

## OVERVIEW OF POLLUTION LEVEL IN THE PORT OF VLORA, ALBANIA

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### ABSTRACT

This study presents data on organic pollutants and physicochemical indicators in water samples collected from the Port of Vlora, Albania, during 2022–2023. The organic pollutants analyzed include organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and benzene—priority substances due to their persistence and toxicity. Physicochemical parameters measured were nutrients (nitrate, nitrite, ammonium, phosphate, total nitrogen, total phosphorus), temperature, pH, conductivity, turbidity, total dissolved solids (TDS), total suspended solids (TSS), dissolved oxygen (DO), biochemical oxygen demand (BOD), and chemical oxygen demand (COD). Vlora, Albania's second-largest port, plays a vital national role and is located in southern Albania within Vlora Bay (Adriatic Sea). The port is influenced by intense maritime and land-based activities, as well as urban runoff, agriculture, and riverine inputs, all of which contribute significantly to pollution. To assess pollution levels, water samples were collected from 12 stations over two years, during March and July of each year (four campaigns in total). Organic compounds were analyzed using a Varian 450 gas chromatograph equipped with electron capture and flame ionization detectors (ECD and FID), while nutrients were measured by UV-VIS spectrophotometry. Other parameters were determined through titration and automatic, semi-automatic, and gravimetric methods. Organic pollutants were detected in all samples, likely originating from agricultural and industrial activities, inputs from the Vjosa River, transportation, atmospheric deposition, and untreated wastewater discharges. Nutrient and physicochemical values indicate that Vlora's marine waters are moderately good but are influenced by human activity. Overall, pollutant concentrations were

comparable to or higher than those reported in previous studies along the Albanian Adriatic coast.

**Keywords:** Organic pollutants, Physico-chemical parameters, Nutrients, GC/ECD/FID, UV-VIS, Vlora Port

## 1. INTRODUCTION

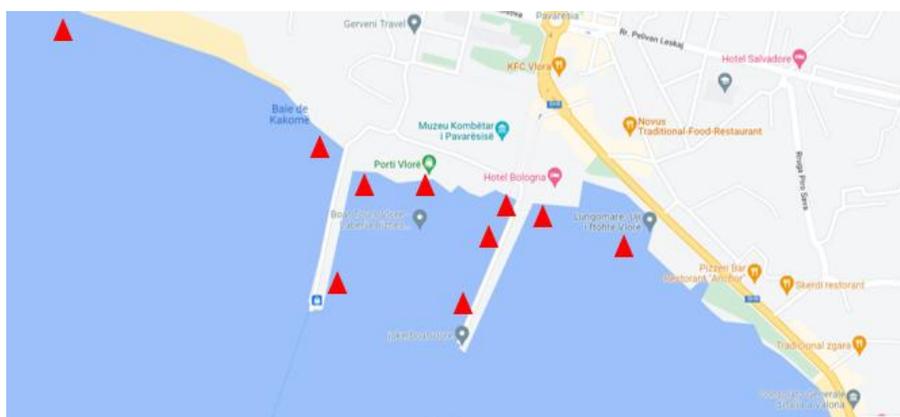
Physicochemical parameters and organic pollutants were measured in the seawater of the Port of Vlora over a two-year period (2022–2023). As Albania's second-largest port, Vlora is characterized by intensive commercial and passenger activity. Numerous studies have shown that port areas are affected by a variety of pollutants that directly impact seawater quality (Mohammed *et al.*, 2011; Nuro *et al.*, 2012; Kane and Lazo 2012; Kane *et al.*, 2015; Froehner *et al.*, 2018). Vlora Bay includes several ports: the main Port of Vlora, the hydrocarbon terminal of Petrolifera, the Delta Forces port, the military port in Orikum, and a fishing port near Zvrnec. The Port of Vlora is also part of the Lungomare Master Plan, which includes the construction of a yacht marina. While the port represents a key development asset for the city, its elevated activity can negatively impact local water quality. Pollution sources in and around the port stem from intensive marine and terrestrial operations, including maritime transport (ships, ferries, boats), anchorage activities, mechanical and technical services, vessel cleaning and sanitization, and import-export operations involving cereals, minerals, hydrocarbons, and the storage of food, chemicals, and other materials near the waterfront. Additionally, vehicular movements such as cars, cranes, and machinery contribute to pollution. Long-term discharges of domestic waste from nearby residents and businesses further increase urban pollution in the area. Furthermore, the structural layout of ports—typically located in deep, sheltered bays—can facilitate the accumulation of pollutants transported from distant sources (Nuro *et al.*, 2012; Kane *et al.*, 2015; Froehner *et al.*, 2018). The potential for such pollution, coupled with limited data on marine water quality in the Port of Vlora, motivated this study.

