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ABSTRACT: This study reports the concentrations of organic pollutants, nutrients, and some physico-chemical parameters in water samples from Vlora Port. Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH) and BTEX (Benzene, Toluene, o-, m- and p-Xyelenes, Ethylbenzene) were analyzed organic pollutants. The levels of NO_3, NO_2, NH_4, N-total, PO_4, and P-total were determined. Temperature, PH, Conductivity, Turbidity, TDS, TSS, DO, BOD and COD were physical-chemical parameters determined in the water samples. Vlora Port is located in the southern part of Albania in Vlora Bay, near Vlora City in the Adriatic Sea. Elevated activities in port areas (terrestrial and marine areas) are the main causes of water pollution. Urban pollution, agriculture, and water currents can influence marine water pollution in this area. To evaluate pollution levels at the port of Vlora, water samples (12 stations) were analyzed over a two-year period (2022 – 2023). Water samples were collected during two seasons: March and July of each year.

Analyses of organic compounds were performed using a gas chromatograph (Varian 450 GC) equipped with ECD and FID detectors. Nutrients were analyzed using the UV-VIS technique. Titration, automatic, semi-automatic, and gravimetric methods were used to determine the physico-chemical parameters. Organic pollutants were detected in all the water samples. Nutrient concentrations and physico-chemical values classified the marine water of Vlora's port as moderately good. Levels of organic pollutants, nutrients, and physico-chemical parameters in water samples from Vlora's port were higher/comparable with those reported in previous studies of the Adriatic Sea (Albania coastline).

KEYWORDS: Organic pollutants, Physical-chemical parameters, Nutrients, GC/ECD/FID, UV-VIS, Vlora's port

INTRODUCTION

This study presents analytical data regarding the physico-chemical parameters and organic pollution measured in the seawaters of Vlora's port, which is the second largest port in Albania. In this port, there are intensive commercial and passenger activities. Many studies have observed that these areas are affected by various pollutants that directly affect seawater quality. The bay of Vlora includes several ports: the cargo and passenger port, the oil port (Petrolifera), the Delta Force port, the military port in Orikum and a fishing port near Zvernec. The cargo and passenger ports in Vlora are considered part of the Lungomare Master Plan. A part of this project is the construction of a yacht port. The luxury marina project includes yacht moorings, complex residential and hotel towers, and commercial areas, such as bars and restaurants. The Port of Vlora is one of the most important development elements in the city. This main maritime port of entry for our country, in addition to important economic aspects, can be simultaneously affected by the pollution that comes as a result of this large volume, both in the number of ships that are handled/anchored and in the variety of goods that pass there.The construction/function of ports promotes the development of these areas and cities, encouraging population growth, economic impact, employment, the development of tourism, and increased communication/ exchange with other countries [1, 2]. Port areas have intense activity not only in marine areas, but also in terrestrial areas near ports. 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 from urban pollution and various businesses operating near port areas can be added. On the other hand, the construction of ports, usually in areas that are deep and protected in the form of a bay, favors the concentration of pollutants inside the port areas. The effects of water currents in ports or new arrivals from rivers/effluents (even distant from the port) can cause pollution from areas that may be far from the ports [1-3]. The possibility of pollution in 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 (physico-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 water in these areas [2, 4-7]. In addition, the concentrations of organochlorine pesticides according to EPA 8081 B, marker PCBs, Benzene, and 13 PAH according to EPA 525 were also determined. These organic pollutants are classified as priority substances because of their persistence and high toxicity. Although some of them are not common pollutants in ports, they have been reported in various works due to various accidents and/or the influence of water currents (). These data will help authorities to determine the quality of marine waters in the main Albanian ports according to national and international norms [6, 8] and identify the possible factors that influence their presence in the analyzed samples.

MATERIAL AND METHODS

Water sampling in Vlora ports

In this study, 12 water and sediment samples from the port area of Vlora were analyzed in mid-May 2023. Six of the samples, UVP1, UVP2, UVP3 (New South Beach), and UVP10, UVP11, and UVP12 (Old Beach in the North), were taken outside the port of Vlora, while the other samples (UVP4 – UVP9) inside the port were distributed to be as representative as possible for the port and its influence in this area. Water samples were collected in March and July for a two-year period (2022 and 2023). These sampling periods represent a normal period for the activities in these ports (March) and intense activity in the port areas (July). At each sampling station, 2.5 L of seawater was collected in glass bottles equipped with Teflon caps, based on the ISO 5667-3:201 Method. The water samples were stored and transported at 4 ^{o}C to the laboratory for further analysis. For each station, the PH, conductivity, dissolved oxygen (DO), TDS, Turbidity, and temperature were determined in the field using a Hanna Multiparameter meter portable equipment (HI98194 Model).

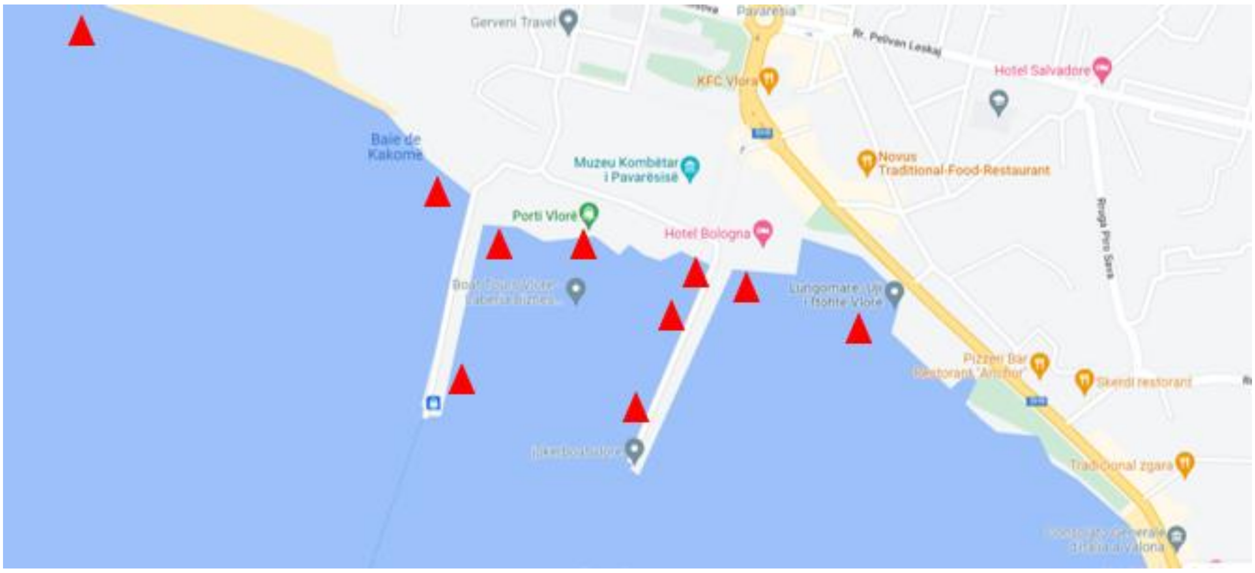

Figure 1. Sampling stations in the main ports of Albania

Determination of BOD_5

VELP brand automatic sensors (respirometers) were used to estimate the 5-day biological oxygen demand (BOD_5) of seawater. The measurements were performed at a concentration of 250 ppm. The samples were placed at 20 ^{o}C for five days, and a direct reading of the BOD value was performed for each sample [9].

Determination of COD

To determine the chemical oxygen demand (COD), SPEC COD digestion tubes were used, which used standard 16-mm tubes pre-prepared with mercury sulfate ($HgSO_4$) were used. Two milliliters of seawater were placed in a pre-filled COD digestion tube, and the cap was closed and mixed vigorously for 1 min. The tube was placed in a thermo-reactor (ECO 16) set at 150 ^{o}C. After heating for 2 h, the samples were cooled at room temperature and then measured in a PF-3 spectrophotometer at wavelengths suitable for COD analysis [9].

Analysis of nutrients and sulfates using SP UV-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_3 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_2 in water was based on the ISO 6777:1984 method for its determination by the colorimetric method at 540 nm. The analysis of NH_4 in water was based on the ISO 7150/1:1984 method for determination using spectrophotometry at 655 nm. N-total was determined by complete disaggregation of the sample with $K_2S_2O_8$ and determination of nitrogen at two wavelengths: 220 nm and 275 nm. All forms of nitrogen were oxidized and measured as NO_3 (Screening Method). P-total was determined using the disaggregation method, which aims to oxidize all forms of phosphorus into PO_4 ions and further determine them using the spectrophotometer method at 880 nm. The analysis of sulfates in water was 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^- (salinity), Ca^{2+} and Mg^{2+} by titration methods

Chloride ions were determined in seawater samples using the argentometric method (4500-Cl- B, Argentometric Method, known as the Mohr method). The data obtained for the chloride ions in seawater were used to calculate the salinity of the samples. The concentration of calcium ions in seawater was determined using the titration method with EDTA in the presence of the indicator Ericrom Black T (3500-Ca B). Magnesium ions have been detected in seawater by titration with $MgCl_2$ of the complex forming Mg^{2+} with EDTA (3500-Mg B, C) [6, 9].

Determination of TSS (Total Suspended Solids) in seawater

The analysis of total suspends solids (TSS) in water was based on its determination by the gravimetric method. The water was filtered using 32 mm diameter glass filters with 0.45 um pores in a vacuum filtration system. TSS content was calculated from the difference in weight before and after filtration. Conditioning and drying of the filters were performed in a thermostat for 8 hours at 105 ^oC [9].

Water treatment for pesticide and PCB analyses

Liquid-liquid extraction was used for the determination of OCPs and PCBs in the water samples. One liter of water samples was extracted with n-hexane (2 × 40 ml) in a separatory funnel. After extraction, the organic phase was dried over anhydrous Na_2SO_4 (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 [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 diameter x 0.25 μm film thickness) on a gas chromatograph (Varian 450 GC) with electron capture detection (ECD detector). Helium was used as the carrier gas (1 ml/min), while nitrogen was used as the makeup gas (24 ml/min). Manual injection was performed in the splitless mode at 280°C. The 21 individuals of organochlorine pesticides according to EPA 8081 B were DDT-related chemicals, HCH isomers, heptachlorides, chlordanes, aldrins, and endosulfanes. PCB analysis was based on the determination of seven PCB markers (IUPAC Nos. 28, 52, 101, 118, 138, 153, and 180). Quantification of OCPs and PCBs was based on the external standard method using five calibration points as follows: 1, 2, 5, 10, and 25 ppb. R2 varied from 0.9452 (Endrin keton) to 0.9965 (b-HCH), and the LOD for each individual OCP and/or PCB markers was 0.05 ppb [3, 4, 11].

Treatment of water samples for PAH analyses

Two-step liquid-liquid extraction (LLE) was used to extract PAHs and Benzene from seawater samples. One liter of water with 40 ml dichloromethane (first step LLE) and then 40 ml hexane (second step LLE) as the extracting solvent were added to a separator funnel. After extraction, the organic phase was dried with 5 g) to anhydrous Na_2SO_4 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 [1, 13-16].

Gas chromatography analysis of PAHs in water samples

Gas chromatographic analyses of PAHs and Benzene 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 ^oC. Nitrogen was used as the make-up gas (25 ml/min). Hydrogen and air were flame detector gases at 30 and 300 ml/min, respectively. EPA 525 Standard Mixture was used for the qualitative and quantitative analyses 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. The quantification of PAHs was based on the external standard method 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] pyerene) to 0.9964 (Anthracene) and the LOD for each PAH (including Benzene) was 0.05 ppm [1, 13, 15].

RESULTS AND DISCUSSION

In this study, water samples from 12 different stations in Vlora’s port, one of the main ports of Albania, were analyzed. Water samples were collected in March and July 2022 and 2023. Organic pollutants and physico-chemical parameters were determined for all the marine water samples. The analysis of organic pollutants included organochlorine pesticides, their degradation products (21 individuals according to EPA 8081 B), PCB markers (seven congeners), Benzene and PAHs (13 individuals according to EPA 525). The physico-chemical parameters of the water samples were determined as follows: temperature, PH, Conductivity, DO, BOD_5, COD, TSS, NO_3, NO_2, NH_4, N-total, P-Total, sulfates, chlorides (salinity), calcium, and magnesium ions. All methods used for the determination of physico-chemical indicators and organic pollutants were based on the Albanian and international norms recommended for these analyses of marine and surface waters.

