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Analyzes of hydrocarbons (PAH, alkanes and BTEX) in marine water of Vlora's port

ABSTRACT

In this study, levels of polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons (n-alkanes) and volatile hydrocarbons were determined in water samples of the port of Vlora which is the second largest port in Albania. It is located in Vlora Bay, near Vlora city. Presence of these pollutants in port area is mainly because of ships transport, commercial/passengers processing and the water currents in-side/out-side the port area. Hydrocarbons (PAHs, n-alkanes and BTEX) are generated mainly by the transport (automobiles, ships, trains, etc), extracting/processing of oil industry, coal mine and other industries. Forest burning and their natural background make them very often in environment.

Water samples were taken in May 2022 in different stations of the Vlora's port (inside and outside its area). Aromatic and aliphatic hydrocarbons were extracted simultaneously using two steps liquid-liquid extraction (LLE) technique. Firstly, dichloromethane (MeCl₂) and after that n-hexane were used as extraction solvents. After extraction, the organic phase was dried with sodium sulfate anhydrous, for water removing. "Clean-up" procedure was realized in an alumina column. After the concentration to 2 ml, the samples were injected in Varian 450 GC equipped with FID detectors. BTEX were analyzed using head space solid phase micro-extraction technique (HS/SPME) by using polydimethylsiloxane fiber (PDMS) followed by GC/FID technique.

PAH, n-alkanes and BTEX were found almost in all water samples of Vlora's port. Their presence could be because of anthropogenic factors (elevated activity and ship transport) in the port area. The levels of hydrocarbons in water samples of Vlora's port were higher / comparable than reported levels for them in other stations of the Adriatic Sea, Albania part.

Keywords: Port of Vlora, PAH, n-Alkanes, BTEX, Water analyze, GC/FID

1. INTRODUCTION

Levels of aliphatic (n-alkanes), polycyclic aromatic (PAH) and volatile (BTEX – Benzene, Toluene, Ethylbenzene, o-, m- and p-Xylenes) hydrocarbons were determined in water samples of the Vlora's port by using gas chromatography technique. The port of Vlora is the second seaport of Albania. It is located in Vlora bay, near the city of Vlora (South-West Albania). The port is part of the Lungomare Master Plan of Vlora. Part of this project is the construction of a yacht port, and some new roads to make the port area most accessible.

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Until now, Vlora's port is mainly in the function of passengers and commercial shipping. In fact, beside Vlora port in the Vlora bay are located some other ports such as hydrocarbon port of Petrolifera (near Zverneci), Marina port for Delta Force (near Radhima), Military Base of Orikumi and a fishing harbor (near Zverneci). In the Vlora bay operates some touristic ships and many private boats (motorized one) that serve mostly for tourist transportation to visit Sazani Island and Karaburuni peninsula. Vlora bay as well as the port of Vlora are impacted by intense ship transport and industrial activity in this area. Due to the geographical position, the bay favors the concentration of pollutants inside of it. Also, can be added the negative impact of Vjosa and Semani rivermouth that bring new arrivals of pollutants (pesticide, hydrocarbons, detergents, etc) from other areas of Albania. These are the main factors of pollution in Vlora bay. Also, the port of Vlora, as

part of Vlora bay, is affected by this pollution adding numerous ships, automobile transport and large commercial activity in this area.

Hydrocarbon pollutants (PAHs and BTEX) are generated mainly by automobile transport, extracting/processing of oil industry, coal mine and other industries. Generally, alkanes are not considered problematic for the environment and organisms in low levels because of their presence in natural background. PAHs and BTEX in marine water were reported in many studies [1-3] generally because of ship transport and/or different accident spills of hydrocarbons. Forest burning and their natural background make them very often in the environment. PAHs (EPA list, 13 most toxic PAHs), Benzene and Toluene are classify as priority substances. These organic pollutants can be found in the atmospheric, aquatic, and terrestrial systems and therefore are closely monitored in the environment. Some of them, such as Benzene or Benzo[a]anthracene are known to be genotoxic, mutagenic, carcinogenic, and/or teratogenic [4]. Low molecular weight PAHs and BTEX move easily in nature with long range distances because of their volatility [4,5]. Higher molecular members of PAHs are relatively immobile due to their large molecular mass. They are less volatile, relatively

insoluble in water, and more lipophilic than the lower molecular members. PAHs are known to stay longer in the environment. Their hydrophobicity has generated a lot of concerns to humans, environment, and aquatic organisms. They associate freely with dissolved organic matter in the surface water through several means of binding and adsorption, especially those with high molecular weights [5,6] and are subsequently deposited in the sediment, thus accumulating to a higher level of toxicity in the aquatic environment. The bioavailability of PAHs to the aquatic animals and also their penetration of dietary sources has thus become unavoidable.

