

ORGANIC POLLUTANTS IN HOT-SPOT AREA OF  
PORTO-ROMANO, ALBANIA

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**Abstract:** Concentrations of organochlorine pesticides, polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH) and BTEX (benzene, toluene, ethylbenzene and xylenes) in marine water and sediment samples of Porto-Romano area are presented in this paper. Porto-Romano is situated in Adriatic Sea, near the city of Durrresi, in central Albania. It is considered as hot-spot, because in this area was located the chemical plant for Lindane production before the 1990s. Water and sediment samples were taken in March 2018 in six stations of Porto-Romano. Liquid-liquid extraction was used for extracting organochlorine pesticides, PCBs and PAHs from water samples. Ultrasonic extraction was used for extraction of organic pollutants from sediment samples. Clean-up procedure was realized in an open-column of Florisil for chlorinated pollutants. Analysis of pesticides and PCBs were realized in HP 6890 Series II, gas chromatograph equipped with  $\mu$ ECD detector. For separation of organochlorine pollutants Rtx-5 capillary column was used. Analysis of PAH and BTEX were realized in Varian 450 GC, gas chromatograph equipped with FID detector and VF-1ms capillary column. BTEX were analyzed using HS-SPME method. Organochlorine pesticides were found in higher levels for both water and sediment samples of Porto-Romano because of the presence of ex-chemical plants in this area for more than 30 year. Lindane and its isomers were not found in high concentration. PCB 28, a volatile congener was found in higher concentrations because of its atmospheric origin. Presence of PCB 138 showed terrestrial origin of PCBs in this area. PAH and BTEX were found only in 30% of the analyzed samples. Their concentration could be because of hydrocarbon activity and ship transport in this area. Mismanagement of ex-chemical plant wastes, urban pollution and recent industrial activity are the main factors of pollution in Porto-Romano area. Presence of organic pollutants in water and sediment samples of Porto-Romano indicates that monitoring of this Hot-spot should be continuous.

## INTRODUCTION

Porto-Romano is situated 7 km north of Durrës city, facing the Adriatic Sea. During communism, the area was known for the chemical plant that produced Lindane for agriculture purposes and sodium dichromate for leather tanning for more than 30 years (Çullaj *et al* 2005). Pesticides were used widely in Albania before the 1990s, especially in the western part of the country (Shkodra, Shëngjini, Durrës, Lushnja, Vlora) where the main agricultural areas are located. DDT, Lindane, HCB, Aldrins and Heptachlors were the most used organochlorine pesticides. Lindane plant was abandoned after the 90' where hundreds of tons of pesticides seriously contaminated the water, soil and air near Porto-Romano. Pesticides with chlorine are usually very stable compounds in the environment. This is the reason why even after three decades, organochlorine pesticides are still detected in water, soil, sediment and biota samples (Como *et al* 2013).

Persistent organochlorines pollutants such as organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) are a group of compounds of great chemical stability and persistence, whose presence in the environment is a clear indication of anthropogenic pollution (Konstantinou *et al* 2006). The massive use of these xenobiotics for agricultural and industrial purposes caused their widespread diffusion to all environmental compartments including a wide range of organisms such as plankton, fish, marine and land mammals and humans (Lekkas *et al* 2004; Neziri *et al* 2010). Several studies have shown that these compounds exert a number of toxic responses including immunotoxicity, reproductive deficits, teratogenicity, endocrine toxicity and carcinogenicity/tumor promotion (Nuro *et al* 2014; Vryzas *et al* 2009). OCPs are the first class of synthetic pesticides, introduced in agricultural and civil uses to counteract noxious insects and insect-borne disease. Most OCPs have been progressively restricted and then banned in the 1970s in most industrialized countries. In Albania organochlorine were used mostly as insecticides until the 90' (Nuro *et al* 2014; Como *et al* 2013).