Organochlorine pesticides

Pesticides and PCBs were determined using GC/ECD, while polycyclic hydrocarbons and benzene derivatives were determined using GC/FID. Figure 2 shows the chromatogram of the port of Vlora for March 2023. Table 1 presents the average organic pollutant concentrations for the four study periods. Organochlorine pesticides were observed in all samples analyzed from the port of Vlora for all periods considered (Figure 3). Their maximum was for the samples analyzed in March 2023 with 14.1 ppb (ug/l), while their minimum for the samples analyzed in March 2022 was 3.8 ppb. The presence of pesticides must be related to previous uses in agricultural areas, not only near the Bay of Vlora, but also to soil erosion and river flows, especially those originating from the Vjosa River. In addition, the influence of sea currents, point sources, and moment values affected the values obtained for the analyzed samples. Figure 4 shows the profile of organochlorine pesticides in water samples from this port. A similar pesticide profile was observed for all four sampling periods. Their profile in water samples was as follows: Endosulfan > Aldrin > HCHs > Heptachlor > Chlordanet > DDT. We added that the pesticide profile is mainly built by the degradation products of some endosulfane, aldrin, heptachlor, and lindane isomers. This may be related to their previous use in agricultural areas near the Bay of Vlora or the new flows of the Vjosa River. These pesticides, which have been used in recent years, are also found as impurities. Total of HCHs (alpha-, beta-, gamma- and delta HCH) was in the range from 0.3 ppb (March 2022) to 2.1 ppb (July 2023). HCHs were found in almost all samples. Heptachlores (Heptachlor and its degradation product Heptachlor epoxide) was found in 64% of analyzed samples with values from 0.4 ppb (March 2022) to 1.5 ppb (July 2022). Chlordanes (alpha- and gamma-chlordanes) were found in less than 50% of the analyzed samples. Their values were from 0.2 ppb (March 2022) to 1.5 ppb (July 2022). Total of Aldrines (Aldrin, Dieldrin, Endrin, Endrin aldehyde and Endrin ketone) were found for all water samples, in each study period with a range between 1.1 ppb (July 2022) to 3.9 ppb (March 2023). DDTs and its related compounds (DDD, DDE and DDT) were dedected in around 32% of water samples with minimum value for March 2022 with 0.1 ppb and maximum in July 2022 with 1.0 ppb. Endosulfanes (Endosulfan I, Endosulfan II and Endosulfan sulfate) were found as primary pollutants in the more than 80% of analyzed samples. Their total was from 0.6 ppb (March 2022) to 6.9 ppb (March 2023). Endosulfan sulfate was the most abundand pollutans especially for some water samples of 2023 study period.

The levels of organochlorine pesticides in the water samples analyzed from the port of Vlora were within the allowable limits defined in the Albanian and EU norms according to Directive 2008/105/EC. The levels of organochlorine pesticides in water and sediment samples from the marine area of the port of Vlora were comparable to those reported earlier for the Gulf of Vlora and Adriatic Sea (Nuro et al 2007; Nuro et al., 2014; Vrizyas et al 2019).

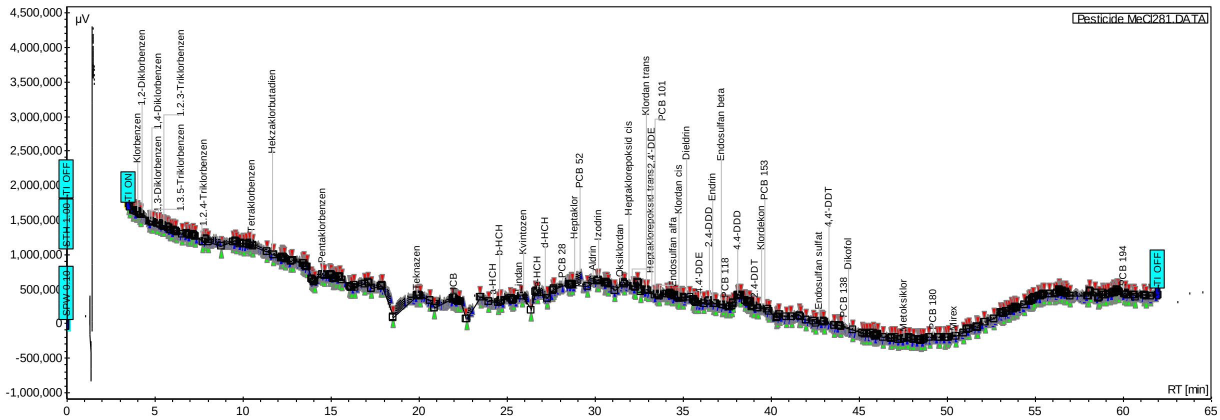

Figure 2. Chromatogram of organochlorine pesticides in water sample UVP6, May 2023

Table 1. Average data for organic pollutants in the four sampling periods for the Port of Vlora

	March 2022	July 2022	March 2023	July 2023
∑ HCHs (ppb)	0.30	1.47	1.58	2.06
∑ Heptachlors (ppb)	0.39	1.45	0.58	0.95
∑ Chlordanes (ppb)	0.23	1.54	0.81	0.63
∑ Aldrins (ppb)	2.18	1.07	3.92	3.60
∑ DDTs (ppb)	0.12	1.02	0.20	0.24
∑ Endosulfanes (ppb)	0.57	1.47	6.91	2.82

∑ **OCPs (ppb)**	3.82	8.16	14.08	10.29
∑ **PCBs (ppb)**	2.21	5.40	8.66	10.23
∑ **PAHs (ppm)**	0.98	5.48	2.65	2.86
∑ **BTEX (ppm)**	1.25	2.51	3.64	3.03

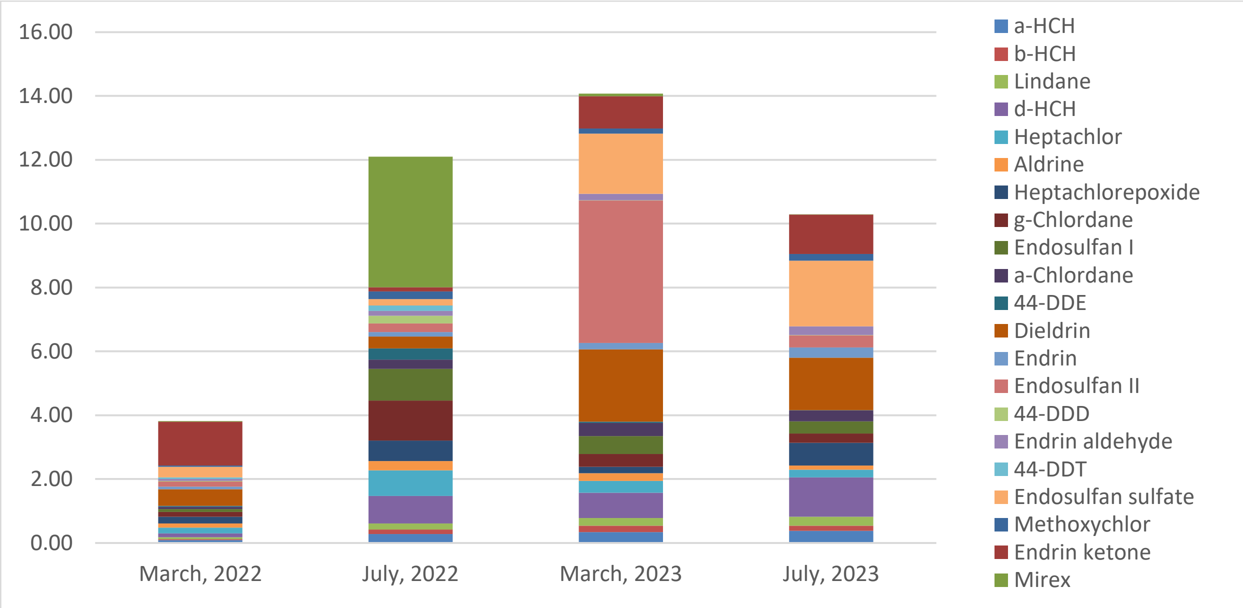

Figure 3. Total organochlorine pesticides in water samples from the port of Vlora