2. MATERIAL AND METHODS

2.1. Sampling of marine water in the port of Vlora

Water samples were taken in 10 different stations of the Vlora's port (6 inside and 4 outside of port area). Marine samples were taken in May 2022. The sampling stations are presented in Figure 1. A quantity of seawater (2.5 liter) was taken from each station in Teflon bottles. The sampling method was based on ISO 5667-3: 2018 [7]. Water samples were transported and conserved at +4°C prior to analyze.

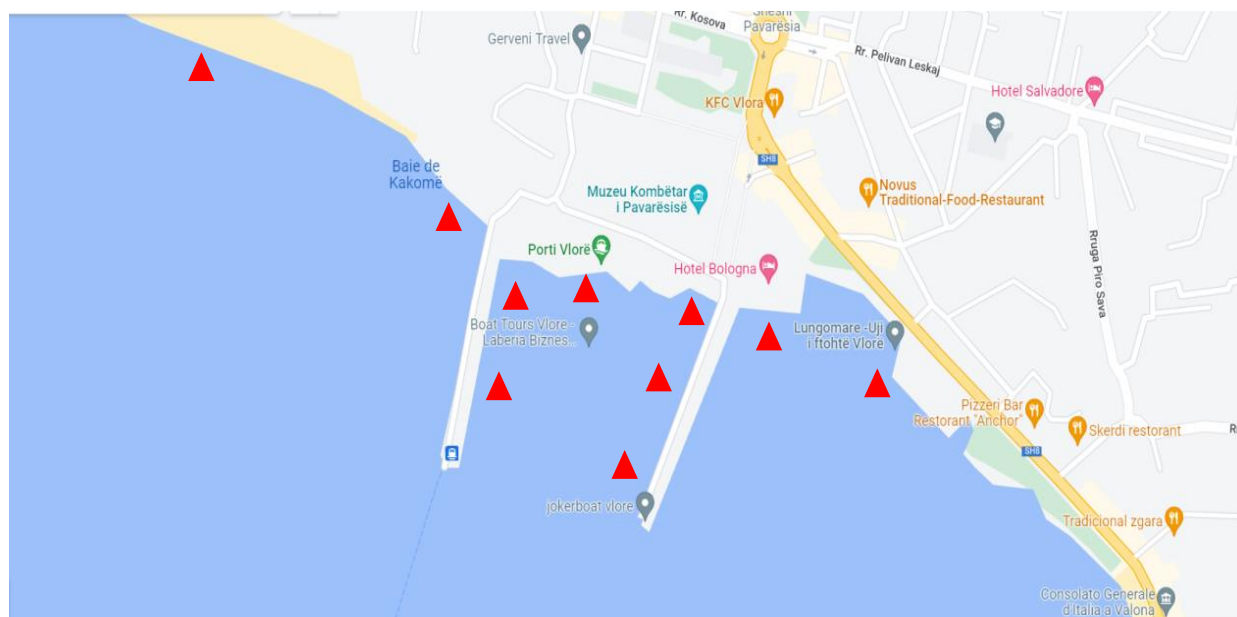


Figure 1. Sampling stations in the port of Vlora, May 2022.

Slika 1. Stanice za uzorkovanje u luci Valona, maj 2022.

2.2. Treatment of water samples for PAH and *n*-alkanes analyzes

Two steps liquid-liquid extraction (LLE) technique was used for extracting PAHs from marine water samples. In a separator funnel, 1 L of

water was treated firstly with 30 mL dichloromethane (first step LLE) and after that with 30 ml *n*-hexane (second step LLE). After extraction, the organic phase was dried with 5 g of anhydrous Na₂SO₄ for water removing. Extracts were

concentrated to 2 mL *n*-hexane using Kuderna-Danish and then were injected in GC/FID apparatus.

2.3. Determination of PAH and *n*-alkanes in water samples

Gas chromatographic analyses of PAHs and *n*-alkanes in seawater samples were realized with a Varian 450 GC instrument equipped with a flame ionization detector and PTV injector. VF-1 ms capillary column (30 m x 0.33 mm x 0.25 µm) was used to isolate and determine simultaneously 13 PAHs according EPA 525 Method and the mixture of C10-C26 *n*-alkanes. Helium was used as carrier gas with 1 mL/min. FID temperature was held at 280°C. Nitrogen was used as the make-up gas (25 mL/min). Hydrogen and air were flame detector gases. Their flow were 30 mL/min and 300 mL/min, respectively. EPA 525 Standard Mixture (Sigma Aldrich) and a mixture of C10-C26 *n*-alkanes (IAEA/MEL laboratory) were used for qualitative and quantitative analyze of PAHs and *n*-alkanes. Analyzes of hydrocarbons was based on simultaneous determination of Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Pyrene, Benz[a]anthracene, Chrysene, Perilene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Indeo[1,2,3-cd]pyrene, Dibenzo[a,b]anthracene, Benzo[g,h,i]perylene. C10, C12, C14, C16, C18, C20, C20x, C22, C24 and C26. Quantification of PAHs and *n*-alkanes was based on external standard method. Six calibration points with concentrations of 1, 5, 10, 25, 50 and 100 µg/L were selected for both, PAHs and *n*-alkanes. Quality assurance procedures included determination of recovery (84.2 – 112.3%), LOD (0.5 µg/L), LOQ (1.5 µg/L), precision, reproducibility and accuracy of the method [8-10].

2.4. HS-SPME technique for determination of BTEX in water samples

Determination of BTEX in water samples was realized using solid phase micro-extraction in static head space mode (HS/SPME) followed by GC/FID technique. 5 mL of water sample was put in a 10 mL head space vial. 100 µm polydimethylsiloxane (PDMS) fiber was used to extract BTEX from water samples. Adsorption process was realized in 50°C for 45 minutes. Desorption process (30 seconds in 280°C) was realized in the PTV injector 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 held at 280°C. Nitrogen was used as the make-up gas (25

mL/min). Hydrogen (30 mL/min) and air (300 mL/min) were flame gases for the FID detector. BTEX Mixture was used for qualitative and quantitative analyze. Five calibration points with concentrations of 1, 5, 10, 25 and 50 µg/L were used for BTEX quantification with external standard method. Method evaluation included recovery (91.3 – 104.6%), LOD (0.5 µg/L), LOQ (1.5 µg/L), precision, reproducibility and accuracy of the method [8].

3. RESULTS AND DISCUSSION

In this study were analyzed PAH, *n*-alkanes and BTEX in marine water samples from port of Vlora, Adriatic Sea. Samples were taken in May 2022. This is the second port of Albania for passengers and commercial shipping. Aliphatic, polycyclic aromatic and volatile hydrocarbons were analyzed using GC/FID techniques. Some of PAHs and BTEX are classified as priority substances because of their stability and toxicity. Intense ship transport at Vlora Bay could be possible factor for the presence of hydrocarbons in area of Vlora's port.

Figure 2 shows totals of 13 PAHs according to EPA 525 Method in water samples of Vlora's port measured by liquid-liquid extraction followed by GC/FID technique. PAHs were detected for all analyzed water samples. Total of PAHs were found in higher concentration for station VW8 located inside the port area with 3.7 µg/L. Average level of PAH in analyzed samples were 0.62 µg/L. Their presence could be because of elevated ship transport in this area. Automobilist transport and any possible accident (hydrocarbon spillage, industrial waste, ect) could be another source of PAH pollution in marine water samples of Vlora's port. The presence of some individual PAHs was noted in higher level. Acenaftilene was found in higher level for VW8, VW1 and VW3 while Anthracene was abundant in VW7, VW8, VW9, VW10 and VW1 stations. The PAH distribution shows that their origin is different for different stations of Vlora port. Also, this could be a momentum value of PAHs for these stations. Profile of PAHs in seawater of Vlora port was: Acenaftilene > Anthracene > Benzo[a]anthracene (Figure 3). Presence of PAHs is mainly because of ship and automobilist transport. PAH levels in seawater samples were in the same range or higher than the reported levels for other stations of Adriatic Sea, Albania [1-3,8,11]. The presence of PAH individuals (Anthracene) was higher than permitted level according to Albanian and EU norms (Directive 2008/105/EC) [12].

