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RESEARCH ARTICLE

DISTRIBUTION OF POLYCYCLIC AROMATIC AND ALIPHATIC HYDROCARBONS IN SURFACE WATER AND SOIL OF PETROCHEMICAL INDUSTRIAL AREA IN BALLSH, ALBANIA

***,1Morsina Çipa, 2Elda Marku and 3Aurel Nuro**

1PhD student at the Program of Chemical Analysis of Matter and Environment, