are pollutants generated by automobile transport, the extracting and processing of oil, coal mining, and other industries.

These hydrocarbons could be found in marine water because of ship transport or accidental spills of hydrocarbons. Forest fires and their natural background make them very common in the environment. These pollutants 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 aquatic ecosystems (Corsi et al., 2010; Nuro et al., 2012). Generally, these compounds are difficult to degrade and can persist for many years, in particular in aquatic ecosystems (Corsi et al., 2010; Nuro et al., 2014). They can be absorbed easily by suspension particles and organic mass in water and concentrate in sediments at levels several times higher than in water (Stogiannidis and Laane, 2015; Wang et al., 2009).

II. Materials and Method

Water and sediment sampling in Saranda port

Water and sediment samples were taken at 11 different stations in the port of Saranda. Samples were taken in February 2023. The sampling stations for water and sediment samples in Saranda Port were the same (Figure 1). A quantity of 2.5 liters of marine water was taken from each station and placed in Teflon bottles. Van Veen grape was used for sediment sampling. The sampling method was based on ISO 5667-3:2018. Water and sediment samples were transported and conserved at +4 oC prior to their analysis.

Figure 1. Sampling stations in the port of Saranda, February 2023

Treatment of water samples for pesticide and PCB analyzes

Liquid-liquid extraction was used for the extraction of organochlorine pesticides and polychlorinated biphenyls from marine water samples. One liter of water and 50 ml of n-hexane as the extraction solvent were added in a separatory funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removal. A florisil column was used for the sample clean-up. 20 ml of n-hexane/dichloromethane (4/1) were used for elution. After concentration to 1 ml hexane, the samples were injected into GC/ECD (Lekkas et al., 2004; Vryzas et al., 2009; Nuro et al., 2012).

Treatment of sediment samples for analyzes of chlorinated pollutants

The sediments were air-dried and then ground in a porcelain mortar. After that, they were sifted. Only the 63 micron fractions were taken into analysis. For the determination of organochlorine pollutants, 5 g of sediment samples were taken from the stations of the Patok Lagoon and placed in a 100 ml beaker, where 40 ml of n-hexane/dichloromethane (3:1) were added as an extraction solvent. Their extraction was carried out in an ultrasonic bath for 60 minutes at 30 oC.After separation of the organic phase, 2 g of anhydrous sodium sulfate was added to remove traces of water. The solvent was evaporated using Kuderna-Danish to 10 ml. Metallic mercury was added to the test tube until the complete removal of sulfur compounds, which are usually found in sediment samples and which hinder the gas chromatographic analysis. The extract is carefully transferred to an open glass column (10 cm x 0.8 cm) packed with florisil. The elution was carried out with 20 ml of n-hexane/dichloromethane (4:1) and collected in Kuderna-Danish, where it was evaporated to blockterm in 2 ml. The extract was injected into the gas chromatograph equipped with an ECD detector.

Gas chromatography analysis of pesticides and PCBs

Organochlorine pesticides and PCBs were analyzed simultaneously using capillary column type Rtx-5 (30 m long x 0.25 mm i.d. x 0.25 μm film thickness) on a gas chromatograph Varian 450 GC with an ECD detector. Helium was used as a carrier gas (1 ml/min) and nitrogen as a make-up gas (24 ml/min).The manual injection was done in splitless mode at 280°C. The organochlorine pesticides detected were DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), HCHs (a-, b-, γ- and d-isomers), Heptachlors (Heptachlor and Heptachlorepoxide), Aldrines (Aldrine, Dieldrine, and Endrin), and Endosulfanes (Endosulfan alpha, Endosulfan beta, and Endosulfat). The 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 was based on an external standard method (Vryzas et al., 2009; Lekkas et al., 2004; Nuro et al., 2014).

Treatment of water samples for PAH analyzes

Two-step liquid-liquid extraction (LLE) was used for extracting PAHs from marine water samples. One liter of water with firstly 30 ml of dichloromethane (first step LLE) and then 30 ml of hexane (second step LLE) as extracting solvents were added in a separator funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removal. Extracts were concentrated to 1 ml hexane using Kuderna-Danish and then injected in GC/FID for qualification and quantification of PAHs (Nuro et al., 2014; Wang et al., 2009; Lekkas et al., 2004).

