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## A survey of water quality in areas of Albanian ports

### ABSTRACT

*This study reports data on physical-chemical parameters and on concentrations of organic pollutants in marine water samples of Albanian ports. Nutrients, PH, temperature, conductivity, TSS, DO, BOD, COD, chlorines, sulfates, magnesium and calcium ions were the indicators used for evaluation of water quality. Also, organic pollutants (organochlorine pesticides, PCBs, PAH and benzene) were determined in seawater samples. Albania is facing by Ionian and Adriatic seas in a coastline of more than 300km. Several ports are in function in Albanian coastline. Ship transport and many activities (automobile transport, mechanical activities, deposits, etc.) are the main factors of water pollution in port areas. Water samples from seven ports (the main Albanian ports) starting from Saranda port in the South to Shengjini port in the North, were analyzed in this study. Sampling was realized in May 2023.*

*Based on physical-chemical indicators the water in the port of Saranda was the cleanest water, while Porto-Romano, Petrolifera and the fishing port in Zvernec was the most polluted one. Organic pollutants were detected in all water samples. Presence of the degradation products of pesticides may be related with previous uses of them. Presence of PCBs can be because of atmospheric deposition (volatile congeners), water currents and mechanical businesses (heavy congeners). PAHs and Benzene were detected on more than 70% of the analyzed samples. Intense ship and automobile transport in the port areas, mechanical businesses discharge and hydrocarbon processing (Petrolifera and Porto-Romano) can be main factor for their presence. Water currents and new arrivals from the rivers can influence the levels and profile of pollutants. The found levels of organic pollutants in water samples of Albanian ports were higher than reported levels in previous studies for the Adriatic Sea (Albania coastline).*

**Keywords:** Albanian ports, Physical-chemical parameters, Organic pollutants, Water analyzes

### 1. INTRODUCTION

Albania facing by Ionian and Adriatic in a coastline of about 316km of which 260 km belong to the Adriatic Sea [1-3]. Trade and communications through the sea have been used since ancient times, which is confirmed by numerous remains found along the coast. Many small harbors and boat anchorages have been and continue to be used along the coast. They are mainly located in small natural bays such as Saranda, Shengjini or in large natural bays such as the bay of Vlora (Note that, in Vlora Bay are several important ports such as Vlora's port, Petrolifera - hydrocarbon port, Marina's port for Delta Force near Radhima, Military Base of Orikum and a fishing harbor near

Zverneci). Some other ports are built artificially such as the port of Durres, Porto-Romano, Petrolifera, etc. The construction/function of ports promote the development of these areas, cities, encourage population growth, impact in economic aspect, employment and nowadays the development of tourism and increased communication/exchange with other countries [1, 2].

In the port areas have an intense activity not only in the marine but also in terrestrial areas near the port. Marine transport of ships/ferries/boats, their anchorages, mechanical/technical services to them, cleaning/sanitization of their interiors, import/export trade (cereals, minerals, hydrocarbons, etc.), the storage of many materials/food/chemicals near the ports, the movements of cars/cranes and other mechanical equipment in port areas are the main reasons why there is generally expected a higher pollution compare to other coastal areas. In many cases, discharges by urban pollution and the various businesses that operate near the port areas can be added. In the

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other side, the construction of ports, usually in areas that have depth and protected in the form of a bay, favors the concentration of pollutants inside the port areas. The effects of water currents in/out ports or the new arrivals from the rivers/effluents (even distant from the port) can bring pollution from areas that may be far from the ports[1-3].

The possibility of pollution for the port areas and the lack of information about the quality of marine waters were the main reasons for undertaking this study in which some of the most important indicators (physical-chemical parameters) such as pH, temperature, DO, BOD, COD, TSS, nutrients and some other ions such as chlorides, sulfates, calcium and magnesium have been determined. The values of these parameters are directly related to the quality of marine waters in these areas [2,4-7]. In addition to them, the concentrations of organochlorine pesticides according to EPA 8081B, marker PCBs, Benzene and 13 PAH according to EPA 525 have also been determined. These organic pollutants are classified as priority substances due to their persistence and high toxicity. Although some of them are not common pollutants of ports, they have been reported in various works due to various accidents and/or the influence of water currents. These data will help us and authorities to determine the quality of marine waters in the main Albanian ports according to national and international norms [6, 8] and also identify the possible factors that influence their presence in the analyzed samples.

## 2. MATERIAL AND METHODS

### *Water sampling in Albanian ports*

To evaluate water quality and water pollution at the ports of Albania and their impact in the sea were analyzed a total of 64 water samples (38 samples inside and 26 samples outside port areas) from seven different ports (Figure 1) starting from Saranda's port (South Albania) to Shengjin's port (North Albania). Sampling stations were as follows: 9 stations at Saranda's port (WSP); 12 stations at Vlore's port (WVP); 8 stations at Petrolifera (WPP); 6 stations at fishing port, Zvernec (WZP); 12 stations at Durres's port (WSP); 9 stations at Porto-Romano (WPR) and 8 stations at Shengjin's port (WSH). Water samples were collected in port areas in May 2023. This sampling period represents a normal period for the activities in these ports. In each sampling station, 2.5 L of sea water were collected in glass bottles equipped with Teflon caps, based in ISO 5667-3: 201 Method [9]. Water samples were stored and transported at 4°C to the laboratory for further analysis. For each station pH, conductivity, DO (Dissolved oxygen) and temperature were determined in field by using

Hanna Multiparameter -portable equipment (HI98194 Model).



Figure 1. Sampling stations in the main ports of Albania

### *Determination of BOD<sub>5</sub>*

VELP brand automatic sensors (respirometers) were used to estimate the 5-day biological oxygen demand (BOD<sub>5</sub>) in seawater. The measurement was carried out at a level of 250 ppm. The samples were placed at 20°C for 5 days, and a direct reading of the BOD value was made for each sample [9].

