

Priority substances in Adriatic Sea, Albanian coastline. Case study: Marine water for Durres and Vlore ports

Bledar Murtaj , Esmeralda Halo , Jonida Tahiraj, Sonila Shehu, Aurel Nuro* 

University of Tirana, Faculty of Natural Sciences, Department of Chemistry, Tirana, Albania

*Corresponding author: aurel.nuro@fshn.edu.al

(Received: May 9, 2024 / Accepted: September 3, 2024)

Abstract

The intense activities in port areas are the main reasons for water pollution by different pollutants. In this study are shown data of priority substances, due to their persistence and potential toxicity to aquatic organisms and human health. Concentration of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH) and BTEX (benzene, toluene, ethyl benzene and o-, m- p-xylenes) were determined in water samples of two main ports of Albania, Durres and Vlore ports. To assess the pollution status of these areas, water samples from inside/outside port areas of Durres and Vlore ports were collected in June 2022. Analyses of the organochlorine compounds and polycyclic aromatic hydrocarbons were performed using a gas chromatograph (Varian 450 GC) equipped with ECD and FID detectors. BTEX was analyzed using the HS/SPME technique, followed by the GC/FID technique for their qualification/quantification. Organochlorine pesticides and their degradation products were detected almost in all analyzed water samples. Their presence could be related to their previous use. PCBs, PAHs, and BTEX were found in more than 80% of analyzed samples. Higher levels were found at stations inside the port areas. Their presence was due to anthropogenic factors (intense activity and ship transport) in these areas. The reported levels of these priority substances in water samples from Durres and Vlore's ports were higher/comparable with those reported levels of them from Adriatic Sea (Albania coast). Water currents and new arrivals from the Albanian rivers can be considered as an important factor for the levels and profiles of analyzed pollutants. Although the production and use of OCPs and PCBs have been banned for decades, their presence continues to be reported because of their high persistence in the environment. This study should encourage the responsible institutions for the continuous analysis of these substances in port areas.

Keywords: durres and vlore ports, organochlorine pesticides, PCBs, PAH, BTEX, water analyse, GC/ECD/FID

Introduction

Many of port operations/means/mechanicals can have environmental impacts on the water and port areas. These operations can have a significant impact primary on water quality and as consequence at the marine life [1, 2]. Liquid/solid wastes from ships and other port activities can result in the pollution inside/outside port areas and harm marine life. In many studies, the marine environment has been established as a primary site for the accumulation of pesticides and other organic compounds [2, 3, 4]. Water and sediment are likely the main means of assessing the degree of marine pollution. The main types of pollutants entering the aquatic environment and their origins are organic compounds represented mainly by polycyclic aromatic hydrocarbons, pesticides, drugs, dioxins, phthalates, or inorganic compounds, which can be represented by metal compounds, nitrogenous materials, and phosphorus. Monitoring of marine pollutants is of great importance [1 – 6]. Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polycyclic aromatic compounds (PAHs) are among the most important persistent organic pollutants (POPs) suggested to be monitored in aquatic environments. These pollutants are well-known for their toxicity, persistence, and easy bioaccumulation affinity [5 – 10]. Persistent organic pollutants have various industrial, anthropogenic, and agricultural applications. For more than 50 years (after the Second World War to 90') organochlorine pesticides have been used widely 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 decreased rapidly after 1990 due to population migration/emigration [3, 4, 9, 19, 20]. PCBs were not used in Albania until 90'.

They can be found only in some electrical transformers that were used in the early 1990s. Note that, they have been reported in many water ecosystems in Albania because of their atmospheric depositions [3, 19, 20]. PAHs and BTEX are pollutants generated by automobile transport, extracting/processing in the oil industry, coal mines, and many other industries. These hydrocarbons can be found in marine water because of ship transport or accidental spills of hydrocarbons. Forest burning and their natural backgrounds make them very common in the environment [1, 3, 6].

The aims of this study were to determine the concentrations of OCPs, PCBs, PAHs and BTEX in seawater collected from two main ports of Albania and to identify potential sources of these contaminants in water. Durres and Vlore ports are located along the Albanian coastline of the Adriatic Sea. Durres is the largest port in Albania. It is an artificial basin formed between two moles and is located in the middle of the Adriatic Sea, to the South of the Durres City. In this port are proceeded around 77% of imports and 89% of Albanian exports. The main activities in this port are general cargo, grains, minerals, containers, and ferry boats. Port of Durres has a fishing harbor located at the northern end of the East Mole. From 2014, the port was ranked as the largest passenger port in Albania and one of the largest passenger ports in the Adriatic Sea. The hydrocarbon ports of Porto-Romano is located near this port (5 km distance). In the near future, the port area will be re-conceptualized and expanded as one of the largest ports of the Mediterranean Sea [3, 4]. The port of Vlore is the second largest port in Albania. It is located in Vlore Bay, near the city of Vlore, southern Albania. The port is considered part of the Lungomare Master Plan of Vlore. Part of this project is the construction of a yacht port and new roads to make the port area the most accessible. Until now, Vlore's port has been mainly a function of passengers and commercial shipping. Except, Vlore port in the Vlore Bay are located some other ports such as petroleum ports (Petrolifera near Zverneci), Marina port for Delta Force (near Radhima), Military Base of Orikumi, and a fishing harbor (near Zverneci). In the Vlore Bay are active some touristic ships and many small boats (motorized ones) which serve for tourist transportation [9].