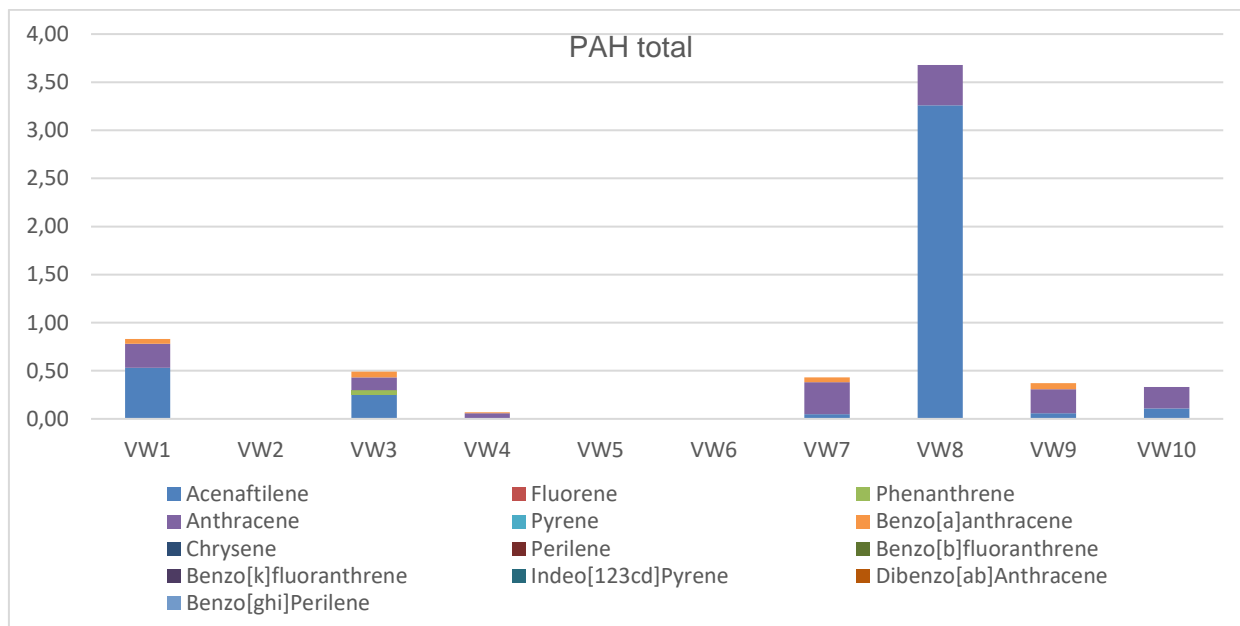


Figure 2. Total of PAHs in water samples of Vlorë's port

Slika 2. Ukupni PAH u uzorcima vode luke Valona

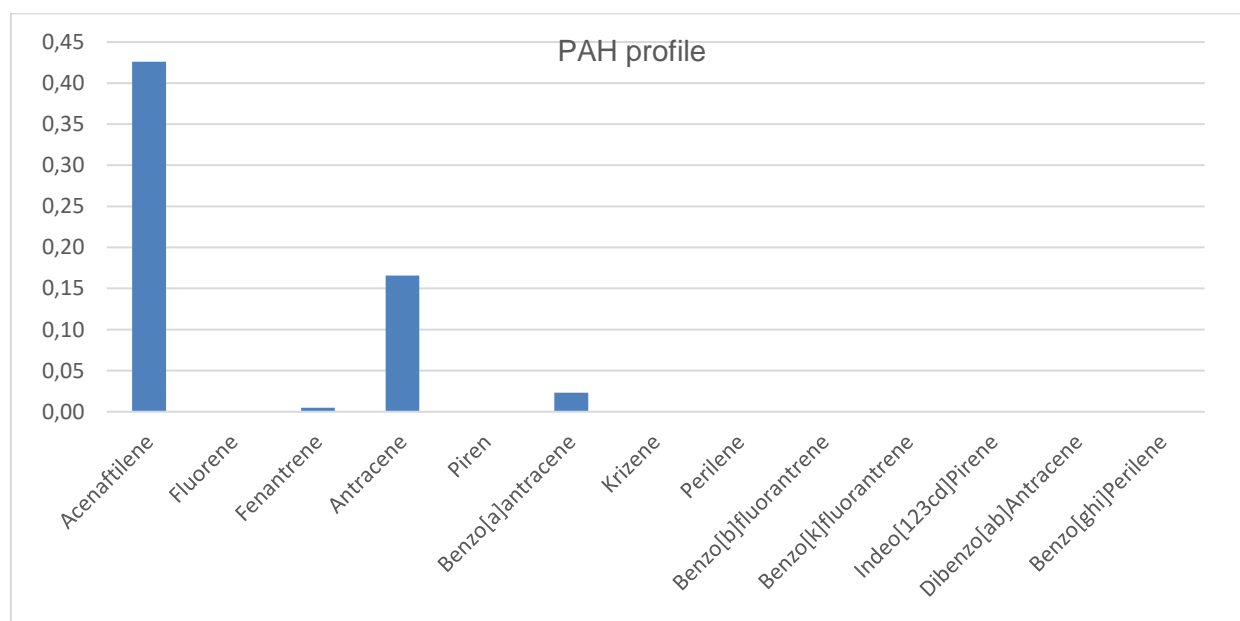


Figure 3. Profile of PAH in water samples of Vlorë's port, May 2022

Slika 3. Profil PAH u uzorcima vode luke u Valoni, maj 2022

Figure 4 shows the total aliphatic alkanes C10-C26 in water samples for the port of Vlorë. Normal alkanes were found in all analyzed samples except VW6 station when they were found lower than LOD levels ($< 0.5 \text{ ug/L}$) for these compounds. Also, aliphatic alkanes (the same as PAHs) were found in higher concentrations for VW8 station with 2.0 ug/L . Their presence can be related to the elevated

ship transport in Vlorë bay as well as at the port area. Automobile transport, the port of hydrocarbons (Petrolifera) any possible accidents/spillage