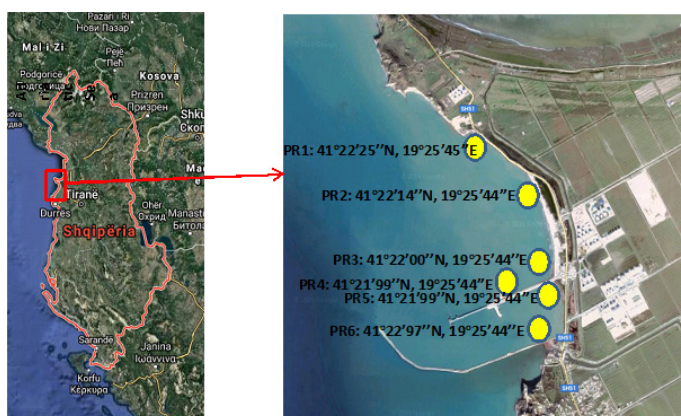
After the communism era, the population of Porto Romano grew constantly, due to free movement of population and migrants from northern areas of Albania. Different families settled in this critically contaminated area of ex-chemical plants. Investments for clean-up of Porto Romano area started in November 2005 as part of a big World Bank-supported project on the Integrated Coastal Zone Management and Clean-up in Albania. Almost 750 tons of pesticides were repackaged in the storage site and transported to a specialized German disposal site in 2006. From 2015 to now in Porto-Romano is constructed and operates the main port for hydrocarbons in Albania. There import / export of GLP, oil, gasoline, etc. is realized. This could be another possibility for contamination of this area due to accidents that may be caused by the transfer of hydrocarbons. Also, a landfill that collects the urban wastes of several cities (Durrës, Rrogozhinë, Peqin, Kavajë) is located near Porto-Romano, which has become quite problematic for

the environment and residents of this area (Borshi *et al* 2016). Unfortunately, Porto-Romano is strongly influenced by anthropogenic activity for a long period of time and became a Hot-spot area of Albania.

## MATERIALS AND METHOD

### Sampling of water and sediment samples in Porto-Romano area

The sampling of water and sediments were realized for six different stations in Porto-Romano area. Water and sediment were sampled in the same stations, in March 2018. The sampling sites are presented in Figure 1. 2.5 L of water were taken from each station. Van Veen grape was used to take sediment samples (1-5m distance to seashore). Water and sediment samples were transported at +4°C. Firstly, sediments were air dried. After that oven (5 hours in 105°C) was used.



**Fig. 1.** The sampling map of water and sediment samples in Porto-Romano (Adriatic Sea), March 2018

### Sample treatments for pesticide and PCB analyzes

*Marine water samples:* Liquid-liquid extraction was used for the simultaneous extraction of organochlorine pesticide and polychlorinated biphenyls from marine water samples of Porto-Romano. 1 l of water and 30 ml n-hexane as extracting solvent were added in a separatory funnel. After extraction the organic phase was dried with 5 g anhydrous  $\text{Na}_2\text{SO}_4$  for water removing. A Florisil column was used for the sample clean-up. 20 ml n-hexane/dichloromethane (4/1) was used for elution. After concentration to 1 ml, the samples were injected in GC/ECD (Lekkas *et al*, 2004; Vryzas *et al*, 2009).

*Sediment samples:* Ultrasonic extraction was used for the extraction of OCPs and PCBs from sediment samples of Porto-Romano areas. 10 g dry sediments and 50 ml n-hexane/dichloromethane (3/1) as extracting solvent were added in glass vial (100 ml) with Teflon cap. After extraction the organic phase was dried with

5g anhydrous Na<sub>2</sub>SO<sub>4</sub> for water removing. Elute was treated with metallic mercury for sulfur removing. A Florisil column was used for final clean-up of samples. 20 ml n-Hexane/dichloromethane (4/1) was used for elution of organochlorine pollutants. After the concentration to 1 ml, the samples were injected in GC/ECD (Vryzas *et al*, 2009; Lekkas *et al*, 2004; Wells and Hess, 2000).

### **Gas Chromatography analyzes of pesticides and PCBs**

Organochlorine pesticides and PCBs were analyzed using capillary column Rtx-5, 30m long x 0.25mm i.d. x 0.25 μm film thicknesses on a gas chromatograph HP 6890 Series Plus with μECD detector. Helium was used as carrier gas and nitrogen as make-up gas. Manual injection was done in split mode (1:50) in 280 °C. The organochlorine pesticides detected were HCHs (α-, β-, γ- and δ-isomers) and the DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), hexachlorobenzene (HCB), heptachlor, heptachlor epoxide, methoxychlor and mirex. Analysis of PCBs was based on the determination of the seven PCB markers (IUPAC Nr. 28, 52, 101, 118, 138, 153 and 180). Quality assurance procedures included the analyses of certified sample IAEA 435 to determine the precision and the accuracy of the method (Vryzas *et al*, 2009; Lekkas *et al*, 2004; Nuro *et al*, 2014).