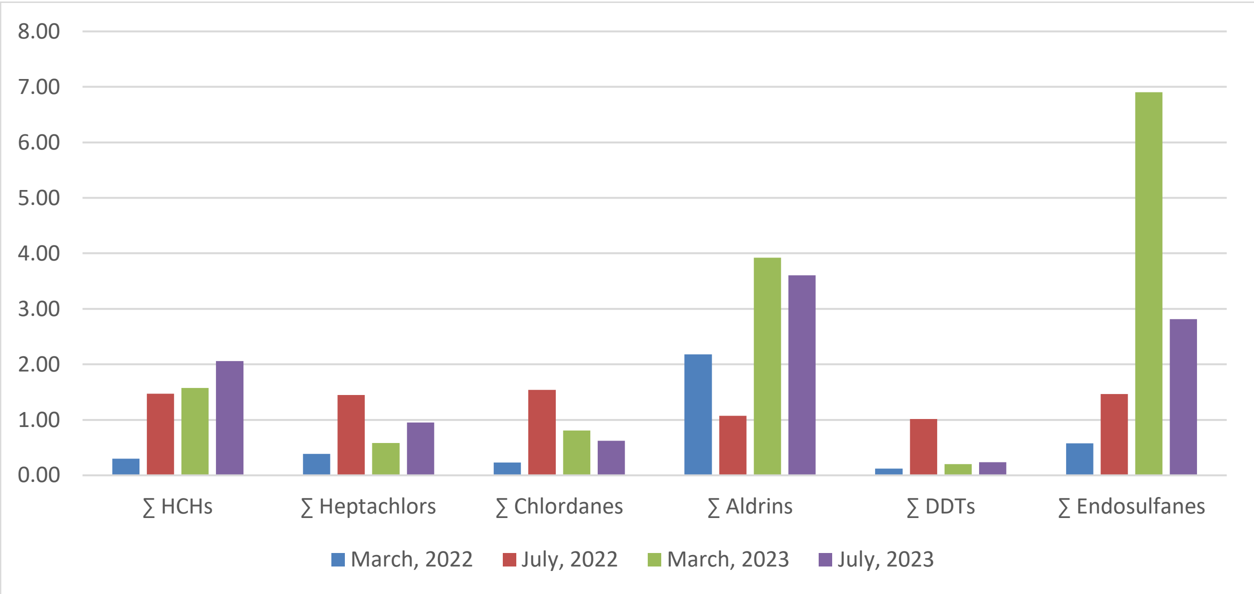

Figure 4. Profile of organochlorine pesticides in water samples from the Port of Vlora

PCB

Marker PCBs were identified in all samples analyzed during the four study periods (Figure 5). Their level was from 2.2 ppb (ug/l) in March 2022 to 10.3 ppb (July 2023). Their presence may be due to atmospheric deposits and mechanical and industrial activities, particularly in the area near the port. The most polluted stations in the analyzed samples were mainly inside the port with levels–2-5 times higher than the stations outside it, so their sources could be accidental spills and/or point sources, or activity mechanics. The profiles of the marker PCBs analyzed in the water samples are shown in Figure 6. There was a similar PCB profile for the four study periods. The profiles were PCB 28 > PCB 52 > PCB 118 > PCB 153 > PCB 101 > PCB 138 > PCB 180. A high concentration of volatile PCBs was noted, with atmospheric deposits as their main source. The presence of heavier PCBs (PCB 153, PCB 138, and PCB 180) should be related to point sources in areas near the port. It should be noted that the individual levels for specific samples had high values. The levels of marker PCBs in the water samples analyzed from the port of Vlora were generally within the permitted limits defined in the Albanian and EU norms (Directive 2008/105/EC). The total concentration for one sample in March 2022 and two samples in July 2023 exceeded their total concentration by 50 ng/l for surface waters. The levels of PCBs in water samples from this marine area were comparable to or higher than those reported in previous studies in other marine ecosystems in Albania (Murtaj et al. 2014; Como et al. 2013, Nuro et al. et al. 2017).