Treatment of sediment samples for PAH analyzes

Only the 63 micron fractions were taken into analysis. For the determination of chlorine-organic pollutants, 5 g of sediment sample was taken from the stations of the Patok Lagoon and thrown into a 100 ml beaker, where 40 ml of n-hexane was added as an extraction solvent. Their extraction was carried out in an ultrasonic bath for 30 minutes at 30 oC. After separation of the organic phase, 2 g of anhydrous sodium sulfate was added to remove traces of water. The solvent was evaporated using Kuderna-Danish to 2 ml. The extract was injected into the gas chromatograph equipped with a FID detector.

Determination of PAH by using GC/FID apparatus

Gas chromatographic analyses of PAHs in water samples were realized with a Varian 450GC instrument equipped with a flame ionization detector and PTV injector. VF-1 ms capillary column (30 m x 0.33 mm x 0.25 μm) was used for the qualification and quantification of 13 PAHs according to the EPA 525 Method. Helium was used as the carrier gas at 1 ml/min. The 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 flow rates of 30 ml/min and 300 ml/min, respectively. EPA 525 Standard Mixture was used for qualitative and quantitative analyses of PAHs. 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 PAHs was based on an external standard method (Nuro et al., 2014; Wang et al., 2009; Lekkas et al., 2004).

III. Result AND Discussion

In this study were evaluated levels of some priority substances (organochlorine pesticides, PCBs, PAH and BTEX) in seawater samples from ports of Durresi and Vlora, Adriatic Sea. Samples were taken in July 2022 because of the intense ship activity during this period (2–3 times higher than in normal periods of the year). These are the main ports of Albania for passengers and commercial shipping. Organochlorine pesticides, their degradation products, and PCB markers were analyzed using GC/ECD techniques. Polycyclic aromatic and volatile hydrocarbons were analyzed using GC/FID techniques. OCPs, PCBs, PAHs, and BTEX were classified as priority substances because of their stability and toxicity. Monitoring them in seawater is important not only for the environment but also for the organisms (including humans).

Organochlorine pesticides were detected in all water samples analyzed from the port of Saranda (Figure 2). The average values of OCPs in sediment were 9.61 ug/kg, while those in water samples were 8.8 ug/l. The highest level of pesticides in the water samples was at station 7 (30.1 ug/l) and station 10 for sediment samples (16.8 ug/kg). The presence of OCPs must be due to their previous uses in agricultural areas near the Saranda, the impact of discharges by rivers and effluents (new arrivals because of soil rinsing from other areas of Albania), water currents inside/outside, punctual sources near the port, etc.

Figure 3 shows the dendogram of the cluster analysis for the total of OCPs in stations in Saranda. It can be seen that there are three main groups of stations. The first group are ST1, SP2, SP3, and SP9, with a similarity level greater than 80%. The similarity with this group is also SP11, but the level of similarity is lower (60%). The second group is the values found for SP7 and SP8. The similarity between the first and second groups is about 55%. The third group is SP4, SP6, SP5, and SP10. The level of similarity between them is 75%. The great similarity of pollution between stations is related to the same origin of pollution in these stations.

Figure 4 shows the profile of OCP in water and sediment samples in the port of Saranda. The profile of OCP classes for water and sediment samples was: Chlordanes > Endosulfanes > Heptachlores > Aldrins > DDTs > HCH. The highest concentrations for pesticide individuals were found for alfa-chlordane, endosulfane sulfate, endosulfane II and endosulfan I. The presence of chlordanes and endosulfanes in higher concentrations could be mainly due to terrestrial sources and water currents (new arrivals from rivers). Physical-chemical properties of pesticides (water solubility, persistence, degradation rate, the ability to bind with suspended matter, etc.) affect their profile. Recent use of these pesticides and punctual sources of these pollutants are not excluded.

Figure 5 shows the dendogram of the cluster analysis for each individual pesticide in the water and sediment samples of the port of Saranda. It can be seen that there is a high level of similarity between 15-DDT and 21-Mirex. After them come: 1-alpha-HCH, 2-beta-HCH, 3-Lindane, 20-Methoxychlor, 18-Endrin aldehyde, and 19-Endrin ketone, which make up the first group at a reliability level greater than 80%. The second group is 11-DDD, 12-Dieldrin, and 13-DDE. The third group is made up of 4-delta-HCH and 5-heptachlor. The level of reliability between these groups is greater than 70%.