### **Treatment of samples for PAH analyzes**

*Marine water samples:* Liquid-liquid extraction was used for the extraction of polyaromatic hydrocarbons from water samples of Porto-Romano areas. 1 L of water and 30 ml dichloromethane as extracting solvent were added in a separatory funnel. After extraction the organic phase was dried with 5 g anhydrous Na<sub>2</sub>SO<sub>4</sub> for water removing. After the concentration to 1 ml, the samples were injected in GC/FID for PAH analyze (Nuro *et al*, 2014; Gustafson and Dickhut, 1997).

*Sediment samples:* Ultrasonic extraction was used for the extraction of polyaromatic hydrocarbons from sediment samples of Porto-Romano areas. 10 gr dry sediments and 50 ml n-hexane as extracting solvent were added in Erlenmeyer (100 ml) with Teflon cap. After extraction the organic phase was dried with 5 g anhydrous Na<sub>2</sub>SO<sub>4</sub> for water removing. A Florisil column was used for the sample clean-up. 20 ml h-hexane was used for elution. After the concentration to 1 ml, the samples were injected in GC/FID (Nuro *et al* 2014; Como *et al* 2013).

### **GC/FID determination of PAHs in water and sediment samples**

Gas chromatographic analyses of PAH in water and sediment samples were realized with a Varian 450 GC instrument equipped with a flame ionization detector and PTV detector. VF-1 ms capillary column (30 m x 0.33 mm x 0.25 μm) was used to isolate and determine 13 PAHs compounds. Helium was used as carrier gas with 1 ml/min. FID temperature was held at 280°C. Nitrogen was used as carrier and make-up gas for both analyses. Hydrogen and air were flame detector gases with 30 ml/min and 300 ml/min, respectively. EPA 525 Mixture was used for qualitative and quantitative of PAH analyse. Quantification of PAH was based on external standards (Nuro *et al*, 2014; Gustafson and Dickhut, 1997).

### HS/SME-GC/FID analyze of BTEX in water and sediment samples

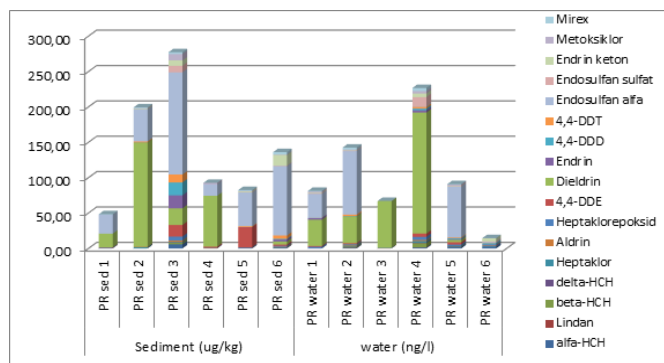
Headspace solid phase micro extraction (HS-SPME) technique was used to trace BTEX in water and sediment samples. 5.0 ml of water sample (or 5 g dry sediment) was placed in a 10 ml headspace vial (5 replicate vials for each sample) to adsorb BTEX. The vials were placed in a heating block for 45 min at 60°C. Extraction of volatile compounds was done using a 100 µm Polydimethylsiloxane fibre in a SPME manual holder. Direct injection in HS mode was performed in 280°C (hold for 20 sec) in a PTV injector. Helium was used as carrier gas in constant flow mode with 0.8 ml/min. FID temperature was held at 280°C. Quantification of BTEX was based on external standards. The method used for determination of VOCs in water samples by capillary GC was optimized for the duration and temperature of extraction, and GC parameters (Mendez *et al*, 2000; Nuro *et al*, 2014; USEPA, 2009).