Materials and Methods

Water sampling in Albanian ports

The water sampling was realized at the end of July, 2022. In Durres Port, 12 water samples (eight samples inside the port area and four samples around it) were collected, and 12 water samples (six samples inside the port area and six samples around it) were collected in Vlore port. This sampling period was chosen because of the intense activities in Albanian ports (from two to three times higher than the normal period). In each sampling point, 2.5 L of sea water were collected in Teflon bottles, based on ISO 5667-3: 201. The water samples were stored at +4°C and transported to the laboratory for further analysis using. The sampling stations for Durres and Vlore ports are shown in Figure 1.

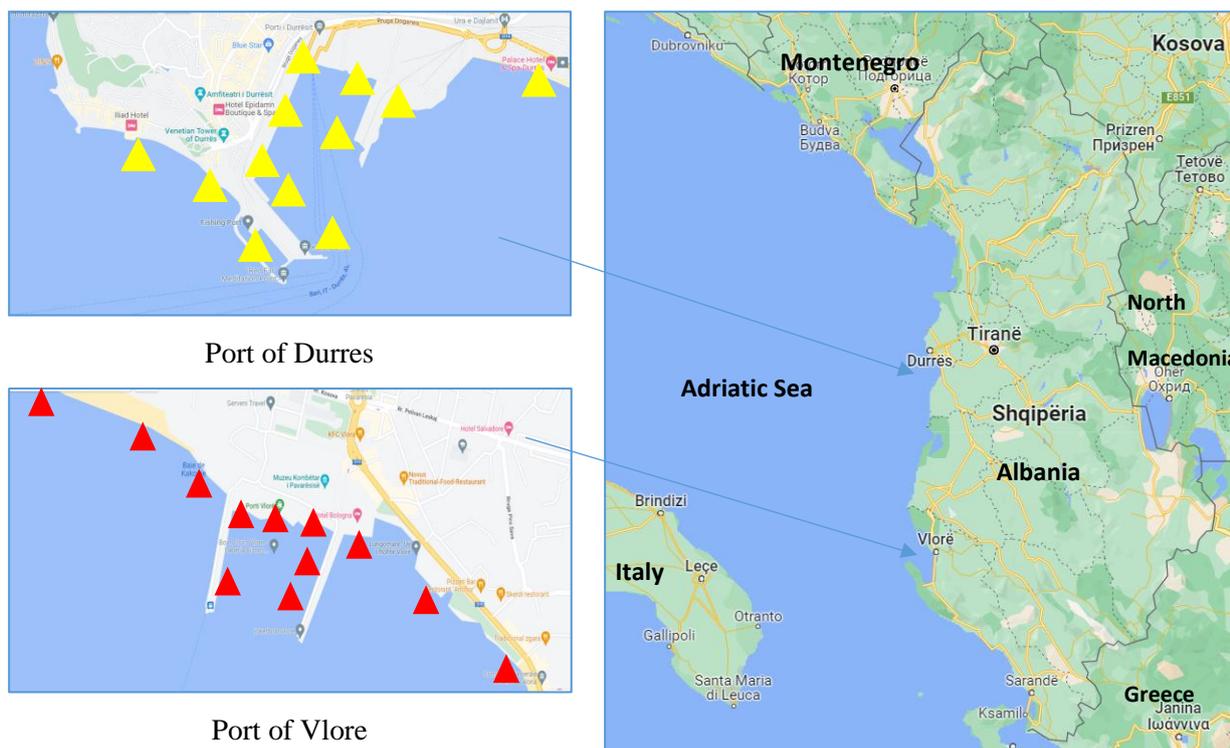


Figure 1. The sampling sites in Durres and Vlore ports, June 2022

Treatment of water samples for pesticides, PCBs and PAHs

Liquid-liquid extraction was used for the determination of OCPs and PCBs in the water samples. One liter of water was extracted using n-Hexane (2 x 40 ml) in a separator funnel. After extraction, the organic phase was dried by using Na₂SO₄ anhydrous (5 g) to remove water. A Florisil column was used for sample cleanup. 20 ml n-Hexane/Dichloromethane (4/1) was used for elution. After concentrating to 1 ml hexane, the samples were injected into the GC/ECD [12, 14, 17, 18 – 21].

Two-step liquid-liquid extraction (LLE) was used to extract PAHs from water samples. One liter of water with 40 ml Dichloromethane (first-step LLE) and 40 ml hexane (second-step LLE) as the extracting solvent was added to a separator funnel. After extraction, the organic phase was dried with 5 g) to Na₂SO₄ anhydrous for water removing. Extracts were concentrated to 1 ml hexane using Kuderna-Danish and then injected into the GC/FID for qualification/quantification of PAHs [4, 16 – 18, 21].

Gas chromatography analyze of organochlorine pollutants

Organochlorine pesticides and PCBs were analyzed simultaneously using capillary column type Rtx-5 (30 m long x 0.25 mm meter x 0.25 μm film thickness gas chromatograph (Varian 450 GC) with electron capture detector (ECD detector). Helium was used as the carrier gas (1 ml/min), and nitrogen was used as the make-up gas (24 ml/min). Manual injection was performed in splitless mode at 280°C. The organochlorine pesticides detected were: DDT-related chemicals (p,p-DDE, p,p-DDD, p,p-DDT), HCHs (α-, β-, γ- and δ-isomers), Heptachlor's (Heptachlor and Heptachlor epoxide); Aldrin's (Aldrin, Dieldrin and Endrin) and Endosulfanes (Endosulfan alpha, Endosulfan beta and Endosulfan sulfate). PCB analysis was based on the determination of seven markers (IUPAC number PCB 28, 101, 118, 138, 153, and 1,80). The quantification of OCPs and PCBs was based on an external standard method [3, 14, 15, 20].

Gas chromatography analysis of PAHs in water samples

The gas chromatographic analyses of PAHs in the water samples were performed using 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 maintained at 280°C. Nitrogen was used as the make-up gas (25 ml/min). Flame detector gases, hydrogen and air were at 30 and 300 ml/min, respectively. EPA 525 Standard Mixture was used for qualitative and quantitative analysis 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. PAH quantification was based on the external standard method [4, 16, 17, 21].

HS-SPME technique for determination of BTEX in water samples

The determination of BTEX in the water samples was performed using solid-phase microextraction in static head space mode (HS/SPME), followed by the GC/FID technique. 5 ml of the water sample was taken in a 10 ml head space vial. A PDMS fiber (100 μm) was used to extract BTEX from the water samples. The adsorption process was performed at 50°C (in a water bath) for 45 min while desorption process (30 seconds at 260°C) was performed using a PTV injector (HS mode was selected) of a Varian 450 GC instrument. VF-1 ms capillary column (30 m x 0.33 mm x 0.25 μm) was used for separation of Benzene, Toluene, Ethyl benzene and Xylene isomers. Helium was used as carrier gas with 1 ml/min. FID temperature was maintained at 260°C. Nitrogen was used as the make-up gas (25 ml/min). BTEX Mixture was used for qualitative and quantitative analyses, based on the external standard method (Nuro et al., 2014). 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 [4, 19].

Results and Discussion

The levels of OCPs, PCBs, PAHs, and BTEX were investigated in the main Albanian ports because of their high toxicity and persistence. These pollutants are classified as priority substances based on Water Framework Directive 2000/60/EC (EC 2000). Organochlorine pesticides were detected in all the water samples analyzed from the ports of Durres and Vlore (Table 1, Figure 2). The total concentration of OCPs in water samples collected in port of Durres ranged from 1.63 $\mu\text{g/l}$ (station D1) to 6.59 $\mu\text{g/l}$ (station D10) with a mean value of 3.61 $\mu\text{g/l}$. Their levels in water samples from port of Vlore were 0.19 $\mu\text{g/l}$ (station V8) to 31.78 $\mu\text{g/l}$ (station V6) with a mean value of 8.16 $\mu\text{g/l}$. Locations near the main drain in the port showed higher levels of OCPs than those around it. The concentration of OCPs in the port of Vlore was higher than that in the port of Durres. This fact can be related to their previous uses in agricultural areas near Vlore Bay (as well as Vlore port), discharges by Vjosa and Semani rivers (new arrival because of soil rinsing from other areas of Albania), geographical position of Vlore Bay, water currents inside and outside Vlore Bay, and punctual sources near the port. In addition, the same factors can affect the levels of OCPs at the port of Durres, although these levels are lower than those in Vlore Bay because of the port's location (it is not inside a bay; therefore, it is more exposed) and stronger water currents outside and inside the port. The profiles of OCPs in water samples in Durres was: HCHs > Heptachlores > Aldrins > DDTs > Chlordanes > Endosulfanes. Higher concentrations were found for δ -HCH, Lindane, α -HCH, DDD and Heptachlor. δ -HCH and β -HCH isomers are more stable against environmental condition than α -HCH and γ -HCH [15, 19, 20]. The residues of δ -HCH and β -HCH can be used as indicators of the historical usage of HCH in agricultural practices. The ratio of α -HCH to γ -HCH was calculated to identify the source of environmental HCHs [15]. Generally, HCHs with a high α -HCH/ γ -HCH ratio (between 5 and 7) originate from technical HCHs, and those with a low ratio (near 0) are primarily sourced from Lindane [3, 15, 19, 20]. In this study, the ratio was 0.79 in Durres samples to Vlore samples was 13.56. Based on these results, the composition of HCHs in water samples was a mixture of technical HCHs and Lindane. Σ DDT concentrations in the water samples ranged from n.d. to 2.149, with a mean value of 0.41 $\mu\text{g/l}$. Among all the OCP compounds, p,p' -DDT had the highest concentration, with an annual average of 0.076 $\mu\text{g/l}$, followed by p,p' -DDE (0.055 $\mu\text{g/l}$), and p,p' -DDD (0.050 $\mu\text{g/l}$). DDT is degraded into DDE under

aerobic conditions and into DDD under anaerobic conditions [3, 15, 20]. Therefore, a ratio of p,p' -DDT/(p,p' -DDE + p,p' -DDD) greater than 1 indicates fresh input, in addition to historical usage (Jiang et al., 2009). In the present study, this ratio was 0.13–4.76 (Mean = 1.47) and 0.08–5.51 (Mean = 1.46) in Durres, respectively; this suggests recent inputs of DDTs into the sea. The Presence of HCHs in higher concentrations could be mainly because of impact of Ex-Lindane plant industry, in Porto-Romano (5 km in North of Durres's port), which for many years discharges its wastes directly to the Adriatic Sea. The presence of DDD and Heptachlor could be a combination of terrestrial (these pesticides have been stored in the port warehouses for a long time) and water currents (new arrivals from the Shkumbini, Erzeni, and Ishmi rivers). The profile of OCPs in the Vlore samples was as follows: Endosulfanes > Heptachlores > Chlordanes > Aldrines > HCHs > DDTs. This profile was different from Durres samples because of their origin is different for both ports. Cyclopentadiene pesticides were detected in higher concentrations. Higher levels of Endosulfane I, Heptachlor, *g*-Chlordane, and Dieldrin were found. This difference may be due to new arrivals from the Vjosa and Semani Rivers and the individual physicochemical properties of the pesticides (water solubility, persistence, degradation rate, ability to bind with suspended matter, etc.). The recent use of these pesticides and the point sources of these contaminants have not been excluded. OCP concentrations in Durres and Vlore water samples were in the same range as those reported in previous studies of the Adriatic Sea [9, 12, 13]. levels of individual pesticides were below the acceptable levels according to the Albanian and EU standards [11].