Another group with a similarity level of about 65% was 7-Heptachlor epoxide, 14-Endrin, and 9-gamma-Chlordane. 8-Endosulfan I and 16-Endosulfan II make up the fifth group with about

60% similarity. 17-endosulfan sulfate and 10-alpha-chlordan have a lower similarity than other pesticides due to high levels in some stations.

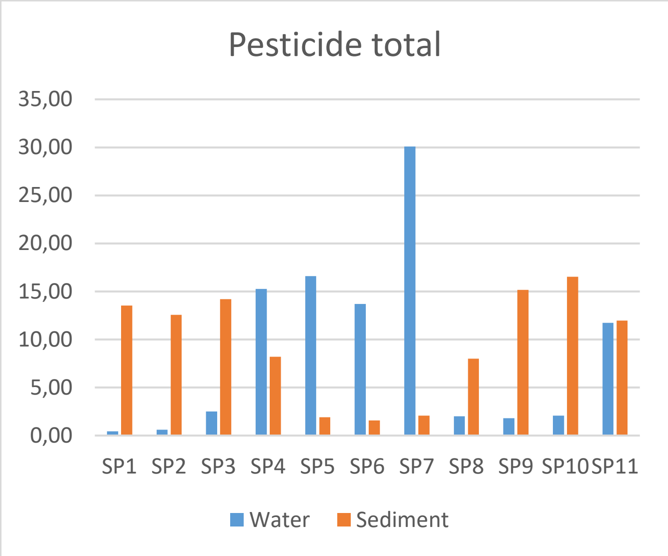

Figure 2. Total of organochlorine pesticides in water and sediment samples of Saranda's port

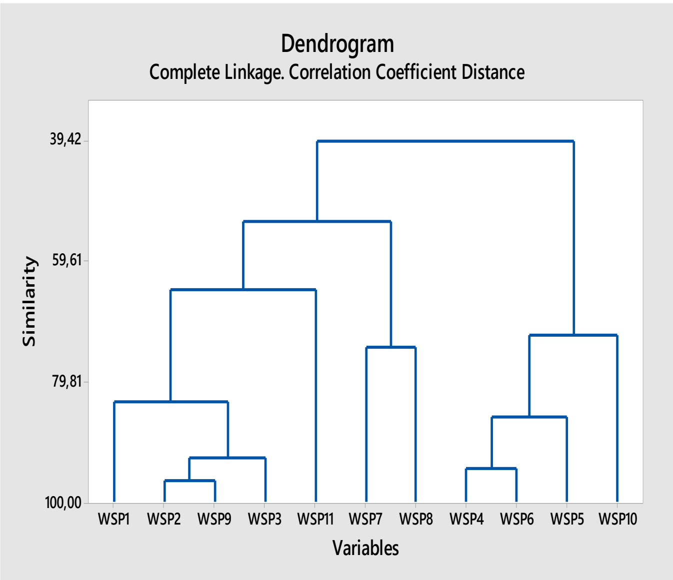

Figure 3. Dendogram of pesticides in sample stations of Saranda's port

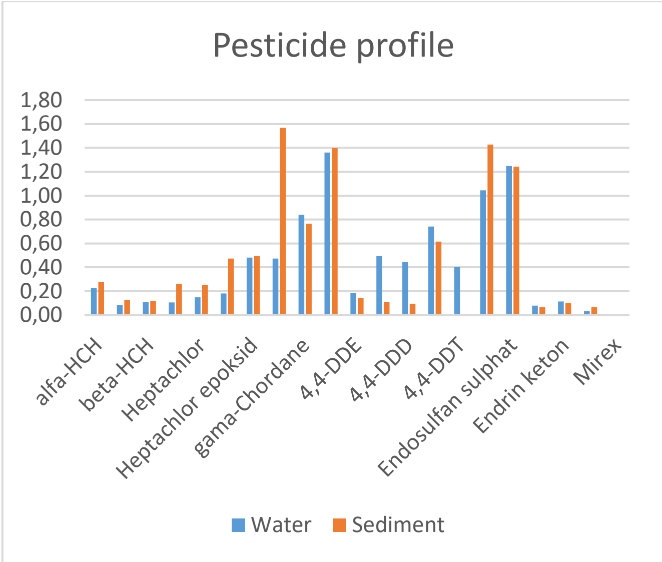

Figure 4. Profile of organochlorine pesticides in water and sediment samples of Saranda's port