### *Determination of COD*

For the determination of chemical oxygen demand (COD), SPEC COD digestion tubes were used, which use standard 16-mm tubes pre-prepared with mercury sulfate (HgSO<sub>4</sub>). 2 ml of seawater was taken in the pre-filled COD digestion tube, close the cap and mix vigorously for 1 minute. The tube was placed in the thermo-reactor ECO 16, set at 150°C. After being heated for 2 hours, the samples were cooled at room temperature, then measured in a PF-3 spectrophotometer at wavelengths suitable for COD analysis [10].

### *Analyse of nutrients and sulfates by using SPUV-VIS method*

The UV-VIS measurements of nutrients (nitrates, nitrites ammonium, N-Total, Phosphates and P-Total) and sulfate ions were carried out in the UV 31 SCAN ONDA model spectrophotometer as follows: The analysis of NO<sub>3</sub> in water is based on the ISO 7890-3: 1988 method for their determination with the spectrophotometry

technique at a wavelength of 420 nm. The analysis of NO<sub>2</sub> in water is based on the ISO 6777: 1984 method for their determination by the colorimetric method at 540 nm. The analysis of NH<sub>4</sub> in water is based on the ISO 7150/1:1984 method for their determination with the spectrophotometry technique at 655 nm. N-total was determined using complete disaggregation of the sample with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and determination of nitrogen at two wavelengths: 220 nm and 275 nm. All forms of nitrogen are oxidized and measured as NO<sub>3</sub> (Screening Method). P-total was determined using the disaggregation method, which aims to oxidize all forms of phosphorus into PO<sub>4</sub> ions and further make their determination using the spectrophotometer method at 880 nm. The analysis of sulfates in water is based on method 9038 for the determination of sulfates by the turbidimetry method at a wavelength of 420 nm [2, 6, 9].

#### *Determination of Cl<sup>-</sup> (salinity), Ca<sup>2+</sup> and Mg<sup>2+</sup> by titration methods*

Chloride ions were determined in seawater samples using the argentometric method (4500-Cl<sup>-</sup> B, Argentometric Method, known as the Mohr method). The data obtained for chloride ions in seawater were used to calculate the salinity of the samples. The concentration of calcium ions in seawater was realized by using the titration method with EDTA in the presence of the indicator Ericrom black T (3500-Ca B). Magnesium ions have been determined in seawater using the titration with MgCl<sub>2</sub> of the complex forming Mg<sup>2+</sup> with EDTA (3500-Mg B, C) [6, 9].

#### *Determination of TSS (Total Suspended Solids) in seawater*

The analysis of total suspended solids (TSS) in water was based on their determination by the gravimetric method. The water is filtered using 32 mm diameter glass filters with 0.45 µm pores in a vacuum filtration system. TSS is calculated from the difference of the weights before and after filtration. The conditioning and drying of the filters was done in the thermostat for 8 hours at 105°C [9].

#### *Water treatment for pesticide and PCB analyses*

For the determination of OCPs and PCBs in water samples was used liquid-liquid extraction. One liter of water sample was extracted with n-hexane (2 x 40 ml) in a separatory funnel. After extraction, the organic phase was dried with anhydrous sodium sulphate Na<sub>2</sub>SO<sub>4</sub> (5 g) for water removal. A florasil column was used for the sample clean-up. 20 ml n-hexane/dichloromethane (4/1) was used for elution. After concentration to 1 ml

hexane, the samples were injected in GC/ECD [3, 4, 11, 12].

#### *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 in diameter x 0.25 µm film thicknesses) on a gas chromatograph (Varian 450 GC) with electron capture detection (ECD 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 splitless mode at 280°C. The 21 individuals of organochlorine pesticides according EPA 8081B were: DDT-related chemicals, HCH isomers, Heptachlor's, Chlordanes, Aldrin's and Endosulfanes. Analysis of PCBs was based on the determination of the seven PCB markers (IUPAC No. 28, 52, 101, 118, 138, 153 and 180). Quantification of OCPs and PCBs was based on external standard method by using five calibration points as follow: 1 ppb, 2 ppb, 5 ppb, 10 ppb and 25 ppb. The R<sup>2</sup> various form 0.9452 (Endrin keton) to 0.9965 (b-HCH) and the LOD for each individual OCP and/or PCB markers was 0.05ppb [3,4,11].

#### *Treatment of water samples for PAH analyses*

Two steps liquid-liquid extraction (LLE) was used for extracting PAHs and Benzene from sea water samples. One liter of water with firstly 40 ml dichloromethane (first step LLE) and after that 40 ml hexane (second step LLE) as extracting solvent was added in a separator funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na<sub>2</sub>SO<sub>4</sub> for water removing. Extracts were concentrated to 1 ml hexane using Kuderna-Danish and then were injected in GC/FID for qualification/quantification of PAHs [1, 13-16].

#### *Gas chromatography analysis of PAHs in water samples*

Gas chromatographic analyses of PAHs and Benzene in water samples were realized with a Varian 450 GC 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 qualification and quantification of 13 PAHs according EPA 525 Method. 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 Standard Mixture was used for qualitative and quantitative analyze of aromatic hydrocarbons. Benzene, 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 external standard method by using six calibration points as follow: 1ppm, 2.5ppm, 5 ppm, 10 ppm, 25 ppm and 50 ppm. The  $R^2$  various form 0.8912 (Indeo [1,2,2-cd] pyrene) to 0.9964 (Anthracene) and the LOD for each PAH (including Benzene) was 0.05ppm[1,13,15].

### 3. RESULTS AND DISCUSSION

In this study, water samples from 64 different stations from the main ports of Albania were analyzed. Water samples were taken in May 2023 from the ports of Saranda, Vlora, Petrolifera, fishing port (Zvernec), Durrës, Porto-Romano and Shengjin. The physico-chemical parameters were determined in water samples were: temperature, pH, Conductivity, DO, BOD5, COD, TSS, NO<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub>, N-total, P-Total, sulfates, chlorides (salinity), ions calcium and magnesium.

The analysis of organic pollutants includes: organochlorine pesticides, their degradation products (21 individuals according to EPA 8081B), PCB markers (7 congeners), Benzene and PAHs (13 individuals according to EPA 525). All methods used for the determinations of physico-chemical indicators and organic pollutants were based on the Albanian and international norms recommended for these analyzes in marine and surface waters.