PCB markers were detected in all analyzed samples from the ports of Durres and Vlore (Table 1, Figure 4). The total concentration of PCBs in Durres port ranged from 0.145 $\mu\text{g/l}$ (station D1) to 13.59 $\mu\text{g/l}$ (station D11) with a mean value of 1.73 $\mu\text{g/l}$, whereas in Vlore samples, PCB markers, ranged from 0.19 (station V8) to 27.47 $\mu\text{g/l}$ (station V7) with a mean value of 5.40 $\mu\text{g/l}$. PCBs were detected at high concentrations in samples from Vlore stations. Their presence in seawater samples from both ports may be related to shipping, industrial activity in the cities of Durres and Vlore, and atmospheric deposition. Oil discharges from machinery operations and activities (in and out of the port) are likely terrestrial sources of PCBs and hydrocarbons in seawater samples from Durres and Vlore. During this period, several large fires were recorded in several cities (Porto Romano landfill near Durres, Selenica and Narta landfills near Vlore), and forest areas (Karabruni, Llogara and Selenica near Vlore) and may represent a further source of contamination in both studies area. Profile of PCB markers in Durres samples was: PCB 118 > PCB 32 > PCB 28 (Figure 5). The PCB profile for the ports of Vlore was PCB 118 > PCB 52 > PCB 101 > PCB 138. High concentrations of PCB 118 were detected in all the water samples. Its origin may be partly terrestrial or partly atmospheric. PCB 52, a volatile congener, was detected in both areas due to atmospheric deposition. PCB levels and profiles were associated with individual concentrations of several congeners. The presence of heavy PCB congeners at some stations was due to punctual sources of these contaminants in both port areas (all of these stations were within port areas). Ship and car transportation could affect the PCB content of the analyzed samples. PCB levels were comparable to those reported in previous studies [3, 9, 19, 20]. Levels of PCB markers were lower than the permitted levels by the Albanian and EU standards [11].

The PAHs were detected almost in all water samples analyzed from Durres and Vlore ports. (Table 1, Figure 6). The average value for 13 PAHs according EPA 525 standard for the port of Durres was 4.57 $\mu\text{g/l}$ and for Vlore's port was 5.48 $\mu\text{g/l}$. The PAHs levels for Durres samples was from 1.97 $\mu\text{g/l}$ (D12) to 8.61 $\mu\text{g/l}$ (D3) and for Vlore samples was from 0.78 $\mu\text{g/l}$ (V10) to 11.49 $\mu\text{g/l}$ (V4). PAHs were found at higher concentrations in the Vlore samples. The main reason could be the effect of water currents in Vlore Bay, which favors the concentrations of pollutants in it. The presence of PAHs in both ports could be due to ship transport, automobilist transport and any possible hydrocarbon accident (in or near the port areas). Mechanical activities near the ports of Durres and Vlore as well as some massive fires near these areas could be important sources of hydrocarbons in marine water. Note that the presence of some individual PAHs was higher in both studied areas. Benzo[k]fluoranthene, Benzo[b]fluoranthene Pyrene, Acenaphthylene, Fluorene, Chrysene was found in higher level for Durres samples while Anthracene and Chrysene were most abundant in Vlore stations (Figure 7). Their profiles in both areas were a combination of their origin by non-pyrogenic hydrocarbons (transport emission, spillage of hydrocarbons, mechanical activities, etc.) and pyrogenic ones (forest and urban waste burning, transport emission, industrial activities, etc.). The differences between Durres and Vlore ports could be connected mainly by geographical position, water currents, and the characteristics of industrial/mechanical activity near respective areas. The momentum values of PAHs for the analyzed samples were not excluded. PAH levels in seawater samples from main Albanian ports were in the same range or higher

than the reported levels for other stations in the Adriatic Sea, Albanian coastline [3, 16 – 20]. The presence of PAH individuals (Anthracene) at some stations was higher than the permitted level according to the Albanian and EU norms [11].