are not excluded to affect in found level. Distribution of *n*-alkanes was different because of their different origin or momentum values. C10 was found in higher level at VW8 station while C18 was detected relatively in high

level for VW10, VW1 and VW3 stations. Presence of C18 is connected with punctual sources of these pollutants in the port area. Profile of aliphatic hydrocarbons was: C10 > C18 > C16 > C24 > C26 > C14 (Figure 5). Presence of C24 and C26

alkanes is an indicator of fuel oil that is used in ship motors. Levels of aliphatic hydrocarbons were higher/comparable with reported data on previous studies on Adriatic Sea, Albanian part [8,11].

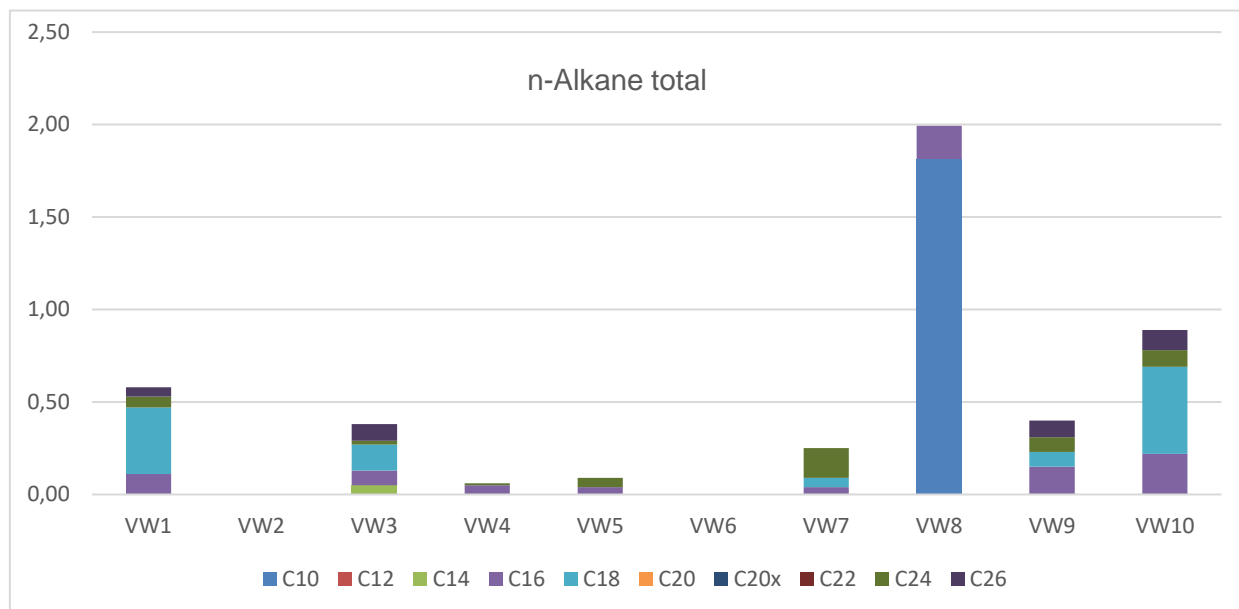


Figure 4. Total of C10-C26 n-alkanes in water samples of Vlorë's port, May 2022

Slika 4. Ukupno C10-C26 n-alkana u uzorcima vode luke Valona, maj 2022.