#### *Physical-chemical parameters*

The average data of measurements of physico-chemical parameters for water samples from port stations in Albania was as follows: The average pH of the water samples was in the range from 7.6 for the port of Saranda to 8.2 in Porto-Romano. These slightly basic pH values are suitable for the growth of living organisms in marine waters. The average seawater temperature at the time of sampling was from 17.6°C in the port of Saranda to 22.8°C for the water of Porto-Romano. These temperatures are normal for the seawater in the month of May. Port water conductivity ranged from 38.8 ms/cm for the port of Shengjin to 60.0 ms/cm for Petrolifera. These values indicate relatively high levels of electrolytes in these waters, which is expected both from the salinity of the sea water and from other ions that come from urban/industrial/agricultural pollution [2, 5, 6].

The maximum value for dissolved oxygen in seawater was for the port of Saranda with 10.8 mg/l, while the minimum value for DO was in the fishing port, Zvernec, with 8.3 mg/l. The limit of 5 mg/l is not exceeded for 2 samples in the fishing port, Zvernec, 2 samples in Porto-Romano and 1

sample in Shengjin port. In general, waters are classified as good according to these DO values. BOD5 values ranged from 25.3 mg/l in the port of Saranda to 132.6 mg/l in Porto-Romano. These values classify the marine waters of the ports as moderately good. The minimum COD value was in the port of Saranda with 50.8 mg/l, while the maximum was again for Porto-Romano with 129.7 mg/l. These values are influenced by the presence of chemicals in the water samples. These COD values classify the analyzed water as very good for Saranda port and moderately good for other ports [5-7]. The analysis of particles in suspension (TSS) showed that their value was from 31.9 mg/l in the port of Saranda to 141.1 mg/l for the port of Shengjin. These values classify the waters of the analyzed ports from good (Saranda port) to moderately good (other ports) [6]. Levels of nutrients in Albanian ports were as follows: The minimum concentration of NO<sub>3</sub> in the waters of the Albanian ports was for the port of Saranda with 0.5 mg/l. Note that, for more than 60% of NO<sub>3</sub> samples were not detected in the water of this port. The maximum was for the samples analyzed from Petrolifera with 8.6 mg/l. The concentration of nitrites in the water samples had an average value from 0.006 mg/l in the waters of the port of Saranda to 0.46 mg/l for the port of Durrës. The average concentration of NH<sub>4</sub> was from 0.004 mg/l (Saranda port) to 0.58 mg/l (Vlora port). N-total in analyzed water samples ranged from 0.17 mg/l for the port of Saranda to 4.93 mg/l in Petrolifera.

The average value of PO<sub>4</sub> was in the interval between 0.026 mg/l in the port of Saranda to 9.0 mg/l for the port of Vlora. P-total measured in water samples was from 0.018 mg/l (Saranda port) to 4.7 mg/l for the port of Durrës. Nutrient values in the waters of Albanian ports indicate an impact of urban waste discharges and agriculture on seawater. Their levels classify the water of ports as moderately good. The flows for the rivers Vjosa and Semani (for the ports of Vlora Bay), Shkumbini, Erzeni, Ishemi (for the ports of Durrës and Porto-Romano) and the rivers Mat and Drin (for the port of Shengjin) have a strong influence on the found values for physical-chemical indicators as well as water quality. Rainfall amount, the direction of the wind and the wave's grade (at the time when the samples were taken) are factors that can affect in momentum values [2, 5 – 7]. The concentration of sulfates in the water samples ranged from 18.2 mg/l in the port of Shengjin to 521.2 mg/l for the fishing port in Zvernec. Their presence must be related to urban pollution, natural background, hydrocarbon spills, ship/automobilist transport, etc. The average value of chlorides and/or salinity in the analyzed port water was from 19.93 g/l (36.0 g/l) in the port of

Vlora to 20.38 g/l (36.8 g/l) in the port of Saranda and in the fishing port in Vlora. The Ionian Sea has a higher salinity than the Adriatic Sea and this was expected for Saranda port, while influence of the Narta Lagoon can affect the increase in chloride values for the fishing port in Zvrnec. The concentration of calcium ions was from 1.13 mg/l for the port of Durres to 7.1 mg/l for the port of Saranda, while the concentration of magnesium ions was from 0.44 mg/l for the port of Vlora to 3.76 mg/l for the port of Saranda. These values are related to both the natural background and the geological structure of the sampling stations [6, 7].

of organochlorine pesticides was as follows: Total of HCHs (a-, b-,  $\gamma$ - and d-isomers of Hexachlorocyclohexane) ranged from 0.4 ug/l (Saranda port) to 6.9 ug/l (Porto-Romano) ; Heptachlor's (Heptachlor and Heptachlorepoxyde) ranged from 0.1 ug/l (Saranda port) to 1.4 ug/l (Porto-Romano); Chlordanes (alpha and gamma-Chlordanes) ranged from 0.2 ug/l (Saranda port) to

1.0 ug/l (Porto-Romano); Aldrin's (Aldrine, Dieldrine, Endrin, Endrin aldehyde and Endrin ketone) ranged from 1.4 ug/l (Saranda port) to 5.3 ug/l (Durres port); DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT) ranged from 0.2 ug/l (ports of Saranda, Vlora, Petrolifera and fishing port of Zvrnec) to 0.9 ug/l (Porto-Romano) and Endosulfanes (Endosulfan alpha, Endosulfan beta and Endosulfan sulfate) ranged from 0.5 ug/l (Saranda port) to 4.0 ug/l (port of Durres). These data clearly shown that the port of Saranda was lower polluted by pesticides due to the stronger currents of the Ionian Sea and the smaller agricultural areas near this port. The most polluted ports with pesticides were Porto-Romano and the port of Durres. The production and storage of pesticides in Porto-Romano for a period of more than 30 years is the main reason. The new arrivals of pesticides from the rivers Shkumbin, Erzen and Ishem have impact on these values.