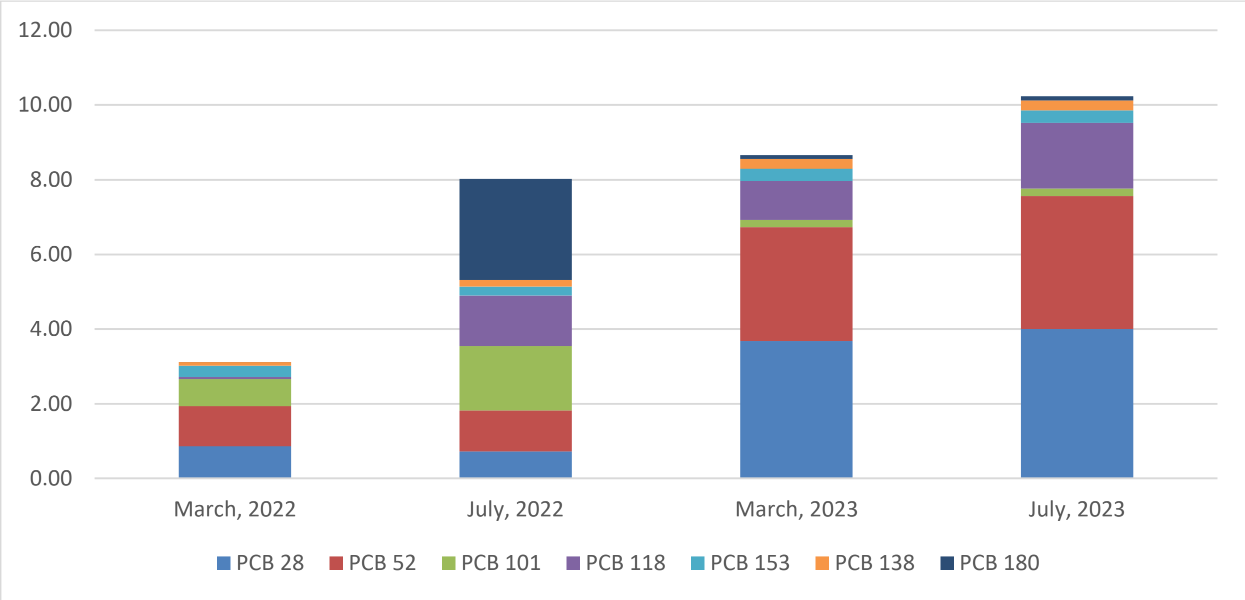

Figure 5. Total marker PCBs in water samples from the port of Vlora

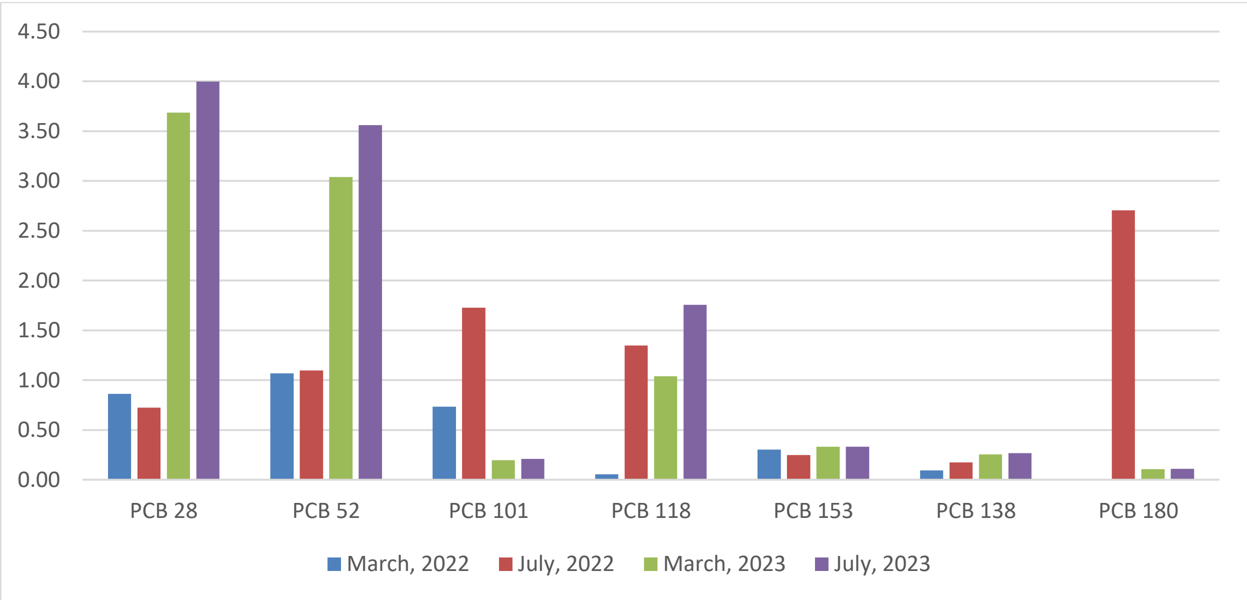

Figure 6. Profile of marker PCBs in water samples from the port of Vlora

Polycyclic aromatic hydrocarbons

Figure 7 shows the total PAHs from the port of Vlora during the four study periods. PAHs were detected in all analyzed samples at a minimum level in March 2022 of 1 ppm (mg/l) and a maximum in July 2022 of 5.5 ppm. The presence of PAH in the water and sediment samples is a consequence of marine and automobile transport, urban spills, fires, natural background, mechanical spills, gas stations, and accidental/intentional spills of hydrocarbons near the study area. In the southern area of the port, high levels of PAHs were found because of the movement and anchoring of small tourist ships in this area. This area and the port area are also affected by automobile transport, urban spills, and businesses near the stations. Figure 8 shows the profile of PAHs in water samples from the port area of Vlora. Again, their profiles were almost the same for the four study periods because of their similar origins. The PAH profile shows that their origin is from small molecular mass PAHs (non-pyrogenic such as Anthracene, Pyrene and Fluorene; their origin is from hydrocarbon spills, mechanical-industrial spills, urban spills, and/or from source point), and PAHs with a large molecular weight (pyrogenic such as benzo [a]anthracene, benzo [b]fluoranthrene, benzo [k]fluoranthrene originating from marine and automobile emissions, industrial processes that take place at high temperatures, burning of forests, and urban waste). The levels of PAHs in the water samples from the port of Vlora were comparable/higher with the levels reported for marine waters of the Adriatic and Mediterranean areas (Magi et al., 2002; Mandi and Frapicini 2013; Mandic and Vrancic 2007). The concentrations of 15 PAH according to EPA 525 do not exceed the permitted levels determined by EU regulations (Directive 2008/105/EC) for surface waters.