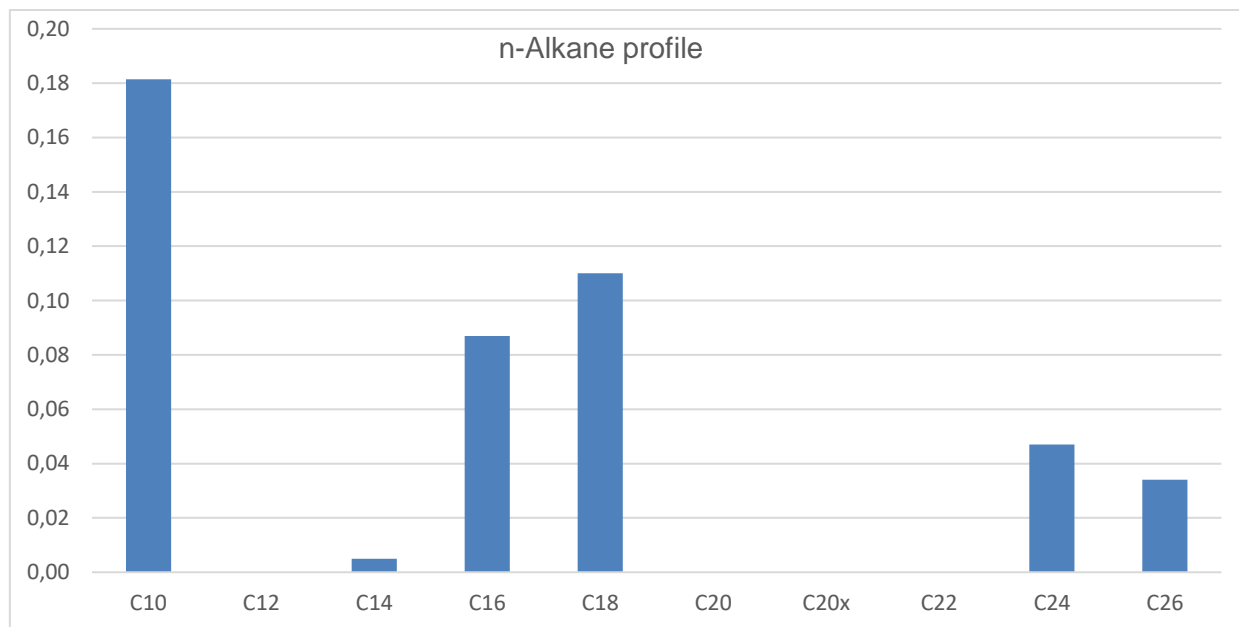


Figure 5. Profile of aliphatic hydrocarbons in water samples of the port of Vlorë

Slika 5. Profil alifatičnih ugljovodonika u uzorcima vode luke Valona

Figure 6 shows totals of Benzene, Toluene, Ethyl benzene, *ortho*-, *meta*- and *para*-Xylenes (BTEX) in water samples of Vlorë's port. Volatile

hydrocarbons were measured by the HS-SPME followed by GC/FID technique. BTEX were detected for 70% of analyzed samples. Also, BTEX

were found in higher concentration for VW8 station with 3.0 ug/L. Benzene was the most frequently volatile compound found in all analyzed samples but Ethylbenzene was found in higher concentration for VW8 station. Profile of BTEX in water samples of Vlora's port was: Ethylbenzene > Benzene > o-Xylene > Toluene. Presence of BTEX could be because of elevated ship transport, automobilist transport and any possible spillage of

hydrocarbons near the area of Vlora's port. A momentum value of BTEX is not excluded. Benzene concentrations were found in low/comparable concentration than reported levels for other stations of Adriatic Sea, Albania [8]. Benzene level was lower than permitted level according to Albanian and EU norms (Directive 2008/105/EC) [12].