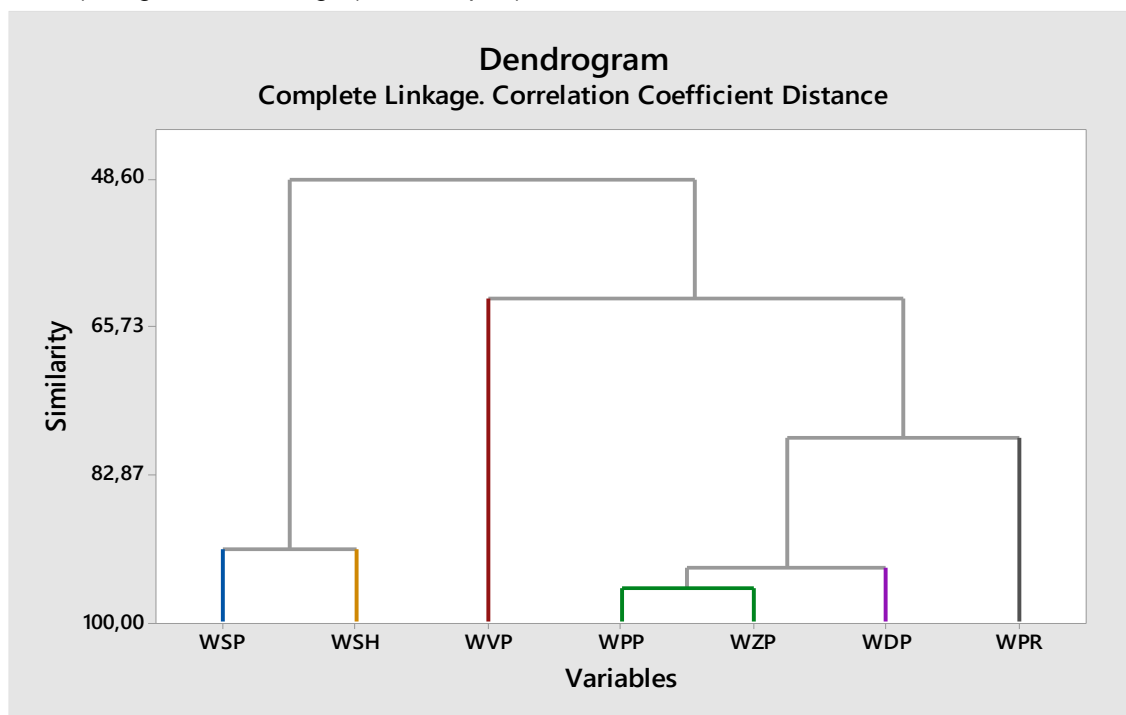


Figure 2. Cluster analyze for distribution of OCPs in Albanian ports

Figure 2 shows cluster analyzes for distribution of OCPs in Albanian ports. The results show that there are two main groups. In the first group were Saranda and Shengjini ports with a similarity level of 92.7%. These groups were built by ports with low level of pesticides. The second group, which is the largest group, includes Petrolifera and the fishing port, Zvrnec (similarity level 95.2%). Connected with them was port of Durres (similarity level 91.3%), Porto-Romano (similarity level 75.3%) and port of Vlora (similarity level 73.2%).

These ports showed higher levels of contamination for some of the individual pesticides and for their total too. Figure 3 shows the multifactorial cluster analysis data for each individual of the analyzed pesticides. There are five main groups of them as follows: The first group has three subgroups, a-HCH and b-HCH (similarity level of 98.6%), d-HCH and Heptachlor epoxide (similarity level of 96.5%) and Aldrine, Chlordane (similarity level of 97.2%) and Endosulfane I (similarity level of 87.1%). First and second subgroups were connected together

with a similarity level of 86.8% and with the third group with a similarity level of 74.3%. In the second group were two subgroups: Lindane, Methoxychlor (similarity level of 97.3%) and Endrin aldehyde (similarity level of 93.2%) are part of the first subgroup, while in the second DDE and DDT (similarity level of 93.5%). They are connected together with a similarity level of 74.4%. Endrin and DDD built together third group with a similarity level of 72.6%. The fourth group was built by Heptachlor, Dieldrine (98.3%), Endosulfan sulfate (86.6%), Endrin ketone (76.3%) and alpha-Chlordane (70.2%). Endosulfane II and Mirex were part of fifth

group with a similarity level of 53.3%. The first and second groups have a similarity level of 51.2%. The connection with the third group was less than 40%, while with the fourth and fifth groups they have a similarity level of less than 10%. These clusters were built by pesticides of the same class and/or the same concentrations. OCP concentrations in the water samples of Albanian ports were in the same range as data reported in previous studies in the Adriatic Sea [3,11,12]. For all analyzed samples levels of individual pesticides were below acceptable levels according to Albanian and EU standards[8].