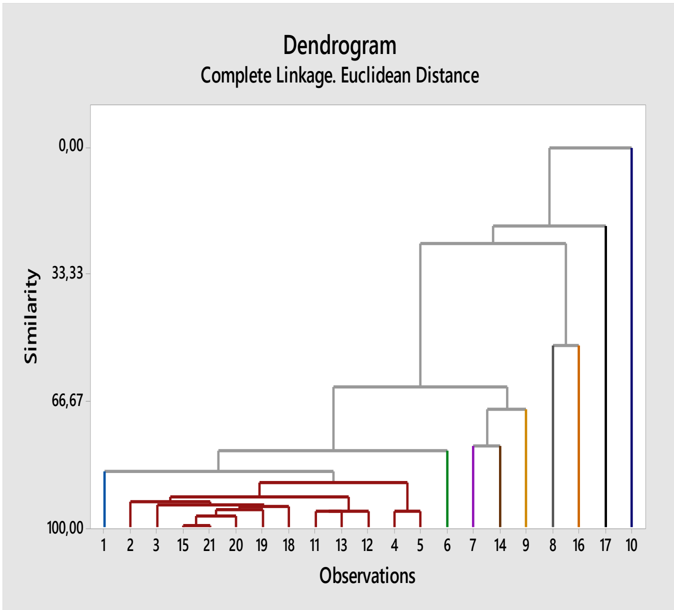

Figure 5. Dendogram of organochlorine pesticides in water and sediment samples

PCB were detected in all water and sediment samples analyzed from the port of Saranda (Figure 6). The average values of PCB in sediment were 4.3 ug/kg, while those in water samples were 4.4 ug/l. The higher level of PCB in the water and sediment samples was in station 6. The presence of PCBs must be due to their atmospheric deposition, mechanical processes, incineration of urban waste, etc.

Figure 7 shows the dendogram of the cluster analysis for the total PCB in the stations of Saranda. It can be seen that there are three main groups of stations. The first group are ST1, SP7, SP3, SP8, and SP9, with a similarity level greater than 90%. The second group is the values found for SP2, SP4, SP5, and SP6. The similarity in the second group was about 85%. The third group is SP10 and SP11. The level of similarity between the first and second groups was about 60%, while the third group has the lowest reliability level (about 37%).

Figure 8 shows the profile of PCBs in water and sediment samples in the port of Saranda. The profile of PCBs in water and sediment samples was: PCB 28 > PCB 52 > PCB 138 > PCB 209 > PCB 180 > PCB 101 > PCB 153 > PCB 138. Volatile PCBs have the highest level, which indicates their atmospheric origin in this area. The presence of heavy PCBs indicates the presence of point sources in these stations.

Figure 9 shows the dendogram of the cluster analysis for each PCB individual in the water and sediment samples of the port of Saranda. It can be seen that there are two main groups: In the first group, there are 1- PCB 28 and 2- PCB 52, which are representatives of volatile PCBs. In the second group, there are 3- PCB 101 and 7- PCB 180 which have similarities with 4- PCB 153 and 5- PCB 118 which have similarities greater than 80 %. This group also includes 8- PCB 209 and 6- PCB 138. These groups represent the two main sources of PCB pollution in the area of Saranda.