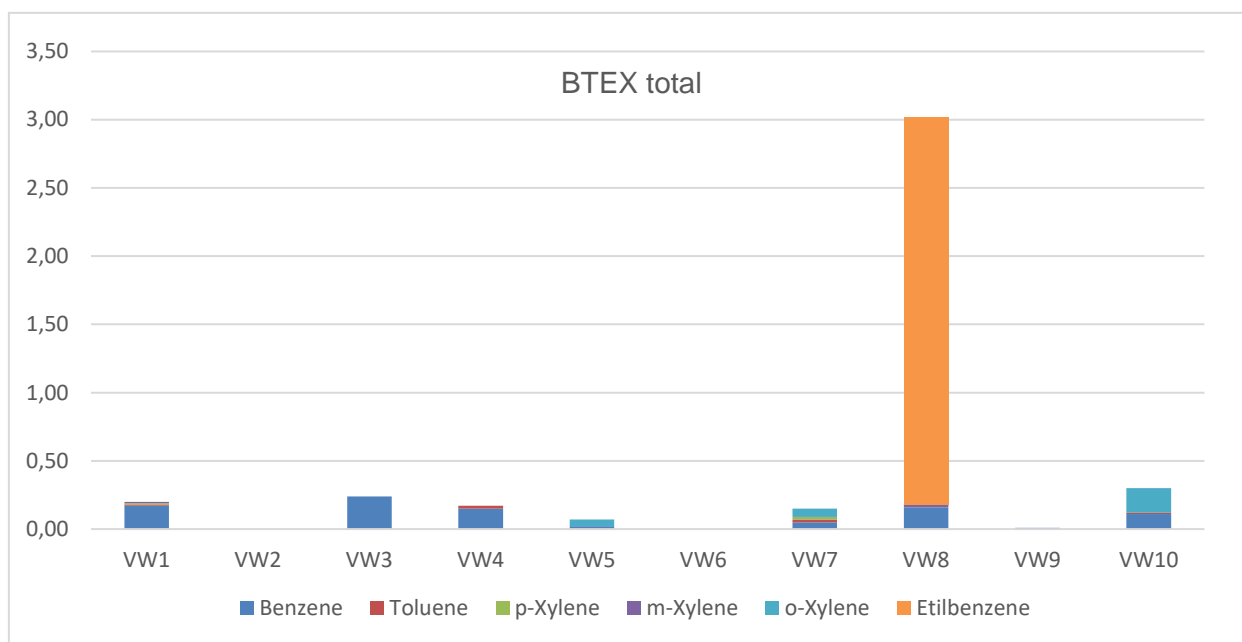


Figure 6. Total of BTEX in water samples of Vlora's port, May 2022

Slika 6. Ukupni BTEX u uzorcima vode luke Valona, maj 2022

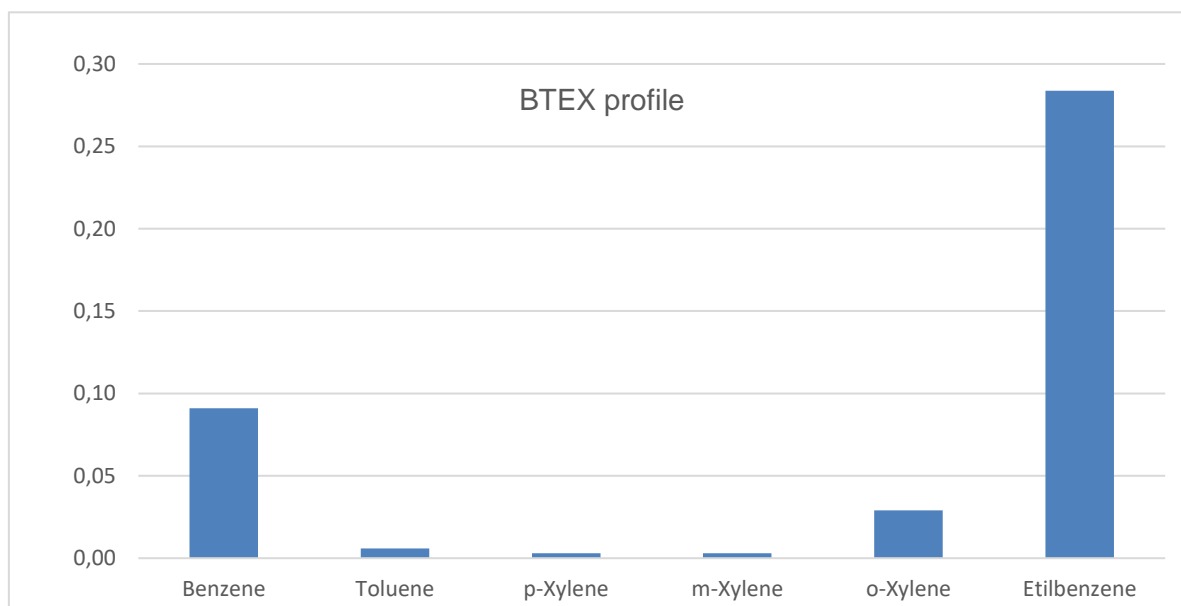


Figure 7. Profile of BTEX in water samples of Vlora's port, May 2022

Slika 7. Profil BTEX-a u uzorcima vode luke Valona, maj 2022

4. CONCLUSIONS

Aliphatic, polycyclic aromatic and volatile hydrocarbons were analyzed in marine water samples for the port of Vlora using GC/FID technique. PAHs, *n*-alkanes and BTEX were found in all water samples of Vlora's port. The higher levels of these pollutants were found for VW8 station, inside the port area. Presence of hydrocarbons in water samples of Vlora's port could be mainly because of elevated ship transport, automobilist transport and any possible accident of hydrocarbons near the port area. Momentum values of them are not excluded. Concentrations of some individual PAHs, *n*-alkanes and BTEX were found in higher concentrations than other hydrocarbons. Generally, found level for PAHs, *n*-alkanes and BTEX were lower than permitted levels for surface waters according to EU Directive 2008/105/EC and Albanian norms. Exception was for Anthracene levels in some stations which was found to be higher than permitted level. Monitoring of hydrocarbons in water of Vlora's port should be continuous because these area could be affected by intense ship and automobilist transport. Elevated activities at Petrolifera, fishing and tourist transport are other possible sources of hydrocarbons in marine water samples of Vlora's port.

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IZVOD

Analize ugljovodonika (pah, alkana i bteks) u morskoj vodi luke valona