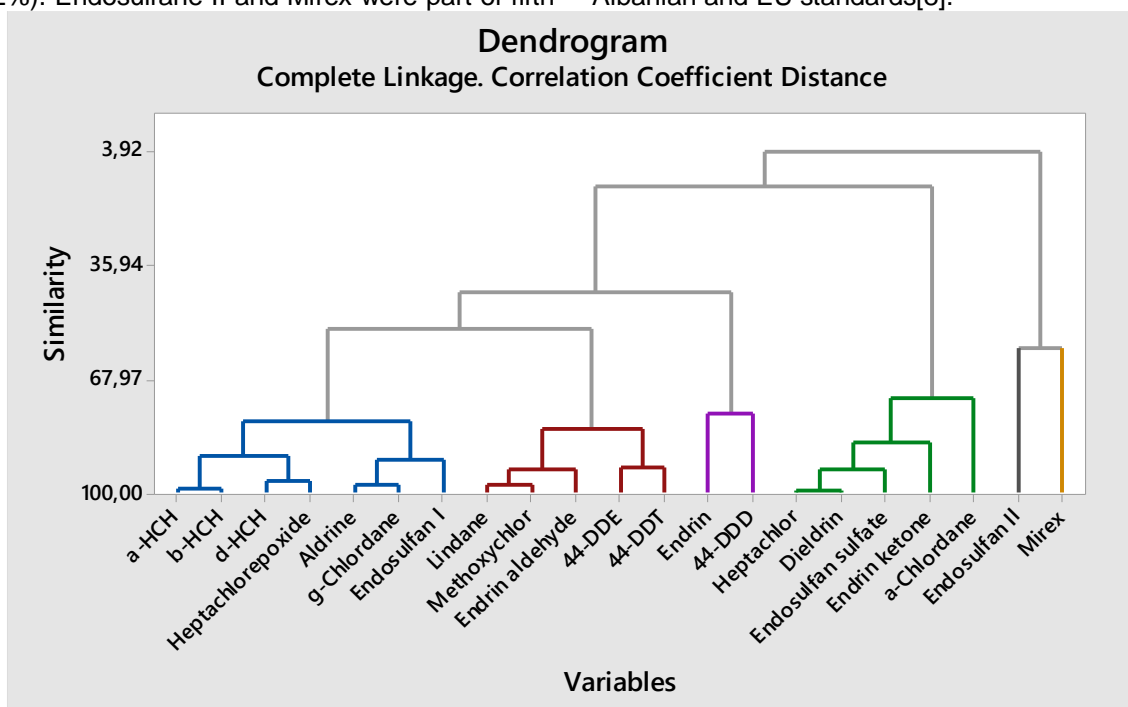


Figure 3. Cluster analyze for organochlorine pesticides (21 individuals) in water samples of Albanian ports

PCB markers were detected in more than 75% of analyzed samples from the Albanian ports. Their total concentrations ranged from 2.9  $\mu\text{g/l}$  (Saranda port) to 15.1  $\mu\text{g/l}$  (Durrës port). Their presence in seawater samples can be related to ship transport/anchorage/repair, industrial/mechanical activity near port areas, atmospheric deposition, water currents, and new arrivals from rivers and/or effluents. Oil discharges from some operations/repair of machineries and activities (in and out of the port) are likely terrestrial sources of PCBs and hydrocarbons in seawater samples. Figure 4 shows cluster analysis data for distribution of PCB markers in Albanian ports. Again, Saranda and Shengjin ports were grouped together with a similarity level of 97.6% because of low levels for PCBs. The higher similarity was for fishing port of Zverneci and Porto-Romano (99.1%) and for Vlora port and Petrolifera (98.2%) which were grouped

together in the second group, with a similarity level of 97.5%. Connected with them was Durrës port with a similarity level of 89.6%. This second group was connected with the first one with a similarity level of 65.2%. Note that water pollution with PCBs for all Albanian ports was almost in the same range (high level of similarity) because of the same pollution origin. Figure 5 shows cluster observation of PCB markers in the water samples of Albanian ports. It was noted that clusters were built in three main groups. In the first group were: PCB 52, PCB 118 (96.1%) and PCB 28 (93.6%). These volatile PCBs were detected frequently in all samples. PCB 153 and PCB 180 (95.2%) were part of the second group which was connected with the first group with a similarity level of 61.1%. The similarity level for PCB 101 and PCB 138 (third group) was 82.2%. The connection of the third group with the first and the second group was with a similarity level of

10.7%. These clusters were results of levels and profiles of PCB markers in water samples of Albanian ports. PCB levels for analyzed sea water samples were comparable to data reported in

previous studies in the Adriatic Sea [3, 11, 12]. The PCB levels were lower than the permitted level by Albanian and EU standards [8].