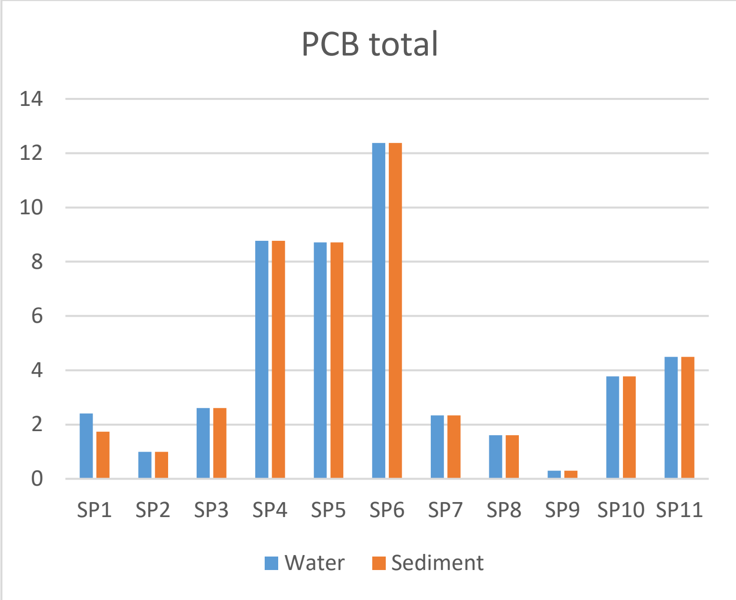

Figure 6. Total of PCBs in water and sediment samples of Saranda's port

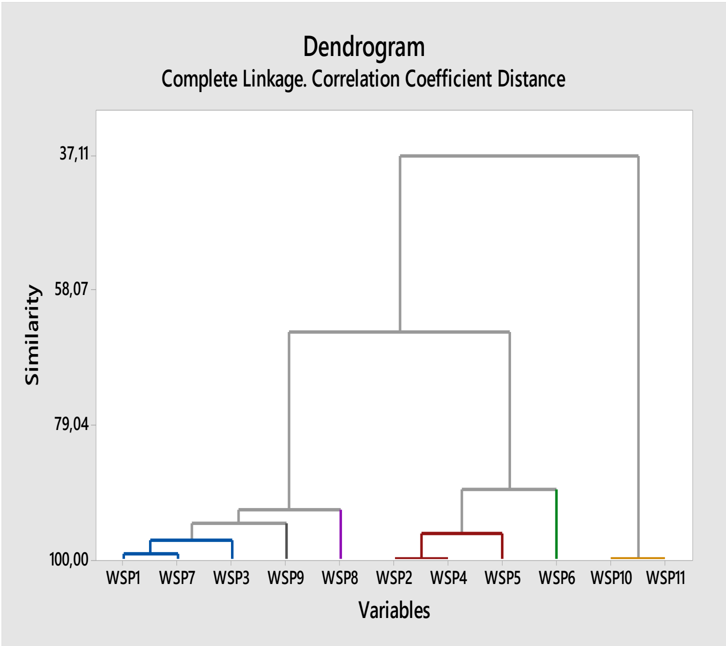

Figure 7. Dendogram of PCBs in sample stations of Saranda's port

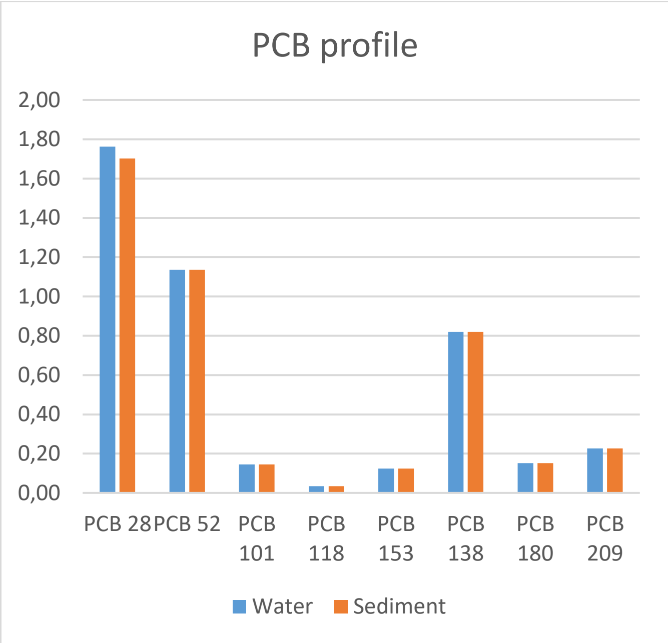

Figure 8. Profile of PCBs in water and sediment samples of Saranda's port

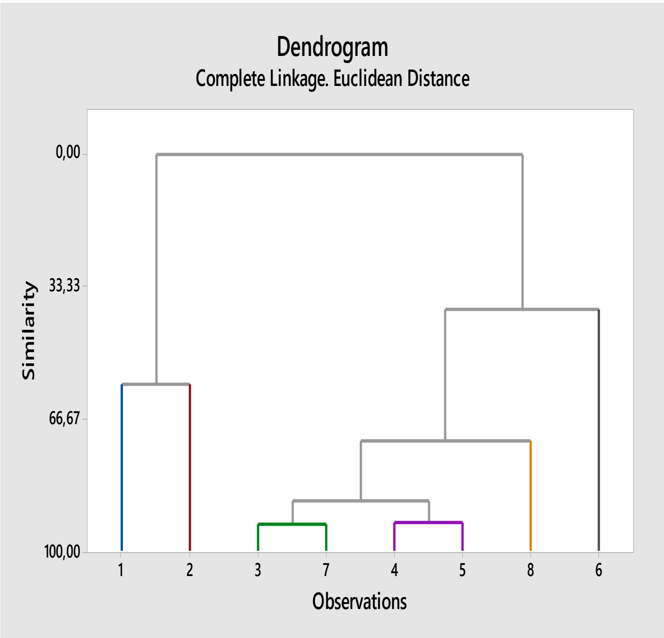

Figure 9. Dendogram of PCBs in water and sediment samples of Saranda's port

AH were detected in all water and sediment samples analyzed from the port of Saranda (Figure 10). The average values of PAH in sediment were 3.0 ug/kg, while those in water samples were 3.6 ug/l. The higher level of PAH in the water samples was in station 2 while in sediment samples was in station 8. The presence of PAH must be due to ship transport, automobile transport, spillages from gas stations and/or accidents, burning processes, etc.

Figure 11 shows the dendogram of the cluster analysis for the total PAH in stations in Saranda. It can be seen that 4 are the main groups of stations. The first group is SP1, SP6, and SP9, with a similarity level of less than 50%. The second group is the values found for SP4, SP5, and SP10. The similarity in the second group was about 65%. The third group is SP8 and SP11 (80%), while the fourth group is SP3 and SP7 (75%). The level of similarity between the groups was about 30%. This fact shows that the origin of pollution at each of the stations is different.

Figure 12 shows the profile of PAH in water and sediment samples in the port of Saranda. The profile of PAH for water samples was: Benzo[f]fluoranthrene > Pyrene > Benzo[ghi]perylene > Benzo[ab]anthracene > Benzo[k]fluoranthrene. The PAH profile in sediment samples was: Fluorene > Benzo[ghi]perylene > Acenaphthylene > Phenanthrene. Pyrogenic PAHs have the highest level in water, while in sediment there are PAHs of natural origin.

Figure 9 shows the dendogram of the cluster analysis for each individual of PAH in the water and sediment samples of the port of Saranda. It can be seen that five are the main groups with a similarity level greater than 65%. First group: 1- Acenaphthylene and 8- Perylene; Second group: 7- Chrysene and 11- Indeo[123cd]Pyrene; Third group: 3- Phenanthrene and 4- Anthracene; Fourth group: 2- Fluorene and 12- Dibenzo[ab]Anthracene and fifth group: 5- Pyrene and 13- Benzo[ghi]Perylene. 10- Benzo[k]fluoranthrene, 6- Benzo[a]anthracene and 9- Benzo[b]fluoranthrene have the lowest level of similarity. This is related to the origin of PAH pollution in the area of the port of Saranda.