## 2. MATERIAL AND METHODS

### Water sampling in Vlora's port

For this study, 12 water and sediment samples were collected from the Vlora Port area during March and July over a two-year period (2022–

2023). March was selected to represent a typical activity period, while July was chosen to capture conditions during peak port activity. Six samples were taken from stations inside the port and six from stations outside, with sampling locations carefully selected to represent the area and the various factors potentially influencing water quality. Sampling was conducted in accordance with ISO 5667-3:201 standard. Several physicochemical parameters were measured on-site at each station using a portable multiparameter meter (HANNA model). Water samples were then stored and transported to the laboratory at +4 °C for further analysis.



**Fig.1.** Sampling stations in the Port of Vlora.

### Physicochemical analyses

pH, conductivity, dissolved oxygen (DO), total dissolved solids (TDS), turbidity, and temperature were measured in the field at each sampling station using a Hanna portable multiparameter meter (Model HI98194). Biochemical oxygen demand (BOD<sub>5</sub>) in seawater was estimated using VELP automatic respirometers. Chemical oxygen demand (COD) was determined with pre-prepared SPEC COD digestion tubes containing mercury sulfate, utilizing a thermo-reactor (ECO 16) and a PF-3 spectrophotometer specifically designed for COD analysis (Baird *et al.*, 2017; Campanelli *et al.*, 2004). Nutrient concentrations—including nitrates (NO<sub>3</sub><sup>-</sup>), nitrites (NO<sub>2</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), total nitrogen (N-total), phosphate (PO<sub>4</sub><sup>3-</sup>), total phosphorus (P-total), and sulfate (SO<sub>4</sub><sup>2-</sup>)—

were measured using a UV-VIS spectrophotometer (UV 31 SCAN, ONDA model). The following standard methods were applied:

- Nitrate ( $\text{NO}_3^-$ ): ISO 7890-3:1988
- Nitrite ( $\text{NO}_2^-$ ): ISO 6777:1984
- Ammonium ( $\text{NH}_4^+$ ): ISO 7150/1:1984
- Total Nitrogen (N-total): Determined by full oxidation of nitrogen species, measured as nitrate (screening method)
- Total Phosphorus (P-total): Oxidation of all phosphorus forms to phosphate, measured spectrophotometrically at 880 nm
- Sulfates ( $\text{SO}_4^{2-}$ ): Determined by turbidimetry (method 9038) at 420 nm (Kane *et al.*, 2015; Baird *et al.*, 2017; Poikane *et al.*, 2019).

Chloride ions ( $\text{Cl}^-$ ) were determined using the argentometric method (4500- $\text{Cl}^-$  B), also known as the Mohr method. These results were subsequently used to calculate the salinity of the seawater samples. Calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) concentrations were measured by complexometric titration with EDTA and appropriate indicators (Baird *et al.*, 2017; Poikane *et al.*, 2019). Total suspended solids (TSS) were quantified using the gravimetric method (Baird *et al.*, 2017).

### **Determination of organochlorine pollutants in seawater samples**

Liquid–liquid extraction was used to determine organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in seawater samples. After extraction, the organic phase was dried over anhydrous sodium sulfate, followed by clean-up using a Florisil column. The concentrated, purified extracts were then analyzed by gas chromatography equipped with an electron capture detector (GC/ECD). A total of 21 organochlorine pesticides, as outlined in EPA Method 8081B, along with 7 PCB marker congeners, were analyzed simultaneously. Separation was achieved using a capillary Rtx-5 column (Lazar *et al.*, 2011; Mohammed *et al.*, 2011; Nuro *et al.*, 2012; Nuro *et al.*, 2014; ISO 5667-3:2018).

### **Determination of PAHs in seawater samples**

A two-step liquid–liquid extraction (LLE) procedure was employed to extract polycyclic aromatic hydrocarbons (PAHs) and benzene from seawater samples. Dichloromethane was used in the first extraction step, followed by hexane in the second. The combined organic phases were then

dried over anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) to remove residual moisture. After concentration, the extracts were analyzed using gas chromatography with a flame ionization detector (GC/FID). Separation and quantification were carried out on a VF-1 ms capillary column, with a total of 13 PAHs determined in accordance with EPA Method 525 (Magi *et al.*, 2002; Froehner *et al.*, 2011; Marini and Frapiccini 2013; Mandić and Vrančić 2017; Naglaa *et al.*, 2018).