Table 1. Data of priority substances concentrations from ports of Durres and Vlore, July 2022

Compounds	Port of Durres						Port of Vlore					
	Mean	Median	Minimum	Maximum	STDV	Count	Mean	Median	Minimum	Maximum	STDV	Count
HCHs (µg/l)	1.37	0.54	0.09	5.65	1.67	12	0.94	0.32	0.14	3.26	1.12	12
DDTs (µg/l)	0.47	0.23	N.D.	2.15	0.58	12	0.90	0.20	N.D.	6.62	1.90	12
Aldrin's (ug/l)	0.61	0.43	0.05	2.10	0.56	12	1.34	0.44	N.D.	6.50	1.87	12
Heptachlors (µg/l)	0.49	0.28	N.D.	1.72	0.56	12	1.68	0.42	N.D.	12.26	3.45	12
Chlordane's (µg/l)	0.38	0.17	N.D.	1.36	0.44	12	1.44	0.12	N.D.	14.29	4.09	12
Endosulfanes (µg/l)	0.27	0.12	N.D.	1.25	0.35	12	1.86	0.19	N.D.	16.85	4.81	12
Pesticides (µg/l)	3.61	3.56	1.63	6.59	1.51	12	8.16	4.65	0.19	31.78	9.40	12
PCBs (µg/l)	1.73	0.66	0.15	13.79	3.82	12	5.40	1.40	0.19	27.47	7.95	12
PAHs (µg/l)	4.57	4.86	1.97	8.61	2.22	12	5.48	4.85	0.78	11.49	3.08	12
BTEX (µg/l)	2.73	2.14	0.24	11.11	2.96	12	2.51	2.29	1.02	4.89	1.36	12

N.D. – Not detected or lowers than Limit of Detection (LOD)