U ovoj studiji utvrđeni su nivoi policikličnih aromatičnih ugljovodonika (PAH), alifatičnih ugljovodonika (n-alkana) i isparljivih ugljovodonika u uzorcima vode luke Valona koja je druga najveća luka u Albaniji. Nalazi se u zalivu Valone, u blizini grada Valone. Prisustvo ovih zagađivača u lučkom području je uglavnom zbog transporta brodova, komercijalne/putničke obrade i vodenih tokova unutar/izvan područja luke. Ugljovodonici (PAH, n-alkani i BTEKS) se uglavnom proizvode transportom (automobili, brodovi, vozovi, itd.), vađenjem/preradom naftne industrije, rudnika uglja i drugih industrija. Paljenje šuma i njihova prirodna pozadina čine ih veoma čestim u okruženju.

Uzorci vode uzeti su u maju 2022. godine u različitim stanicama luke Valona (unutar i van njenog područja). Aromatični i alifatični ugljovodonici su ekstrahovani istovremeno korišćenjem tehnike ekstrakcije tečnost-tečnost u dva koraka (LLE). Kao rastvarači za ekstrakciju prvo su korišćeni dihlorometan (MeCl₂), a zatim n-heksan. Posle ekstrakcije, organska faza je osušena sa anhidrovanim natrijum sulfatom, radi uklanjanja vode. Procedura „čišćenja“ je realizovana u koloni glinice. Nakon koncentracije do 2 ml, uzorci su ubrizgani u Varian 450 GC opremljen FID detektorima. BTEKS je analiziran korišćenjem tehnike mikro-ekstrakcije čvrste faze (HS/SPME) uz upotrebu polidimetilsiloksanskih vlakana (PDMS), praćeno GC/FID tehnikom.

PAH, n-alkani i BTEKS pronađeni su skoro u svim uzorcima vode luke Valona. Njihovo prisustvo može biti zbog antropogenih faktora (povećana aktivnost i brodski transport) u području luke. Nivoi ugljovodonika u uzorcima vode luke Valona bili su viši/uporedivi od prijavljenih nivoa za njih u drugim stanicama Jadranskog mora, deo Albanije.

Ključne reči: Luka Valona, PAH, n-alkani, BTEKS, analiza vode, GC/FID

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