### 3. RESULTS AND DISCUSSION

#### Physical-chemical parameters

The seawater temperature during sampling was consistent with the seasonal norms for March and July in Vlora Bay, Adriatic Sea. The pH values ranged from 7.5 to 8.4, indicating that water quality at Vlora Port can be classified as very good (Poikane *et al.*, 2019), although some signs of potential pollution were noted. Dissolved oxygen (DO) levels during the four sampling campaigns ranged from 8.1 to 11.2 mg/L, suggesting the seawater is suitable to support marine life. Biochemical oxygen demand ( $\text{BOD}_5$ ) values varied between 12.5 and 46.0 mg/L, classifying the water as good regarding organic matter content and biodegradability. Chemical oxygen demand (COD) values ranged from 25.1 to 84.9 mg/L, likely reflecting the presence of various chemicals associated with intense industrial and commercial activities in the port area. These values indicate a moderately good water quality status (Poikane *et al.*, 2019). Total dissolved solids (TDS) averaged between 84.9 and 125 mg/L, while total suspended solids (TSS) ranged from 26.4 to 107.3 mg/L, both reflecting good water quality.

The average nutrient concentrations were as follows: nitrate ( $\text{NO}_3^-$ ) ranged from 2.5 to 6.8 mg/L; nitrite ( $\text{NO}_2^-$ ), 0.09 to 0.27 mg/L; ammonium ( $\text{NH}_4^+$ ), 0.1 to 0.6 mg/L; total nitrogen (N-total), 0.5 to 4.5 mg/L; phosphate ( $\text{PO}_4^{3-}$ ), 1.0 to 6.0 mg/L; and total phosphorus (P-total), 0.8 to 4.6 mg/L. These levels classify the seawater quality as ranging from good to moderate (Poikane *et al.*, 2019). Such concentrations likely reflect the influence of urban runoff, ship discharges, agricultural inputs (including fertilizers and pesticides), and riverine inflows. The effects of tidal movements and water currents, both inside and outside the port, as well as inputs from the Vjosa River, are also important contributors. Sulfate ( $\text{SO}_4^{2-}$ ) concentrations ranged between 271.9 and 514.8 mg/L, possibly

linked to urban wastewater, hydrocarbon contamination, or riverine discharges. Chloride ( $\text{Cl}^-$ ) levels varied from 16.1 to 19.1 g/L, corresponding to salinity values of 29.0 to 34.4 g/L. Calcium ( $\text{Ca}^{2+}$ ) concentrations ranged from 61.4 to 74.8 mg/L, while magnesium ( $\text{Mg}^{2+}$ ) ranged from 33.3 to 50.6 mg/L. These values are likely influenced by the geological characteristics of Vlora Bay, marine water exchange, and Vjosa River inputs.

**Table 1.** Data on physical-chemical parameters, nutrient and main ions in water samples of Vlora's port

Physico-chemical parameters	March 2022	July 2022	March 2023	July 2023	WQI EC Standards
Temperature (OC)	17.48	24.79	17.67	22.92	NA
PH	7.51	8.38	7.74	7.92	6.5 – 8.5
Conductivity (MS/CM)	33.65	41.25	52.33	45.36	NA
DO (mg/l)	10.97	8.11	11.18	8.23	> 4 mg/l
BOD 5 (mg/l)	12.49	46.04	23.36	34.35	< 3 mg/l
COD (mg/l)	25.1	71.9	48.54	84.92	< 25 mg/l
Turbidity (FNU)	232.49	146.04	173.36	134.35	NA
TDS (mg/l)	125.1	121.9	148.54	84.92	500 mg/l
TSS (mg/l)	107.32	37.49	60.75	26.44	25 mg/l
NO3 (mg/l)	2.54	3.39	6.84	6.34	45 mg/l
NO2 (mg/l)	0.12	0.09	0.1	0.27	0.1 mg/l
NH4 (mg/l)	0.13	0.39	0.58	0.25	0.05 mg/l
N-Total (mg/l)	0.51	1.06	2.97	4.46	10 mg/l
PO4 (mg/l)	1.04	2.8	6.03	3.73	0.5 mg/l
P-Total (mg/l)	0.83	0.16	4.58	1.99	0.1 mg/l
SO4 (mg/l)	312.06	411.11	271.94	514.81	200 – 400 mg/l
CL- (g/l)	16.05	18.21	17.93	19.06	NA
Salinity (g/l)	28.97	32.85	32.36	34.4	NA
CA+2 (mg/l)	62.68	61.4	73.94	74.78	75 – 200 mg/l
MG+2 (mg/l)	40.56	33.3	45.43	50.58	30 – 100 mg/l