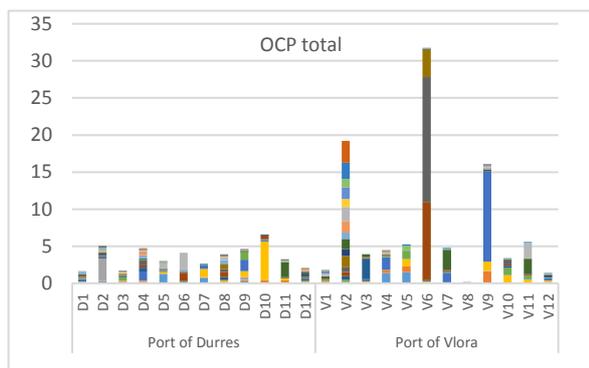


Figure 2. Total of organochlorine pesticides in Durres and Vlore ports

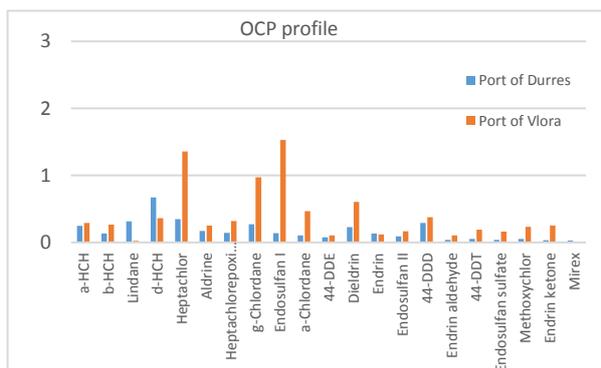


Figure 3. Profile of organochlorine pesticides in Durres and Vlore ports

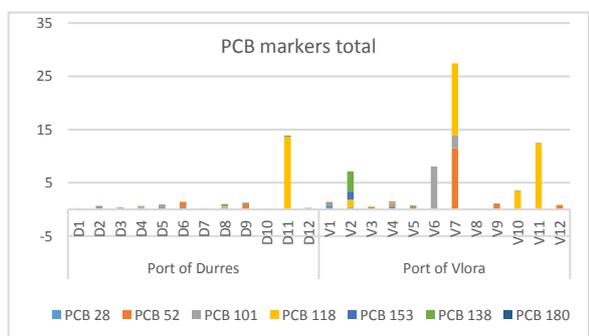


Figure 4. Total of PCBs in Durres and Vlore ports

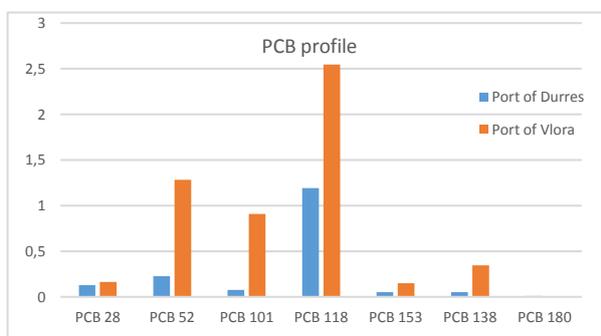


Figure 5. Profile of PCBs in Durres and Vlore ports

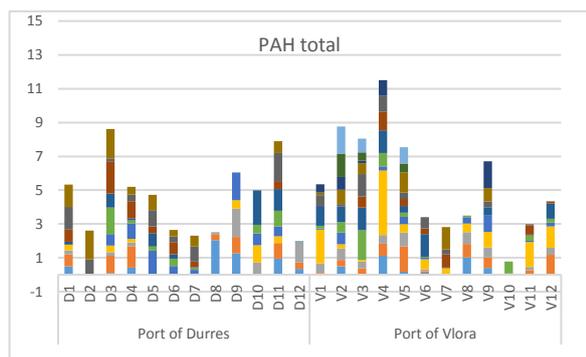


Figure 6. Total of PAHs in Durres and Vlore ports

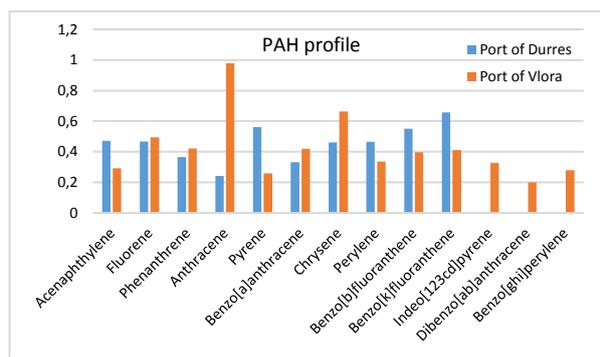


Figure 7. Profile of PAHs in Durres and Vlore ports

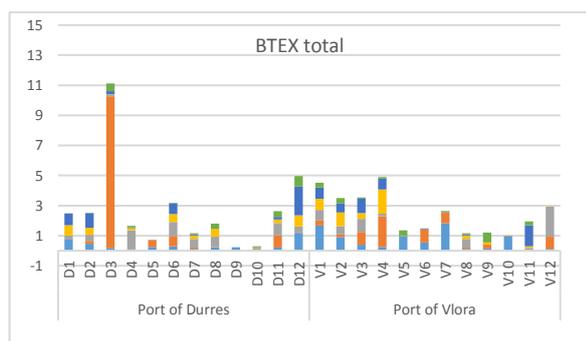


Figure 8. Total of BTEX in Durres and Vlore ports

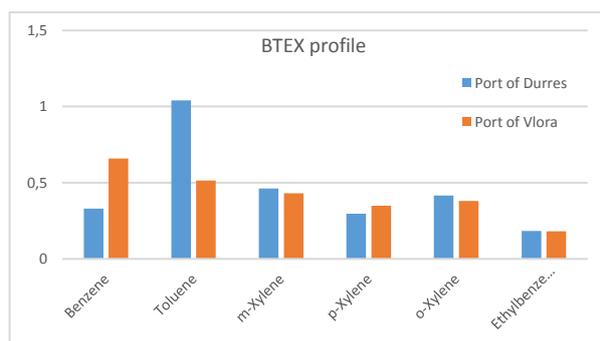


Figure 9. Profile of BTEX in Durres and Vlore ports

Benzene, Toluene, Ethyl benzene, orto-, meta- and para-Xylenes (BTEX) were found almost in all water samples of Durres and Vlore ports. Average of BTEX for Durres port (2.73 ug/l) was almost the same with Vlore samples (2.51 ug/l). The total was slightly higher in Durres because of the abundant level of Toluene at D3 station (Table 1, Figure 8). Total of BTEX ranged between 0.24 ug/l (D9) to 11.11 ug/l (D11) at Durres samples and from 1.02 ug/l (V10) up to 4.89 ug/l (V4) at samples taken in port of Vlore. Profile of BTEX in Durres stations was: Toluene > m-Xylene > o-Xylene > Benzene > p-Xylene > Ethylbenzene and their profile for Vlore samples was: Benzene > Toluene > m-Xylene > o-Xylene > p-Xylene > Ethylbenzene (Figure 9). Benzene and Toluene were the most frequently volatile hydrocarbons found in analyzed samples but the presence of Xylene isomers was found in higher concentrations in some stations (D1, D6, D12, V1, V2, V3, V4, V11 and V12). Presence of BTEX in seawater samples could be because of elevated ship transport, automobilist transport and any possible accident of hydrocarbons near the areas of Durres and Vlore ports. Also, the momentum values of the BTEX for both ports were not excluded. Benzene concentrations were found to be higher/comparable to the reported levels for other stations in the Adriatic Sea, Albanian region [20]. Benzene level was lower than permitted level according to Albanian and EU norms [11] exclude its level for some stations of Durres (three stations) and Vlore (one station).

Data on priority substances in the ports of Durres and Vlore were processed using multivariate cluster analysis. From the processing of the data for the main groups of priority substances, three main groups were identified (Figure 10). The greatest similarity in the first group was between HCHs, DDTs and Aldrin's. Their similarity exceeded 70%, followed by heptachlors, which had lower similarity. In the second group, Chlordanes and Endosulfans showed high similarity, with a similarity of over 80%. This group was similar to Group 1, with a confidence level of more than 40%. In Group 3, the greatest similarity was observed between PAHs and BTEX, with greater than 50% similarity. The similarity between Group 3 and the other groups was approximately 30%. The data for endosulfans (15%), total pesticides (2%), and PCBs showed the least similarity to the other groups. The similarity of these groups can be attributed to the nature of the substances (organochlorine compounds show similarity, hydrocarbons show similarity), the timing of their use, and their respective physicochemical properties (solubility, degradation rate, etc.).

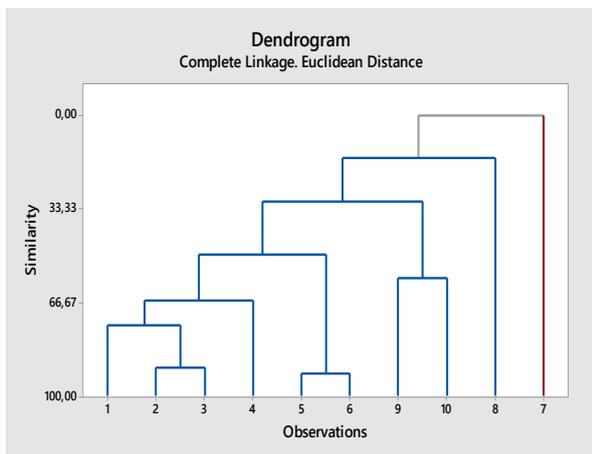


Figure 10. Cluster analyze for primary substances in water samples of Albanian ports (1 = Σ HCHs, 2 = Σ DDTs, 3 = Σ Aldrines, 4 = Σ Heptachlors, 5 = Σ Chlordanes, 6 = Σ Endosulfanes, 7 = Σ Pesticides, 8 = Σ PCBs, 9 = Σ PAHs and 10 = Σ BTEX)