## RESULTS AND DISCUSSION

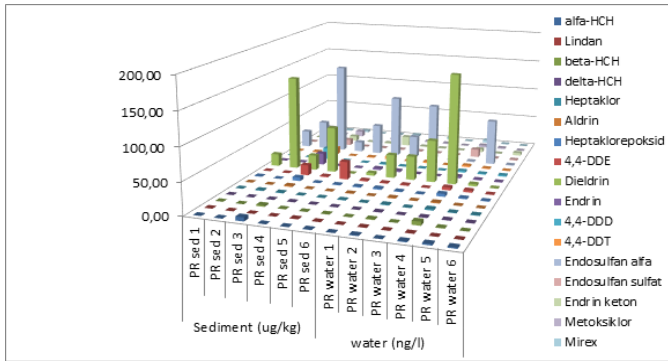
Determination of organochlorine pesticides, their residues, polychlorinated biphenyls, PAH and BTEX was realized in water and sediment samples of Porto-Romano, Durres, Albania. Water and sediment samples were taken in 6 different stations. Liquid-liquid technique was used for extraction of OCPs, PCBs and PAHs in water samples while ultrasonic bath was used for sediment samples. GC/ECD technique was used for determination of organochlorine pesticides and PCBs. Qualitative and quantitative analyze of PAHs were realized by GC/FID technique. BTEX analyze were performed using HS/SPME technique with PDMS fiber followed by gas chromatography flame ionization detector in both, water and sediment samples.

Figure 2 shows the total of organochlorine pesticides in water samples of Porto-Romano, March 2018. Organochlorine pesticides were detected in all samples. Mean concentration of pesticides were: in water samples 89.9 ng/L and in sediment samples 136.7 ng/g. Abandoning of pesticides for a several years near Porto-Romano is the main factor for their presence in this ecosystem. The higher concentration was in sediment samples because of adsorption process and their slow degradation. Distributions of organochlorine pesticides in water and sediment samples of Porto-Romano (**Figure 2**) were built by some individual pesticides such as Dieldrin and Endosulfan alfa found in higher concentration for some stations. Distribution of pesticides and their residues was the same for all samples because of the same pollution origin. Pesticide residues were found in higher concentrations because of previous use of pesticides and their degradation process. Figure 3 shows profiles of organochlorine pesticides in water and sediment samples of Porto-Romano. Their profile in water samples was: Dieldrin > Endosulfan alfa > Endosulfan sulfat, while in sediment samples was: Endosulfan alfa > Dieldrin > DDE > Endrin keton > Endrin. Profile of pesticides was connected with individual levels of pesticides in different samples.

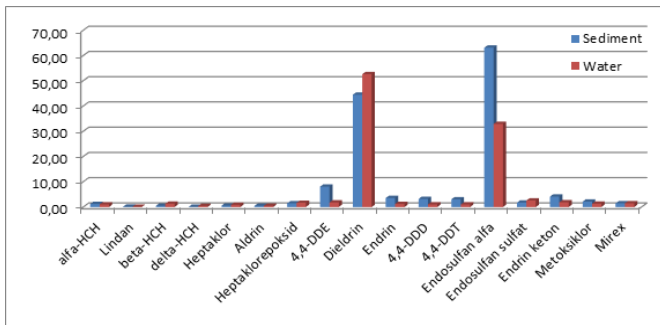
Mean concentration of Lindane and its isomers in water samples was 2.8 ng/L and in sediment samples was 1.9 ng/g. Lindane was detected for 50% of studied samples. Their profile was: Beta-HCH > alfa-HCH > Lindane > delta-HCH. This fact is because of HCH isomer stability and its individual physical and chemical characteristics. Total of HCHs was lower than permitted levels in water and sediment samples. These levels were lower than previous reports for this area (Borshi *et al* 2016). Heptachlors were found in higher concentration in water samples (2.6 ng/L) than in sediment samples (2.0 ng/g). This could be connected with new arrival from terrestrial sources. Their presence was lower than permitted levels in water and sediment samples. Mean concentration of Aldrins was: in water samples 56.2 ng/L and in sediment samples 52.7 ng/g. Dieldrin was found in higher level for both samples. Aldrines could be in use in this area under a false trademark or could be any punctual source near Porto-Romano area for this pollutant. Total of Aldrin's were higher than permitted levels in water and sediment samples. Mean concentration of DDT and its degradation products in water samples was 5.2 ng/L and 16.3 ng/g in sediment samples. DDTs were found in higher concentration in sediment samples because of their previous use. DDT was detected for only in one water sample and in two sediment samples. Total of DDTs were lower than permitted levels in water and sediment samples. Mean concentration of Endosulfanes in water samples was 35.8 ng/L and in sediment samples 65.7 ng/g. Endosulfan alfa was found in higher level for all levels. Total of Endosulfanes were lower than permitted levels in water, and sediment samples. Organochlorine pesticide levels were lower/comparable than reported levels in other studies for Porto-Romano. Presence of Dieldrin and Endosulfan alfa was higher because of recent use for this pesticide in agricultural areas near Porto-Romano. New arrivals from terrestrial sources or use of this pesticide under a false mark could be some reasons for their presence.



**Fig. 2.** Total of organochlorine pesticides in water and sediment samples of Porto-Romano



**Fig. 3.** Distribution of organochlorine pesticides in water and sediment samples of Porto-Romano



**Fig. 4.** Profile of organochlorine pesticides in water and sediment samples of Porto-Romano

Figure 5 shows the total of PCB markers in water and sediment samples of Porto-Romano. Mean concentration of PCB markers in water samples was 53.6 ng/L and in sediment samples 56.9 ng/g. PCB markers were found for all studied samples. Their presence could be because of atmospheric depositions or terrestrial sources. Discharging of wastes from some mechanical businesses near Porto-Romano could affect found level and their profile. Distribution of PCBs is shown in Figure 6. Distributions of PCBs were the same for all samples. This could be because the same pollution origin of PCBs in water and sediment samples of Porto-Romano. PCB 28 was found in higher level for all samples. This fact is connected with atmospheric origin of PCBs in this area. PCB 138 was found in higher level for PRW4 station. This could be a momentum value or a punctual source near PRW4 station. Profiles of PCBs (Figure 7) were: PCB 28 > PCB 138 > PCB 153 > PCB 118. The levels of PCBs in water and sediment samples of Porto-Romanos were lower than reported levels for the previous studies (Borshi *et al*, 2016).