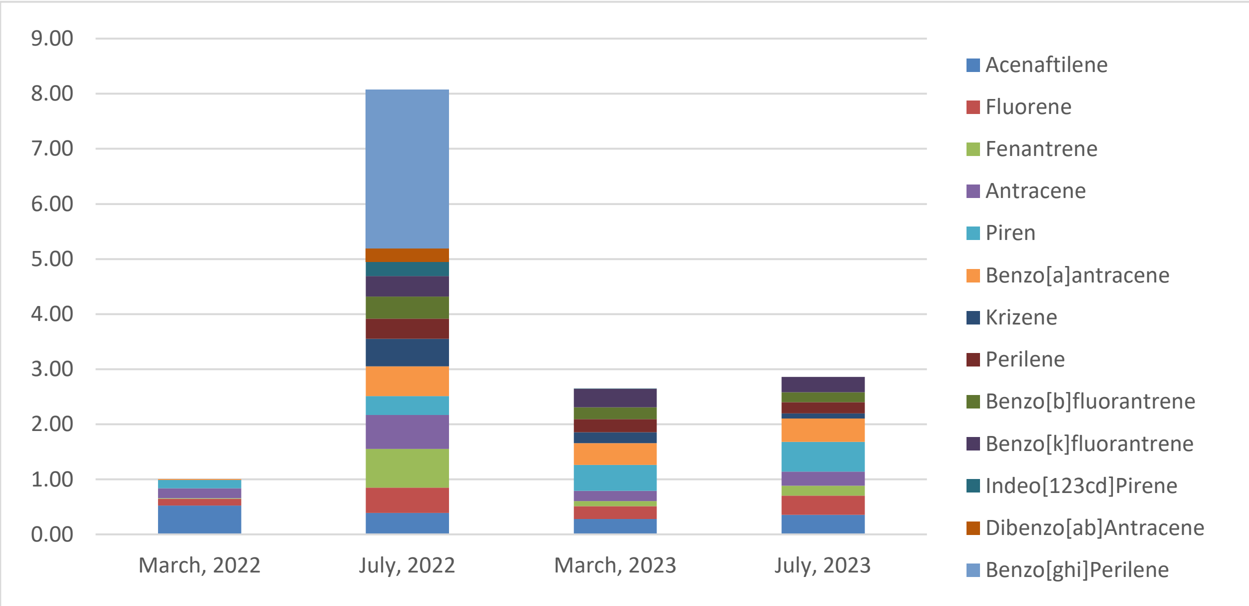

Figure 7. Total PAHs in water samples from the Port of Vlora

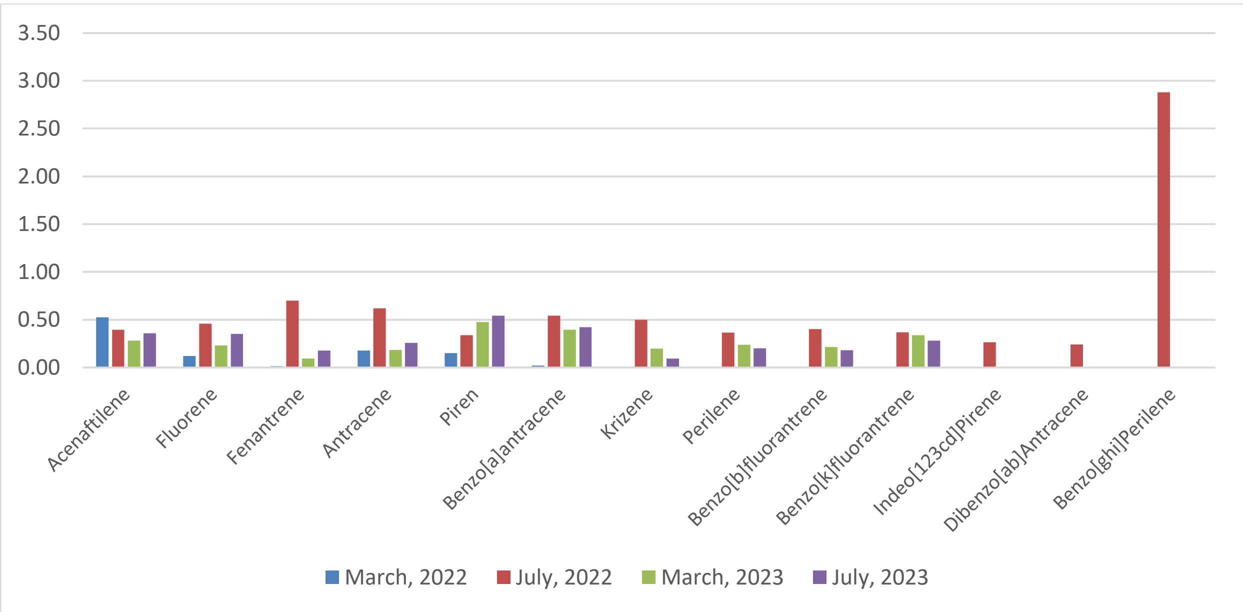

Figure 8. Profile of PAHs in water samples from the port of Vlora

BTEX

Figure 9 shows the total BTEX for the water samples from the port of Vlora for the four study periods. BTEXs were detected in approximately 70% of the samples analyzed from the Port of Vlora. The minimum level of BTEX for the water samples was observed in March 2022 at 1.3 ppm (mg/l), whereas the highest level was observed in March 2023 and July 2022 at 3.5 ppm. The presence of BTEX in the water samples indicates that the current values may be influenced by hydrocarbon spills or emissions from marine and automobile transport. This is also supported by the fact that the stations most polluted with BTEX were inside and south of the port. Their origin is the same as that of other hydrocarbons, such as marine and automobile transport, mechanical-industrial activity, and urban spills. Figure 10 shows the profile of BTEXs in water samples from the port of Vlora. The profile of the BTEXs was almost the same for all study periods because of the same origin of pollution.

Their profile was: Benzene > Xylene > Toluene > Ethylbenzene. This profile shows that their origin is mainly marine and automobile transport, fuel stations, and urban or mechanical-industrial spills. The levels of BTEXs in water samples from this area were comparable/higher than the levels reported for marine waters for the Adriatic and Mediterranean seas (Magi et al., 2002; Mandi and Frapicini 2013; Mandic and Vrancic 2007). The concentrations of Benzene and Toluene exceeded the permitted levels determined by the EU regulations (Directive 2008/105/EC) in only two cases for the UVP3 and UVP4 stations.