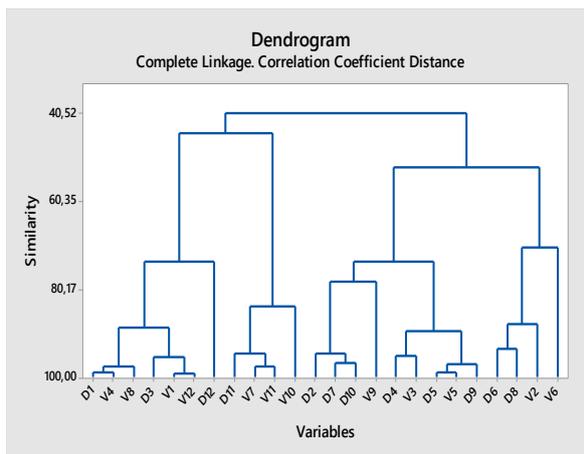


Figure 11. Cluster analyze for the pollution of each station for the ports of Durres and Vlore

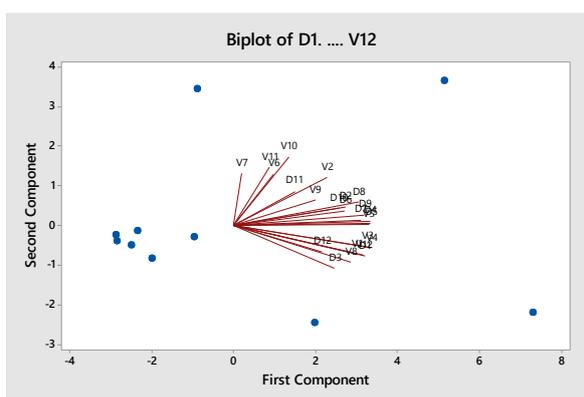
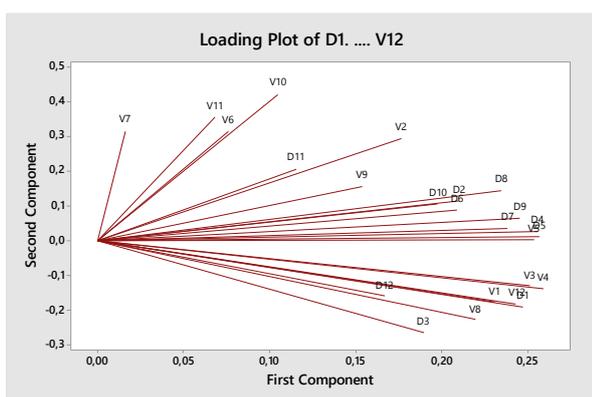
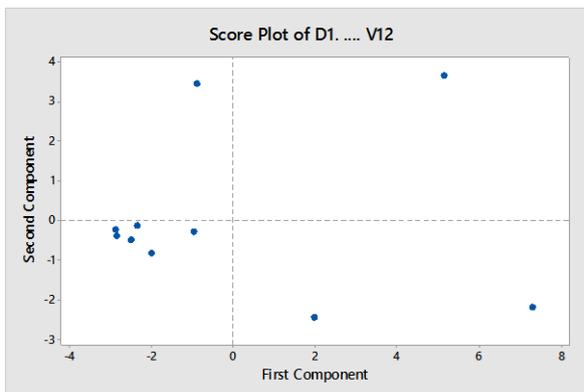
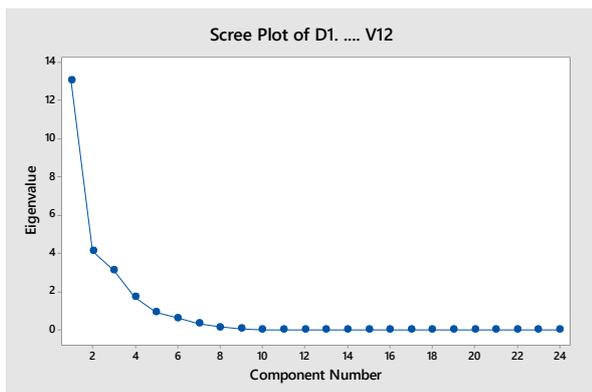


Figure 12. PCA statistical analyze for priority substances in the ports of Durres and Vlore, June 2022

A cluster analysis of the contamination levels at each station (Fig. 11) revealed seven groups sharing a similarity greater than 90%. Five groups showed similarities above 80% and two major groups showed similarities above 40%. The main groups consisted of sampling stations inside and outside the port. There were no visible differences between Durres and Vlore stations. They are interspersed among themselves according to their pollution levels. This is related to the same origin of pollution in the marine waters of the Durres and Vlore ports. Individual levels of some pollutants also led to differences between the stations. These facts can also be seen from the treatment of the data with multivariate principal component analysis (PCA),

where most of the stations are grouped together with a high level of similarity (Figure 12). Eigen values for these stations ranged from 0.98-1.25. Only four stations (D11, V2, V6, and V9) showed notable differences from the other stations. The changes observed for these stations were related to the high levels of some individuals (PCB 118, Methoxychlor, Endosulfane I and Heptachlor).