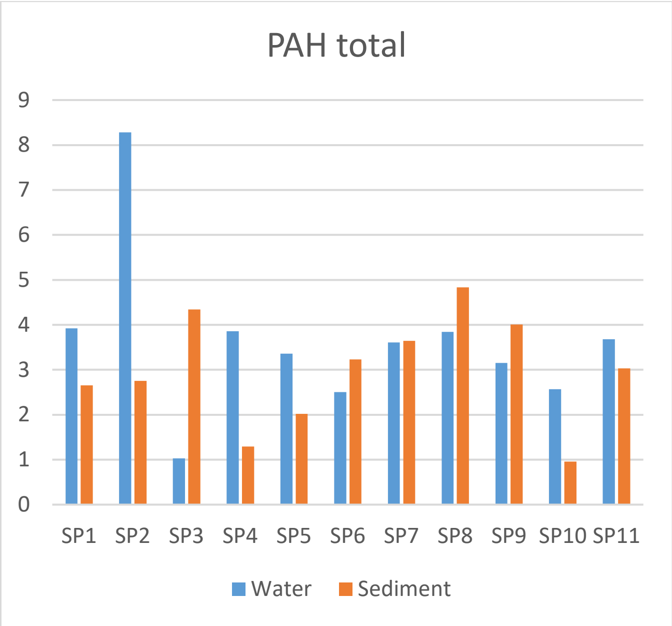

Figure 10. Total of PAH in water and sediment samples of Saranda's port

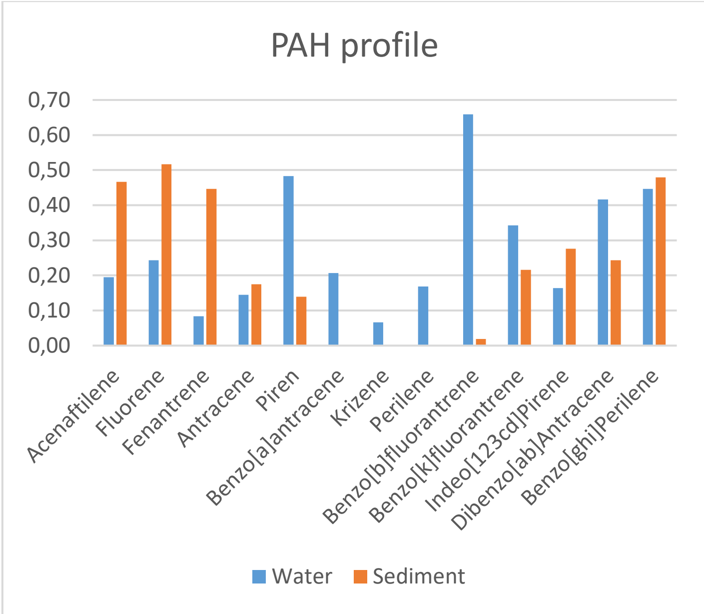

Figure 12. Profile of PAH in water and sediment samples of Saranda's port

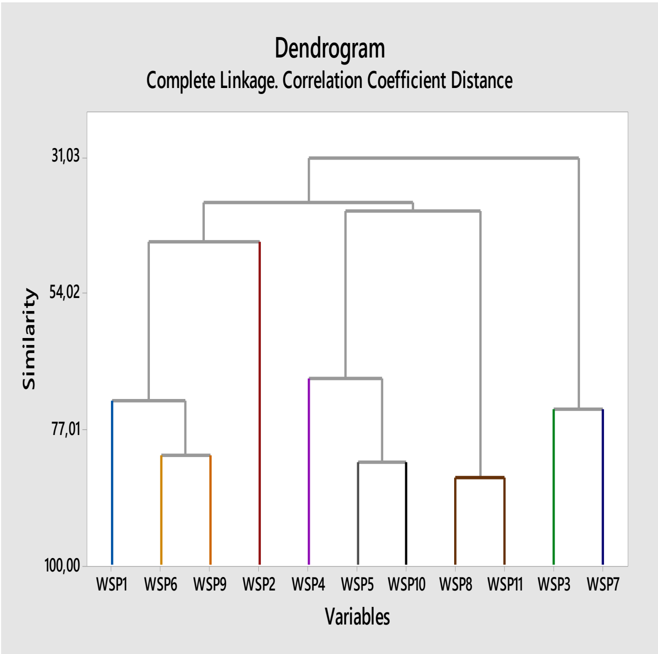

Figure 11. Dendogram of PAHs in sample stations of Saranda's port

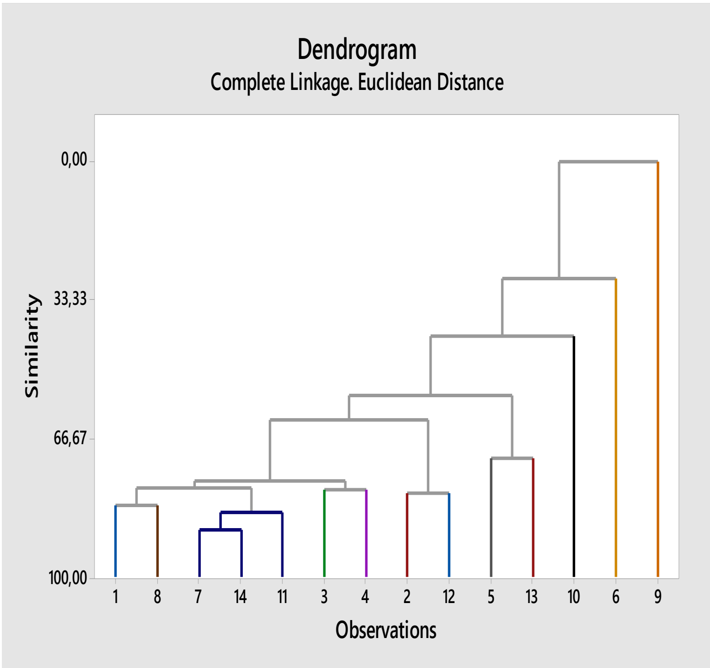

Figure 13. Dendogram of PAH in water and sediment samples of Saranda's port

IV.CONCLUSION

Priority substances were found in all water samples from Saranda Port. The levels of organochlorine pesticides, PCBs, and PAHs were found in water and sediment samples from the port of Saranda because of elevated activity near this area. Pesticides were found due to their previous uses in agricultural areas near the port, new arrivals by rivers/efluents, water currents, punctual sources near the ports, etc. Degradation products of pesticides were found at higher levels compared to their active products. This fact is connected with the previous use of pesticides in Albania and their degradation process. The presence of PCBs and PAHs in seawater and sediment samples can be related to elevated ship transport, industrial activity in the cities of Durresi and Vlora, and atmospheric deposition. Mechanical activities could be a terrestrial source of PCBs and hydrocarbons in the stations of Saranda Port.

Levels of individual organochlorine pesticides, PCBs, and PAHs in water and sediment samples from Saranda Port were lower than permitted levels for surface waters according to EU Directive 2013/39 and Albanian norms. Monitoring of organic pollutants in the water of Saranda Port should be continuous because this area could be affected by many sources of pollution.

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VI. REFERENCES

[1] Akkanen J, Tuikka A, Kukkonen JVK (2005) *Comparative sorption and desorption of benzo[a]pyrene and 3,4,3',4'-tetrachlorobiphenyl in natural lake water containing dissolved organic matter.* Environ Sci Technol 39(19):7529–7534