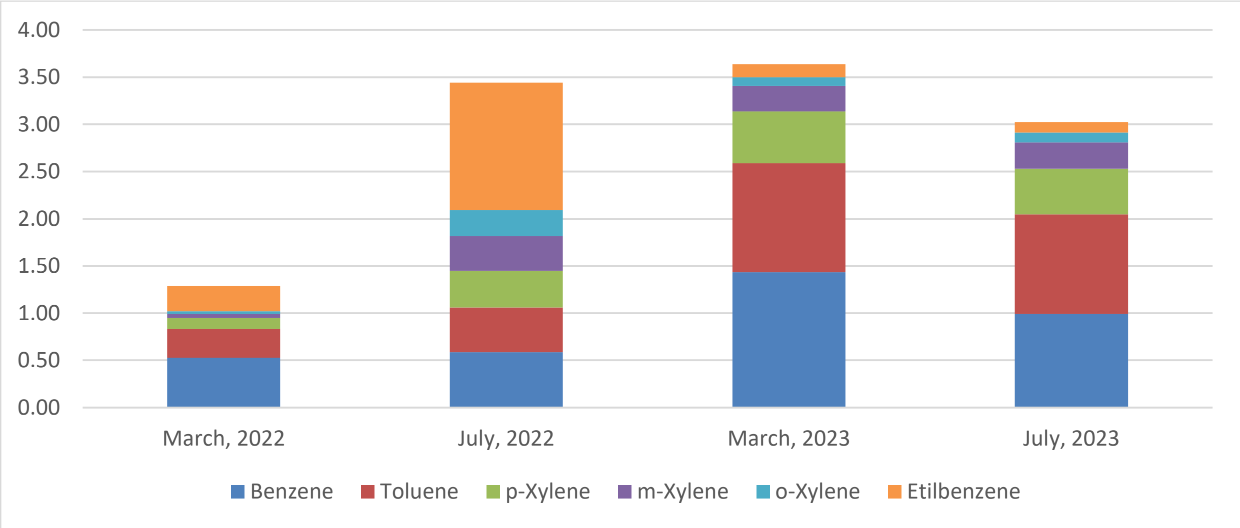

Figure 9. Total BTEXs in water samples from the port of Vlora

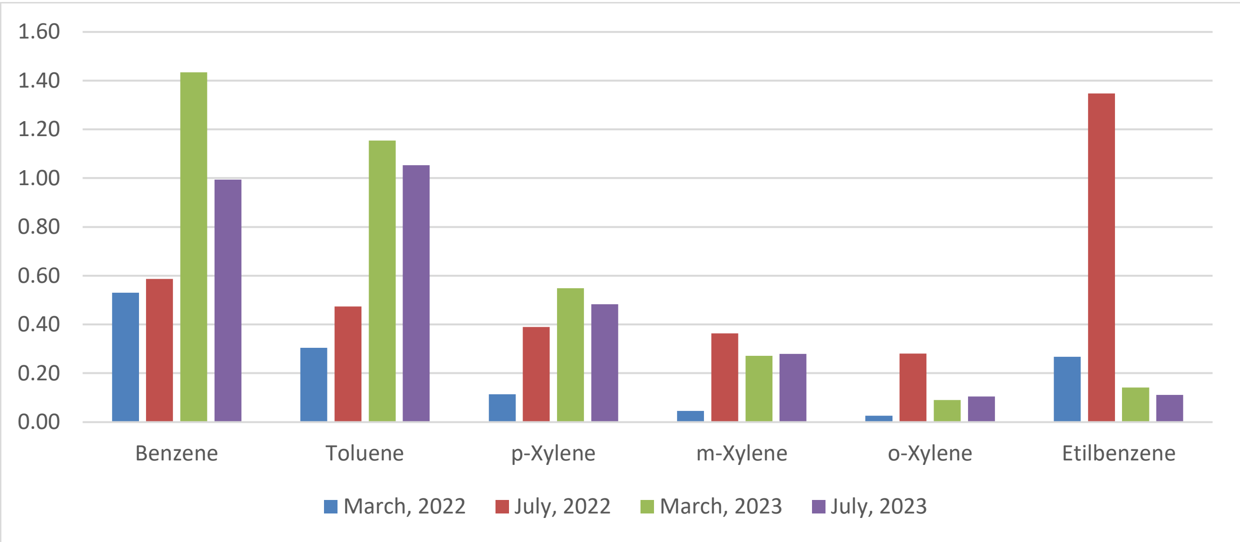

Figure 10. Profile of BTEXs in water samples from the Port of Vlora

Physico-chemical data

In this study, the physico-chemical parameters of seawater samples from the port of Vlora were analyzed in four study periods (March and July for two years, 2022 and 2023). The average data of the measurements of physico-chemical parameters for water samples from the Vlora port stations are presented in Table 2.

The temperature of the seawater at the time of sampling ranged from 17.5 °C in March (for both years) to 24.8 ºC (for July 2022). These are usual temperatures for March and July in Vlora bay, Adriatic Sea.

The pH values of the water samples ranged from 7.5 (March 2022) to 8.4 (July 2022). These slightly basic values may be the result of the urban wastewater discharge near the port area. Based on the PH values, the water of Vlora's port can be classified as very good, but the tendecy of pollution is exist.

The average values for dissolved oxygen in seawater for the port of Vlora for the fourth study period was from 8.1 mg/l (July 2022) to 11.2 mg/l (March 2023). These values were higher than > 5 mg/l classifying that seawater is suitable for the growth of organisms in this area.

Mean BOD_5 values range from 12.5 mg/l (March 2022) 46.0 (July 2022). These intervals of values classify the waters of the Port of Vlora as good in terms of their water quality based on this parameter.

The average values for the chemical oxygen demand (COD) was from 25.1 mg/l (March 2022) to 84.92 mg/l (July 2023). These relatively high values must be related to the presence of chemicals in the seawater, which is mainly due to the intense activity of processing goods in this area. This COD value classifies the water of the port of Vlora as moderately good.

Turbidity values range from 134.4 FNU (July 2023) 232,5 FNU (March 2022). These values classify the water of the Vlora port as good.

The average values of TDS (total disolved solids) were found in the range from 84.9 mg/l (July 2023) to 125 mg/l (March 2022). These values classify the water of the Vlora port as good.

Analysis of particles in suspension (TSS) showed that their average value ranged from 107.3 mg/l (March 2022) 26.4 mg/l (July 2023). These values classify the water of the Vlora port as good.

The average concentration of nutrients was as follows:

- Minimum for NO_3 was in March 2022 (2.5 mg/l) and maximum in March 2023 (6.8 mg/l)
- Minimum for NO_2 was in July 2022 (0.09 mg/l) and maximum in July 2023 (0.27 mg/l)
- Minimum for NH_4 was in March 2022 (0.1 mg/l) and maximum in March 2023 (0.6 mg/l)
- Minimum for N-total was in March 2022 (0.5 mg/l) and maximum in July 2023 (4.5 mg/l)
- Minimum for PO_4 was in March 2022 (1.0 mg/l) and maximum in March 2023 (6.0 mg/l)
- Minimum for P-total was in March 2022 (0.8 mg/l) and maximum in March 2023 (4.6 mg/l)

The nutrient values in the analyzed samples were higher than those reported for Vlora Bay, except for the values in March 2022. Generally, these values classify seawater as good to moderate. This value may be related to the urban runoff from cities or ships in this area. The influence of water currents inside and outside the port, river arrivals, agricultural activity (fertilizer and pesticide), and momentum values were not excluded. Note that, for the sampling period in July, there was a large increase in the number of tourists. An increase in the population by almost five times compared to the normal population of the city of Vlora is accompanied by a significant increase in urban waste.

Analysis of sulfates in water samples of Vlora’s port showed their presence at the range level between 271.9 mg/l (March 2023) to 514.8 mg/l (July 2023). Their presence must be related to urban pollution, hydrocarbon spills, or the impact of new arrivals from the Vjosa River and other effluents.

The average value of chlorides in the water of the port of Vlora was from 16.1 g/l or calculated as the salinity of these waters 29.0 g/l (March 2022) to 19.1 g/l or 34.4 g/l. This value can be related to the quantity of sweet water that brings Vjosa, other effluents, and Vlora city. The increase in chlorine (salinity) values in July can be attributed to the relatively high temperatures of the seawater during this period.

Levels for Ca ions were from 61.4 mg/l (July 2022) to 74.8 mg/l (July 2023) while for the Mg ions were between 33.3 mg/l (July 2022) to 50.6 (July 2023). The presence of calcium and magnesium ions could be related to the geological construction of Vlora Bay and the impact of seawater currents and Vjosa flows.

From the analysis of the physico-chemical parameters, we can say that the waters of the port of Vlora are good, but care must also be taken because there is a tendency for them to be affected by anthropogenic activities. This is due to the activity in the port, in the areas near it, as well as from urban pollution. The positioning of many residences, hotels, and businesses very close to marine areas is a factor that is directly reflected in the values of these water quality parameters.