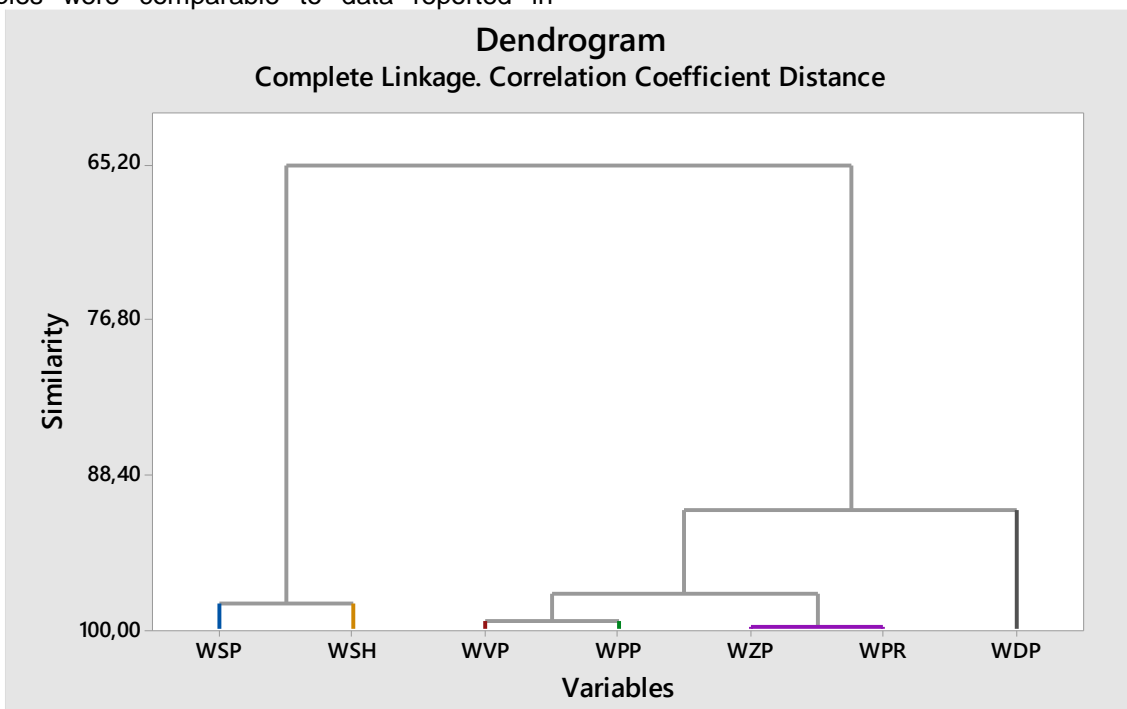


Figure 4. Cluster analyze for distribution of PCBs in ports of Albania

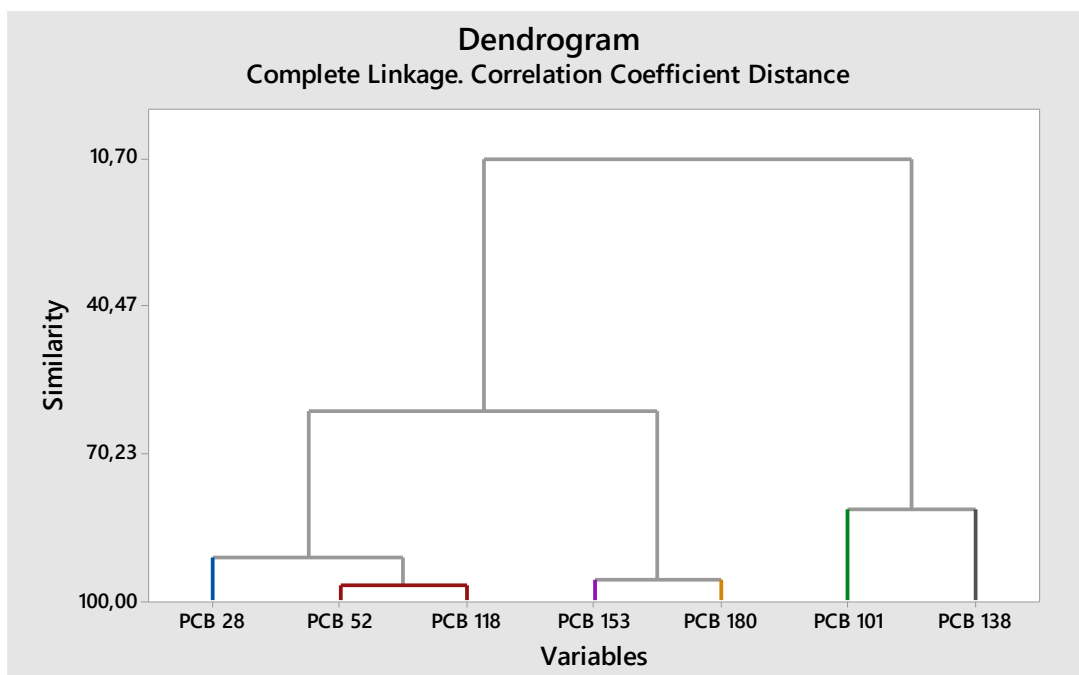


Figure 5. Cluster analyze for PCB markers in water samples of Albanian ports

PAHs and Benzene were detected in more than 60% of water samples analyzed from Albanian ports. The average value for 13 PAHs according EPA 525 standard was between 0.6 mg/l (Saranda port) and 2.9 µg/l (Petrolifera, hydrocarbon port of

Vlora) while for Benzene from 0.4 mg/l (Saranda port) to 2.2 mg/l (Porto Romano). The main reasons of hydrocarbon presence could be ship transport and any possible accident of hydrocarbons (in the port areas or near it),

mechanical activities near the port as well as some massive fires near these areas could be sources of hydrocarbons in marine water. Note that, the presence of some individual PAHs were found in higher level for some stations in Petrolifera, Durres and Porto-Romano. PAH presence was a

combination of non-pyrogenic PAHs (transport emitting, spillage of hydrocarbons, mechanical activities, etc) and pyrogenic PAHs (forest and urban waste burning, transport emitting, industrial activities, etc).