## Organic pollutants

Organochlorine pesticides (OCPs) were detected in all seawater samples collected from the Port of Vlora during the four sampling campaigns. The highest concentration was observed in March 2023, reaching 14.1 ppb ( $\mu\text{g/L}$ ), while the lowest was recorded in March 2022 at 3.8 ppb. The presence of OCPs is likely attributable to historical agricultural practices in the broader Vlora region, as well as to soil erosion and riverine inputs, particularly from the Vjosa River. In addition to these terrestrial sources, marine currents, point-source discharges, and seasonal variations may have influenced the detected concentrations. Across all four sampling periods, a consistent pesticide profile was identified, suggesting stable and ongoing contamination sources. This profile was dominated by degradation products of several persistent pesticides, notably endosulfan, aldrin, heptachlor, and isomers of lindane. Their presence can be linked to past agricultural applications and potentially to continued inputs via riverine transport. Furthermore, these compounds may persist as residual contaminants or impurities in materials currently used or discharged in the area.

Marker polychlorinated biphenyls (PCBs) were detected in all seawater samples collected during the four sampling campaigns. Concentrations ranged from 2.2 ppb ( $\mu\text{g/L}$ ) in March 2022 to a peak of 10.3 ppb in July 2023. The presence of PCBs is likely associated with atmospheric deposition, as well as mechanical and industrial activities in and around the port area. Notably, the highest concentrations were recorded at sampling stations located within the port, where levels were 2 to 5 times greater than those measured at stations outside the port. This spatial distribution suggests that the primary sources of PCB contamination are point-source discharges, accidental spills, or localized mechanical operations within the port infrastructure.

A particularly high concentration of volatile PCB congeners suggests that atmospheric deposition is a significant pathway for PCB contamination. Conversely, the detection of heavier PCB congeners—such as PCB 153, PCB 138, and PCB 180—further supports the influence of point-source pollution originating from industrial or port-related activities in the vicinity. Polycyclic aromatic hydrocarbons (PAHs) and BTEX compounds (benzene, toluene, ethylbenzene, and xylene) were detected in nearly all seawater samples. Concentrations ranged from a minimum of 1 ppm ( $\text{mg/L}$ ) in March 2022 to a maximum of 5.5 ppm in July 2022. The

presence of PAHs in the marine environment is attributed to various sources, including marine and automotive transport, urban runoff, industrial discharges, combustion processes, natural environmental degradation, fuel handling at gasoline stations, and accidental or deliberate hydrocarbon spills in the surrounding area. Elevated PAH concentrations were particularly notable in the southern section of the port, a zone frequently used for the docking and movement of small tourist vessels. This area is further impacted by vehicular emissions, urban wastewater discharges, and commercial activities situated near the sampling stations. The PAH profile indicates a mixed origin. Low molecular weight (non-pyrogenic) PAHs—such as anthracene, pyrene, and fluorene—are predominantly associated with petroleum spills, mechanical and industrial leaks, urban runoff, and localized point sources. High molecular weight (pyrogenic) PAHs—including benzo[a]anthracene, benzo[b]fluoranthene, and benzo[k]fluoranthene—are typically derived from combustion-related processes, such as emissions from marine and automotive engines, high-temperature industrial activities, forest fires, and urban waste incineration.

These findings underscore the complex interplay of anthropogenic and natural factors contributing to the contamination profile in the Port of Vlora.

**Table 2.** Average data of organic pollutant levels on Vlora’s port

	March 2022	July 2022	March 2023	July 2023	Directive 2008/105/EC
∑ HCHS (ug/l)	0.30	1.47	1.58	2.06	0.02 ug/l
∑ Heptachlors (ug/l)	0.39	1.45	0.58	0.95	0.01 ug/l
∑ Chlordanes (ug/l)	0.23	1.54	0.81	0.63	0.01 ug/l
∑ ALDRINS (ug/l)	2.18	1.07	3.92	3.60	0.01 ug/l
∑ DDTS (ug/l)	0.12	1.02	0.20	0.24	0.025 ug/l
∑ endosulfan (UG/L)	0.57	1.47	6.91	2.82	0.05 ug/l
∑ OCPS (ug/l)	3.82	8.16	14.08	10.29	NA
∑ PCBS (ug/l)	2.21	5.40	8.66	10.23	NA
∑ PAHS (ug/l)	0.98	5.48	2.65	2.86	NA for PAH 2.4 ug/l for naphthalene 0.05 for Benzo[a]anthracene