Table 2. Statistical data for physico-chemical parameters of water samples from the port of Vlora

Physical-chemical parameters	March 2022	July 2022	March 2023	July 2023
Temperature (ºC)	17.48	24.79	17.67	22.92
PH	7.51	8.38	7.74	7.92
Conductivity (ms/cm)	33.65	41.25	52.33	45.36
DO (mg/l)	10.97	8.11	11.18	8.23
BOD_5 (mg/l)	12.49	46.04	23.36	34.35
COD (mg/l)	25.10	71.90	48.54	84.92
Turbidity (FNU)	232.49	146.04	173.36	134.35
TDS (mg/l)	125.10	121.90	148.54	84.92
TSS (mg/l)	107.32	37.49	60.75	26.44
NO_3 (mg/l)	2.54	3.39	6.84	6.34
NO_2 (mg/l)	0.12	0.09	0.10	0.27

NH_4 (mg/l)	0.13	0.39	0.58	0.25
N-total (mg/l)	0.51	1.06	2.97	4.46
PO_4 (mg/l)	1.04	2.80	6.03	3.73
P-total (mg/l)	0.83	0.16	4.58	1.99
SO_4 (mg/l)	312.06	411.11	271.94	514.81
Cl^- (g/l)	16.05	18.21	17.93	19.06
Salinity (g/l)	28.97	32.85	32.36	34.40
Ca^{2+} (mg/l)	62.68	61.40	73.94	74.78
Mg^{2+} (mg/l)	40.56	33.30	45.43	50.58

CONCLUSIONS

The analyses of organic pollutants and the determination of physico-chemical parameters in water samples from the port of Vlora were carried out during four study periods (March and July for the years 2022 and 2023). Sampling and analytical measurement procedures were carried out at 12 stations, eight of which were in the area inside the port and four stations outside it (two in the south and two in the north). Organochlorine pesticides were detected in almost all the analyzed samples. Their presence must be related to previous uses, new flows from the Vjosa River and other effluents, the washing of agricultural lands near the Gulf of Vlora, sea currents, and point sources. The pesticide profile is built mainly from the degradation products of the pesticides Aldrin, Endosulfan and HCH. PCBs were detected in approximately 70% of the analyzed samples. Their presence is due to atmospheric deposits and mechanical-industrial activity in the port area in particular and in the Vlora area in general. Aromatic and volatile polycyclic hydrocarbons were detected in more than 50% of the analyzed samples. They were detected not only in the stations inside the port but also in the stations outside the port. Their presence is influenced by marine and automobile transport, hydrocarbon spills, urban spills, and fire, etc. This fact is also supported by their profile, which is mainly related to the similar profile of hydrocarbons used as fuel in ships and/or cars. Emissions from mechanical businesses and transport have their own impacts on PAH and BTEX profiles. In general, the individual levels of organochlorine pesticides, PCBs, PAHs and Benzene in the water of the Port of Vlora were within the limits allowed according to Directive 2008/105/EC. Higher levels of some individuals were observed at some stations. Their concentrations in the water samples were comparable/higher than those reported for the Gulf of Vlora and Adriatic Sea. Analyses of organic pollutants should be performed using GC/MS/MS and LC/MS/MS.

The water in the port area has a slightly basic PH as a result of urban water discharge in the port of Vlora but is accessible for the organism to grow. The average values for DO, BOD_5, and COD indicate that harbor water is suitable for the growth of organisms in this area. The high value of COD should be mainly related to the presence of chemicals in the seawater, which comes mainly from the intensive activity in this area. These nutrient levels were relatively higher than those reported in previous studies in this area. The impact of agriculture may also be significant at these levels. The presence of sulfates is mainly related to urban pollution, hydrocarbon spillages, and/or the impact of ships and automobilistic transport. Concentrations of the analyzed ions (Cl^-, Ca^{2+}, and Mg^{2+}) could be related to the natural background of the Adriatic Sea or influenced by external factors, such as seawater currents inside or outside the port, and the impact of flow for some important rivers of Albania. The levels found for the water of the Port of Vlora classify these waters as good or moderately good. Analyses of physico-chemical parameters in the water of the port of Vlora should be performed periodically by the laboratories of the respective agencies because their monitoring keeps the pollution of these areas under control. Continuous analyses of the port area should be carried out, not only because a trend of anthropogenic influence on the water quality of the port of Vlora was observed.

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CONFLICT OF INTEREST

"The authors declare that they have no conflict of interest."

REFERENCES

1. Froehner S., Rizzi J., Vieira LM., Sanez J., (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. Kane S, Lazo P, Qarri F (2015) "Environmental situation of Vlora Bay, Albania based on physic-chemical parameters of seawater", Austin Journal of Hydrology, Volume 2/1 ISSN: 2380-0763

3. Nuro A., Marku E., Shehu M. "Organchlorinated pesticide residues in marine water in the South of Albania". International Journal of Ecosystems and Ecology Sciences (IJEES), Vol 2, Issue, Fq. 27-34 (2012)
4. 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
5. Kane S, Lazo P (2012) "Assessment of environment situation and water quality of Vlora Bay and Narta Lagoon by nutrients and heavy metals determination". International Interdisciplinary Conference, Vlorw, Albania, 26-28 Nwntor, Libri i Abstrakteve: ISBN 978-9928-4000-2-4
6. Poikane S, Kelly GM, Herreroa SF, Pitt Jo-A, Jarvie PH, Claussen U, Leuja W, Solheim LA, Teixeira H, Phillips G. 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. ISSN 0048-9697; https://doi.org/10.1016/j.scitotenv.2019.133888
7. Campanelli A., Fornasiero P., Marini M., (2004) Physical and chemical characterization of the water column in the Piceno coastal area (Adriatic Sea). Fresen Environ Bull. Vol. 13: 430-435
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. Baird R., Eaton A., Rice E., (2017) Standard Methods for Examination of Water and Wastewater, 23rd Edition, ISSN 55-1979, https://doi.org/10.2105/SMWW.2882.216
10. ISO 5667-3:2018, Water quality — Sampling — Part 3: Preservation and handling of water samples.
11. 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
12. 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. 121-129
13. Naglaa A. El-Naggar, Hosny I. Emara, Madelyn N. Moawad, Yosry A. Soliman, Abeer A. M. El-Sayed (2018) Detection of polycyclic aromatic hydrocarbons along Alexandria's coastal water, Egyptian Mediterranean Sea, The Egyptian journal of aquatic research, Volume 44, Issue 1, Pages 9-14
14. 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
15. 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
16. 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, Vol. 90, issue 6, pp. 1839-1846