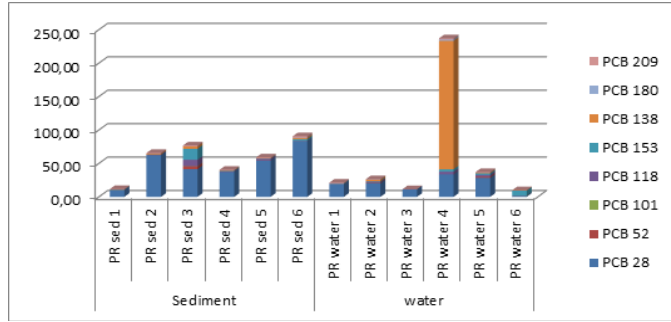


Fig. 5. Total of PCB markers in water samples of Porto-Romano

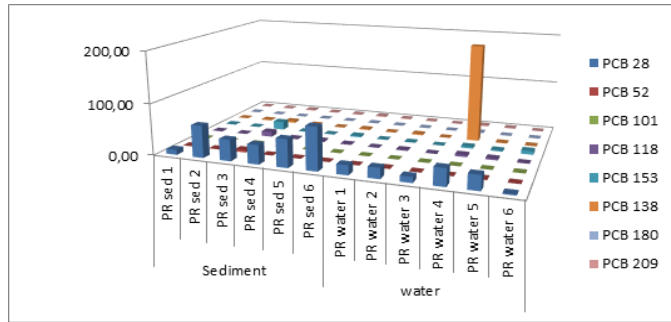


Fig. 6. Distribution of PCB markers in water samples of Porto-Romano

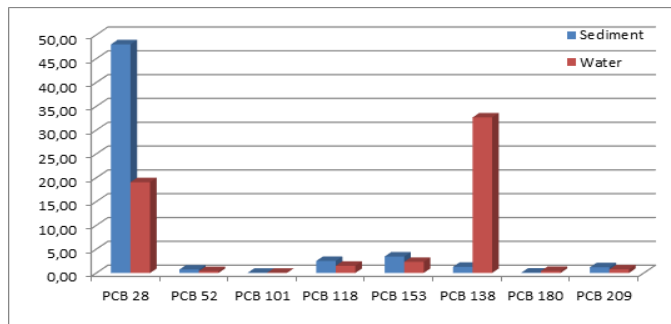
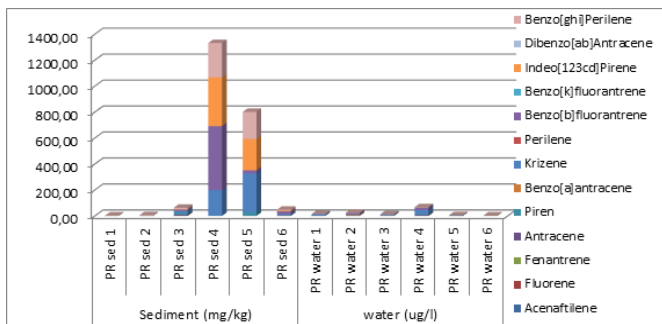


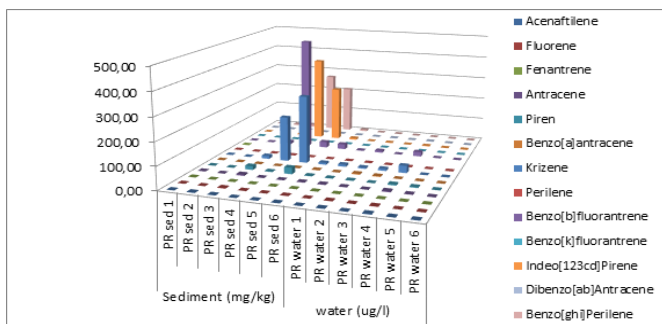
Fig. 7. Profile of PCB markers in water samples of Porto-Romano



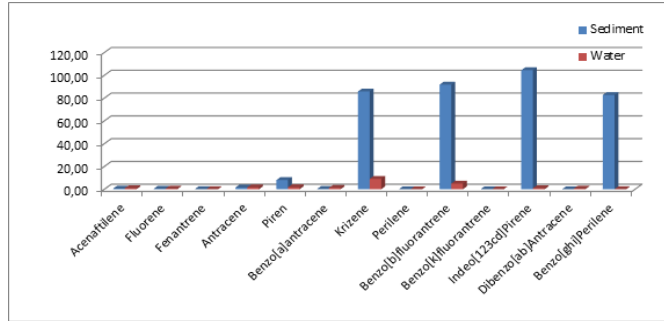
Figure 8 shows the total of PAH in water and sediment samples of Porto-Romano. Mean concentration of PAH in water samples was 21.2 ug/L and in sediment samples was 345 ug/g. PAHs were found for all studied samples. Total of PAHs were in higher concentration for PR5 and PR6 sediment stations. Their presence could be because of terrestrial sources, hydrocarbon activity and ship transport in Porto-Romano area. Distribution of PAHs (**Figure 9**) was the same for all water and sediment samples because of the same pollution origin. The presence of some individual PAHs for PR4 and PR5 sediment samples in high concentrations was noted. This could be connected with a punctual source because of hydrocarbon activity in this area. Car transport near the stations could be another factor. Profile of PAHs (Figure 9) for sediment samples were: Indeo[1,2,3]Pyrene > Benzo[ghi]perilene while in water samples was: Benzo[b]fluoranthrene > Chrysene. PAH levels in water samples of Porto-Romano were higher than reported levels for other ecosystems of Albania (Nuro *et al*, 2014). Total of PAHs were lower than permitted level (50 ng/L) for surface waters conform Directive 2008/105/EC. Presence of PAHs in sediments was higher than permitted levels for PR5 and PR6 stations.