Conclusions

Priority substances were detected almost in all water samples from Durres and Vlore ports. Owing to the geographical location of Vlore Bay favors high levels of organochlorine pesticides, PCBs, and PAHs in water samples from Vlore Port. Pesticides were found due to past use in agricultural areas near both ports, new arrivals from rivers, water currents, and punctual sources near the ports. Pesticide degradation products were found at higher concentrations than the active products. This was related to the previous use of pesticides in Albania and their degradation processes. The presence of PCBs, PAHs and BTEX in seawater samples in both ports may be related to shipping/automobilist transport, mechanical/industrial activity in the cities of Durres and Vlore, and atmospheric deposition. Mechanical activity may be a terrestrial source of PCBs and hydrocarbons in the seawater samples from Durres and Vlore. Several large fires were recorded near these areas during this study period, could affect in the contamination levels for both ports. The levels of individual organochlorine pesticides, PCB markers, PAHs and Benzene in water samples from both ports were lower than the permitted levels for surface waters according to EU Directive 2013/39 and Albanian norms. An exception was for some individuals (at some stations), which had relatively higher concentrations than others. The monitoring of organic pollutants in the waters of Durres and Vlore ports is ongoing, as these areas can be affected by many sources of pollution. This study should encourage the responsible institutions for the continuous analysis of these substances in port areas.

Acknowledgement

Authors thanks Tirana University about financial support of this study in frame of project entitled "Analyzes of priority substances in water samples of main Albanian ports" as part of program: "UT-Research, Excellence and Innovation" (2021 – 2024).

References

- [1] Froehner S., Rizzi J., Maria V. L., Sanez J., (2018) PAHS in water, sediment and biota in an area with port activities, Arch. Environ. Contam. Toxicol., 75(2):236-246, doi: 10.1007/s00244-018-0538-6
- [2] Mohammed A., Peterman P., Echols K., Feltz K., Tegerdine G., Manoo A., Maraj D., Agard J., Orazio C. (2011) Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in harbour sediments from sea lots, Port-of-Spain, Trinidad and Tobago, Mar Pollut Bull, Vol.62(6):1324-32, doi: 10.1016/j.marpolbul
- [3] Borshi Xh, Nuro A, Macchiarelli G, Palmerini G.M, "Analyzes of Some Chlorinated Pesticides in Adriatic Sea. Case study: Porto-Romano, Adriatic Sea, Albania" Journal of International Environmental Application and Sciences (JIEAS) 2016; Vol. 9(4): 521-424.
- [4] Borshi Xh, Nuro A, Macchiarelli G, Palmerini M.G, Determination of PAH and BTEX in Water Samples of Adriatic Sea using GC/FID, Int.J.Curr.Microbiol.App. Sci 2018; Vol. 5(11): 877-884
- [5] Li, J., Zhang, G., Qi, S., Li, X., Peng, X., 2006. Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China. Sci. Total Environ. 372, 215–224.
- [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] 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.
- [9] 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): “Ecotoxicological assessment of Vlore 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: Vlore Gulf [Tursi & Corselli]*: pp. 116 – 120. DOI:10.2112/SI_58_1.
- [10] Chen MY, Yu M, Luo XJ, Chen SJ, Mai BX (2010) The factors controlling the partitioning of polybrominated diphenyl ethers and polychlorinated biphenyls in the water-column of the Pearl River Estuary in South China. *Mar Pollut Bull* 62:29–35. <https://doi.org/10.1016/j.marpolbul.2010.09.018>
- [11] 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
- [12] EU (2007) “Guidance Document On Pesticide Residue Analytical Methods”, (ENV/JM/ENV/JM/MONO (2007;17)
- [13] ISO 5667-3:2018, Water quality — Sampling — Part 3: Preservation and handling of water samples.
- [14] Lekkas Th., Kolokythas G., Nikolaou A., Kostopoulou M., Kotrikla A., Gatidou G., Thomaidis N.S., Goulinopoulos 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
- [15] Li, J., Zhang, G., Qi, S., Li, X., Peng, X., 2006. Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China. *Sci. Total Environ.* 372, 215–224.
- [16] 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
- [17] 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
- [18] 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
- [19] 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
- [20] 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
- [21] Yang, J., Qadeer, A., Liu, M., Zhu, J., Huang, Y., Du, W., Wei, X., 2019. Occurrence, source, and partition of PAHs, PCBs, and OCPs in the multiphase system of an urban lake, Shanghai. *Appl. Geochem.* 106, 17–25.
- [22] Lazar B, Maslov L, Romanić SH, Gračan R, Krauthacker B, Holcer D, Tvrtković N., Accumulation of organochlorine contaminants in loggerhead sea turtles, *Caretta caretta*, from the eastern Adriatic Sea. *Chemosphere*. 2011, Vol. 82(1): pp. 121-9. doi: 10.1016/j.chemosphere.2010.09.015

- [23] Storelli MM, Barone G, Marcotrigiano GO., Polychlorinated biphenyls and other chlorinated organic contaminants in the tissues of Mediterranean loggerhead turtle *Caretta caretta*. *Science of Total Environment*, 2007; Vol. 373(2-3): pp. 456-63. doi: 10.1016/j.scitotenv.2006.11.040
- [24] Orós J, González-Díaz OM, Monagas P., High levels of polychlorinated biphenyls in tissues of Atlantic turtles stranded in the Canary Islands, Spain. *Chemosphere*. 2009 Jan;74(3):473-8. doi: 10.1016/j.chemosphere.2008.08.048