[2] Corsi I., Tabaku A., Nuro A., Beqiraj S., Marku E., Perra G., Tafaj L., Baroni D., Bocari D., Guerranti C., Cullaj A., Mariottini M., Shundi L., Volpi V., Zucchi S., Pastore A.M., Iacocca A., Trisciani A., Graziosi M., Piccinetti M., Benincasa T., Focardi S. (2010): “Ecotoxicologial assessment of Vlora Bay (Albany) by a biomonitoring study using an integrated approach of sub-lethal toxicological effects and contaminants levels in bioindicator species”. Journal of Coastal Research, Special Issue 58 - Coastal Research in Albania: Vlora Gulf [Tursi & Corselli]: pp. 116 – 120. DOI:10.2112/SI_58_1

[3] Directive 2008/105/EC of The European Parliament And Of The Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council

[4] ISO 5667-3:2018, Water quality — Sampling — Part 3: Preservation and handling of water samples

[5] Lekkas Th., Kolokythas G., Nikolaou A., Kostopoulou M., Kotrikla A., Gatidou G., Thomaidis N.S., Golfinopoulos S., Makri C. (2004) *Evaluation of the pollution of the surface waters of Greece from the priority compounds of List II, 76/464/EEC Directive, and other toxic compounds,* Environment International, Volume 30, Issue 8, Pp. 995–1007

[6] Magi E., Bianco R., Ianni C., Di Carro M. (2002) *Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea,* Environmental pollution, Vol. 119, Pp. 91–98

[7] Mandić J. and Vrančić M.P. (2017) *Concentrations and origin of polycyclic aromatic hydrocarbons in sediments of the middle Adriatic Sea,* Acta Adriatica: International Journal of Marine Sciences, Vol 58(1), Pp. 3 - 24, 2017

[8] Marini M. and Frapiccini E. (2013) *Persistence of polycyclic aromatic hydrocarbons in sediments in the deeper area of the Northern Adriatic Sea (Mediterranean Sea),* Chemosphere, Volume 90, issue 6, pp. 1839-1846

[9] Murtaj B., Nuro A., Como E., Marku E., Mele A. (2013) “Study of Organochlorinated Pollutants in Water Samples of Karavasta Lagoon” Science Bulletin of Faculty of Natural Sciences, Tirane, Nr 14 Pp 178-185

[10] Nuro A., Marku E., Murtaj B., Mance S., (2014) “Study of Organochlorinated Pesticides, their Residues and PCB Concentrations in Sediment Samples of Patoku Lagoon” International Journal of Ecosystems and Ecology Sciences (IJEES), Vol 2, Issue 1, Pp. 15-20

[11] Stogiannidis E, Laane R (2015) *Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: an overview of possibilities.* Rev Environ Contam Toxicol 234:49–133.

[12] Wang B, Yu G, Yu YJ, Huang J, Hu HY, Wang LS (2009) *Health risk assessment of organic pollutants in Jiangsu Reach of the Huaihe River,* China. Water Sci Technol 59(5):907–916