**Fig. 8.** Total of PAHs in water and sediment samples of Porto-Romano, March 2018

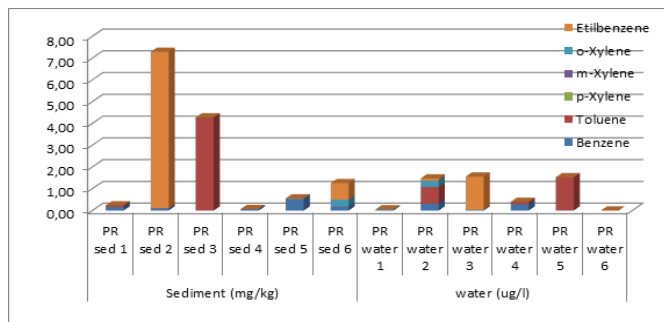


**Fig. 9.** Distribution of PAHs in water and sediment samples of Porto-Romano



**Fig. 10.** Profile of PAHs in water and sediment samples of Porto-Romano

Total of BTEX in water and sediment samples for each of the studied stations of Porto-Romano was given in Figure 11. Mean concentration of BTEX in water samples was 0.8 µg/L and in sediment samples was found to be 2.6 µg/g. BTEX were found almost for all studied samples. Their presence could be the same as PAH (terrestrial sources, hydrocarbon activity and ship transport in Porto-Romano). Distribution of BTEX in water samples of Porto-Romano is shown in Figure 12. BTEX were shown to have the same distribution because of the same pollution origin. Profile of BTEX in water and sediment samples of Porto-Romano (Figure 13) were: Ethylbenzene > Toluene > Benzene > Xylenes. BTEX levels in water samples of Porto-Romano were lower/comparable than reported levels for other ecosystems of Albania (Nuro *et al*, 2014). Benzene concentration was lower than permitted level (10 ng/L) for surface waters conform Directive 2008/105/EC.



**Fig. 11.** Total of BTEX in water and sediment samples of Porto-Romano

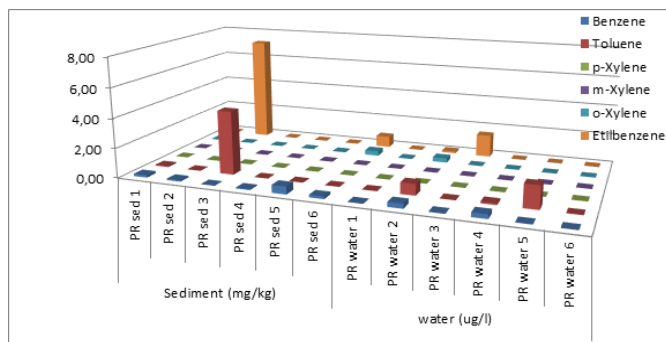


Fig. 12. Distribution of BTEX in water and sediment samples

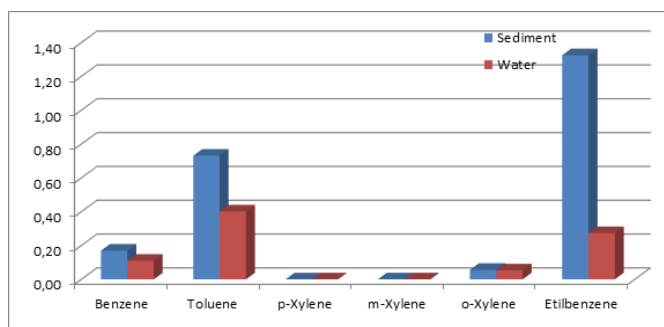


Fig. 13. Profile of BTEX in water and sediment samples of Porto-Romano, March 2018

## CONCLUSIONS

Determination of organochlorine pesticides, PCBs, PAH and BTEX was realized in water and sediment samples of Porto-Romano, Durres, Albania. GC/ECD technique was used for determination of organochlorine pesticides and PCBs. Qualitative and quantitative analyze of PAHs were realized by GC/FID technique. BTEX analyses in water and sediment samples were performed using HS/SME-FID technique. Organochlorine pesticides were found in higher level in sea water and sediment samples of Porto-Romano. OCP levels could be associated mainly with old pollution in this area from ex-chemical plant. Abandoning of pesticides for a long time near Porto-Romano is the main factor for their presence in this ecosystem. The higher concentration was in sediment samples because of adsorption process. Distributions of organochlorine pesticides in water and sediment samples of Porto-Romano were built by some individual pesticides. Organochlorine pesticide levels were lower or comparable than reported levels in other studies for Porto-Romano area. Presence of Dieldrin and Endosulfan