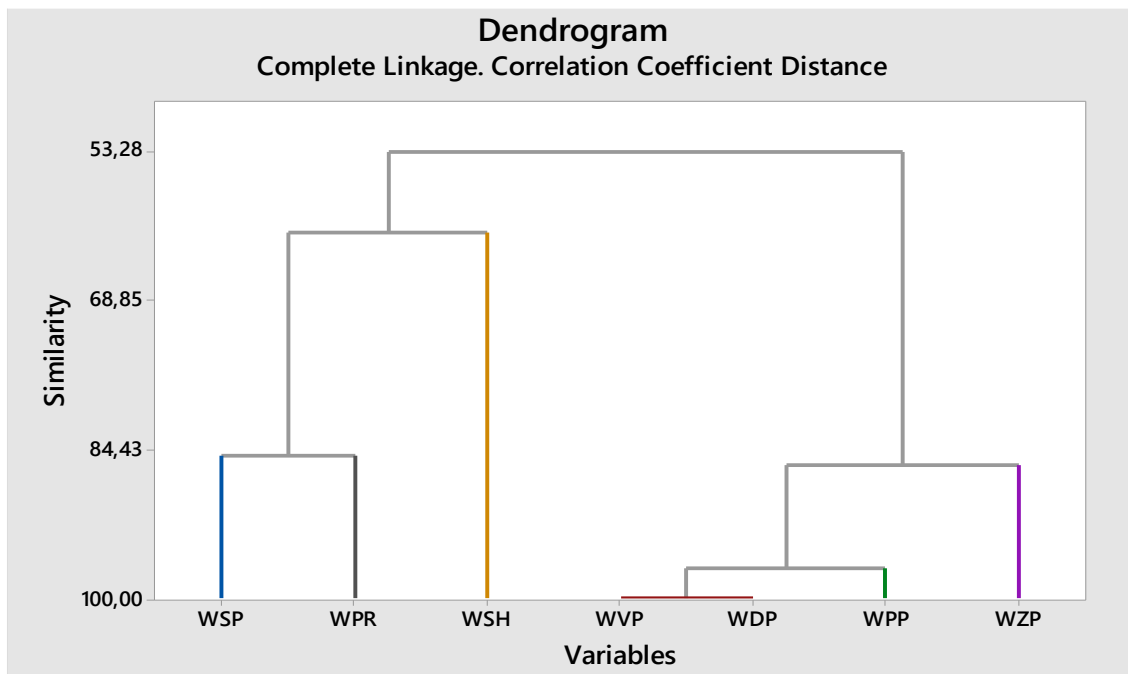


Figure 6. Cluster analyze for distribution of PAHs in water ports

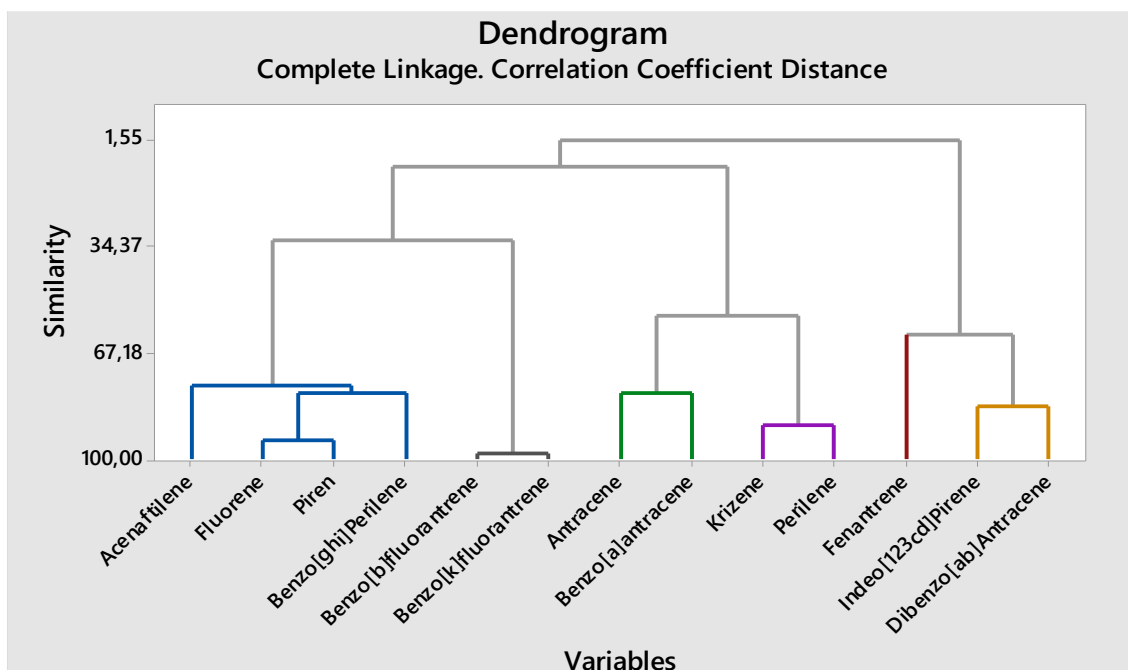


Figure 7. Cluster analyze for 13 individuals of PAHs in water samples of Albanian ports

Figure 6 shows cluster analyze data for distribution of 13 PAH according EPA525 in Albanian ports. In the first group were Saranda, Porto-Romano (84.5 %) and Shengjin ports (60.2

%) while in the second group were ports of Vlora, Durres (99.3%), Petrolifera (95.6%) and fishing port of Zverneci (85.1%). Both groups were linked together with a similarity level of 53.3%. Figure 7



shows clusters for PAHs in Albanian ports. It was noted presence of five main groups (clusters) as follows: In the first group were: Acenafilene, Fluorene, Pyrene and Benzo [ghi]perilene with a similarity level between 93.2 – 72.1%. In the second group were Benzo[b] fluornathrene and Benzo[k] fluoranthrene (98.3%) which was connected with first group (34.4%). In third group was Anthravene and Benzo[a] Anthracene (73.8%) while in the fourth group were Chrysene and Perilene (79.3%). These groups were connected together (50.2%) and with previous groups (7.3%). The last group was built by Indeo[123cd]Pyrene and Dibenzo[ab]anthracene (74.5%) and Fenantrene (65.7%). These clusters were results of levels and profile of PAHs in water samples. PAH levels in analyzed samples were in the same range/higher than the reported levels for other stations of Adriatic Sea, Albania [1, 13-16]. The presence of Benzene and Anthracene for some stations was higher than permitted level according to Albanian and EU norms [8].

#### 4. CONCLUSIONS

Data of physical-chemical parameters and the determination of organic pollutants in the water of the Albanian ports, shown that the waters of the port of Saranda were cleaner (very good) than other ports. The waters of the other ports were classified as good to moderately good. Anthropogenic activity can influence water quality. This comes mainly from the activities in the port areas, but also from urban pollution and/or agriculture, which are relatively far from the ports but flows from rivers and sea currents can affect them. The values reported in this paper generally do not have significant differences with previous works for the Adriatic Sea [2, 4, 5], however it can be said that these are momentum values and can be change quickly. For this, recommend that the physical-chemical parameters should be kept under continuous monitoring by the relevant institutions.

Pesticides, PCBs and PAHs were detected in water samples of Albanian ports. Their presence could be because of ship/automobilist transport, elevated activity near port areas, new arrivals from rivers, water currents, punctual sources, accidents, etc. Pesticide degradation products were found in high concentrations because of their previous use. The presence of PCBs and PAHs can be related to the transport, industrial/mechanical activity, atmospheric deposition and water currents. Statistical analysis of cluster showed a good connection between the pollutant levels and profile for each class of them. Levels of individual organochlorine pesticides, PCB markers, Benzene and 13 most toxic PAHs according to EPA in water samples were generally lower than permitted levels

for surface waters according to EU Directive 2013/39 and Albanian norms. Exception was for some individuals (in some stations) found relatively in higher concentration than others. Monitoring of organic pollutants in Albanian ports should be ongoing, because can be identify many sources of pollution that can affect them. Generally, their concentrations in water samples were similar to the reports made for the Adriatic Sea [3, 4, 11-16]. Continuous analysis of organic pollutants is recommended to realize by using GC/MS/MS and LC/MS/MS techniques.