alfa was higher because of new arrivals from terrestrial sources or use of these pesticides under false trademarks. PCB markers were found for all stations. Their presence could be mainly because of atmospheric depositions. Discharging of wastes from some mechanical businesses near study area could affect level and profile of PCBs. PCB 28 was found in higher level in all samples. PCB 138 was found in high level in PR4 station. Levels of PCBs in water and sediment samples of Porto-Romano were lower than reported levels for the previous studies (Borshi *et al*, 2016). PAHs were found for all studied samples. Total of PAHs were in higher concentration in PR5 and PR6 sediment stations. Their presence could be because of hydrocarbon activity and ship transport in Porto-Romano area. PAH levels in water samples of Porto-Romano were higher than reported levels in other ecosystem in Albania (Nuro *et al*, 2014). BTEX were found for all studied samples. Their presence could be the same as PAH. BTEX levels in water samples of Porto-Romano were lower/comparable than reported levels in other ecosystem in Albania (Nuro *et al*, 2014). Analyze of organic pollutants in Porto-Romano must be continued because of anthropogenic impact in this Hot-Spot area.

#### CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this article. It was written after the proposal of the first author (A.N.) and all the other authors (E.M. and B.M.) contributed equally to the discussions of the text.

#### REFERENCES

1. Borshi Xh., Nuro A., Macchiarelli G., Palmerini M.G. “Determination of PAH and BTEX in water samples of Adriatic Sea” *International Journal of Current Microbiology and Applied Sciences* ISSN: 2319-7706 Volume 5 Number 11 (2016) pp. 877-884
2. Como E., Nuro A., Murtajn B., Marku E., Emiri A. (2013): Study of Some Organic Pollutants in Water Samples of Shkumbini River”, *International Journal of Ecosystems and Ecology Sciences (IJEES)*, Vol 8, Issue 4; 573-579
3. Çullaj A., Hasko A., Miho A., Schanz F., Brandl H., Bachofen R., (2005): Overview on Albanian natural waters and the human impact. *Environment International* 31(1):133-146
4. 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
5. EU (2007) “Guidance Document On Pesticide Residue Analytical Methods”, (ENV/JM/ ENV/JM/MONO (2007;17)

6. Gustafson E., Dickhut M., (1997): Distribution of polycyclic aromatic hydrocarbons in southern Chesapeake Bay surface water: evaluation of three methods for determining freely dissolved water concentrations. *Environment Toxicology Chemistry* 16, 452–461
7. Konstantinou I.K., Hela D. G., Albanis T. A. (2006) The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels, *Environmental Pollution*, Volume 141, Issue 3, Pp. 555–570
8. Lekkas Th., Kolokythas G., Nikolaou A., Kostopoulou M., Kotrikla A., Gatidou G., Thomaidis N.S., Goufopoulos 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
9. Menéndez J C F, Sánchez L. F, Uría J E S, Martínez E F, Sanz-Medel A. (2000): Static headspace, solid-phase microextraction and headspace solid-phase microextraction for BTEX determination in aqueous samples by gas chromatography. *Anal Chim Acta*; p. 415:9-20
10. Nezirli A., Marku E., Nuro A. (2010): Identification of Polychlorinated biphenyls in Shkodra Lake water using bottle sampling and passive sampling technology, *Asian Journal of Chemistry*, Vol 22, Nr. 10; 7850-7856
11. Nuro A., Marku E., Murtaç B. (2014): Determination of PAH and BTEX levels in water sampling using GC/FID technique. Case study: Patoku Lagoon, *International Journal of Ecosystems and Ecology Science (IJEES)* Volume 4/2; 195-200. ISSN: 2224-4980
12. USEPA, (2009): Method EPA 524. 3: Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry
13. Vryzas, Z., Vassiliou, G., Alexoudis C., Papadopoulou-Mourkidou E. (2009) Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece, *Water Research*, Volume 43, Issue 1, Pp. 1–10
14. Wells DE., Hess P. (2000): Determination and evaluation of chlorinated biphenyls. In: Barceló E (2007) Sample handling and trace analysis of pollutants, techniques, applications and quality assurance. Elsevier, Amsterdam; 239–285