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#### 5. REFERENCES

- [1] S. Froehner, J. Rizzi, L.M. Vieira, J. Sanes (2018) PAHS in water, sediment and biota in an area with port activities, Arch. Environ. Contamination Toxicology, 75(2):236-246, doi: 10.1007/s00244-018-0538-6.
- [2] S. Kane, P. Lazo, F. Qarri (2015) Environmental situation of Vlora Bay, Albania based on physical-chemical parameters of seawater, Austin Journal of Hydrology, 2, 112-119.
- [3] A.Nuro, E.Marku, M.Shehu (2012) Organochlorinated pesticide residues in marine water in the South of Albania". International Journal of Ecosystems and Ecology Sciences, 2, 27-34.
- [4] A.Mohammed, P.Peterman, K.Echols, K.Feltz, G. Tegerdine, A. Manoo, D. Maraj, J. Agard, C. Orazio (2011) Polychlorinated Biphenyls (PCBS) and Organochlorine Pesticides (OCPS) in Harbour Sediments from Sea Lots, Port-of-Spain, Trinidad and Tobago, Mar Pollut Bull, 62(6), 1324-32, doi: 10.1016/j.marpolbul
- [5] S.Kane, P.Lazo (2012) Assessment of environment situation and water quality of Vlora Bay and Narta Lagoon by nutrients and heavy metals determination. International Interdisciplinary Conference, Vlore, Albania, 26-28 November, ISBN 978-9928-4000-2-4.
- [6] S. Poikane, G.M. Kelly, S.F. Herreroa, Jo-A. Pitt, P.H. Jarvie, U. Claussen, W. Leuja, L.A. Solheim, H. Teixeira, G. Phillips (2019) Nutrient criteria for surface waters under the European water framework directive: current state- of-the-art, challenges and future outlook. Science of the Total Environment, 695, 133888. <https://doi.org/10.1016/j.scitotenv.2019.133888>
- [7] A. Campanelli, P. Fornasiero, M. Marini, (2004) Physical and chemical characterization of the water column in the Piceno coastal area (Adriatic Sea). Fresen Environ Bull. 13, 430-435.
- [8] [8] 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.
- [9] ISO 5667-3:2018, Water quality — Sampling — Part 3: Preservation and handling of water samples.
- [10] R. Baird, A. Eaton, E. Rice (2017) Standard Methods for Examination of Water and Wastewater, 23rd Edition, <https://doi.org/10.2105/SMWW.2882.216>.
- [11] A. Nuro, E. Marku, B. Murtaj, S. Mance (2014) Study of Organochlorinated Pesticides, their Residues and PCB Concentrations in Sediment Samples of Patoku Lagoon" International Journal of Ecosystems and Ecology Sciences (IJEES), 2(1), 15-20.
- [12] P. B. Lazar, L. Maslov, S.H. Romanić, R. Gračan, B. Krauthacker, D. Holcer, N. Tvrković (2011) Accumulation of organochlorine contaminants in loggerhead sea turtles, *Caretta caretta*, from the eastern Adriatic Sea. *Chemosphere*.82(1), 121-129.
- [13] A. Naglaa El-Naggar, I. Hosny Emara, N. Madelyn Moawad, A. Yosry Soliman, A. M. Abeer El-Sayed (2018) Detection of polycyclic aromatic hydrocarbons along Alexandria's coastal water, Egyptian Mediterranean Sea, The Egyptian journal of aquatic research, 44(1), 9-14.
- [14] E. Magi, R. Bianco, C. Ianni, M. Di Carro (2002) Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea, *Environmental pollution*, 119, 91–98.
- [15] J. Mandić, M.P. Vrančić (2017) Concentrations and origin of polycyclic aromatic hydrocarbons in sediments of the middle Adriatic Sea, *Acta Adriatica: International Journal of Marine Sciences*, 58(1), 3 - 24.
- [16] M. Marini, E. Frapiccini (2013) Persistence of polycyclic aromatic hydrocarbons in sediments in the deeper area of the Northern Adriatic Sea (Mediterranean Sea), *Chemosphere*, 90(6), 1839-1846.

## IZVOD

### ISTRAŽIVANJE KVALITETA VODE NA PODRUČJIMA ALBANSKIH LUKA

Ova studija daje podatke o fizičko-hemijskim parametrima i koncentracijama organskih zagađivača u uzorcima morske vode albanskih luka. Hranljivi sastojci, PH, temperatura, provodljivost, TSS, DO, BPK, COD, hlor, sulfati, joni magnezijuma i kalcijuma bili su indikatori koji su korišćeni za ocenu kvaliteta vode. Takođe, u uzorcima morske vode utvrđeni su organski zagađivači (organohlorni pesticidi, PCB, PAH i benzen). Albanija je suočena sa Jonskim i Jadranskim morem na obali dužoj od 300 km. Nekoliko luka je u funkciji na albanskoj obali. Brodski transport i mnoge delatnosti (automobilski transport, mašinske delatnosti, nanosi i dr.) glavni su faktori zagađenja vode u lučkim područjima. U ovoj studiji analizirani su uzorci vode iz sedam luka (glavnih albanskih luka) počev od luke Saranda na jugu do luke Shengjini na severu. Uzorkovanje je realizovano u maju 2023. godine.

Na osnovu fizičko-hemijskih pokazatelja voda u luci Saranda je bila najčistija voda, dok su Porto-Romano, Petrolifera i ribarska luka u Zvernecu bila najzagađenija. U svim uzorcima vode otkriveni su organski zagađivači. Prisustvo proizvoda razgradnje pesticida može biti povezano sa njihovom prethodnom upotrebom. Prisustvo PCB-a može biti zbog atmosferskog taloženja (isparljivi kongeneri), strujanja vode i mehaničkih poslova (teški kongeneri). PAH i benzen su detektovani na više od 70% analiziranih uzoraka. Intenzivan brodski i automobilski transport u lučkim oblastima, istovar mehaničkih preduzeća i prerada ugljovodonika (Petrolifera i Porto-Romano) mogu biti glavni faktor njihovog prisustva. Vodeni tokovi i novi dolasci iz reka mogu uticati na nivoe i profil zagađivača. Pronađeni nivoi organskih zagađivača u uzorcima vode albanskih luka bili su viši od nivoa prijavljenih u prethodnim studijama za Jadransko more (obala Albanije).

**Ključne reči:** albanske luke, fizičko-hemijski parametri, organski zagađivači, analize vode

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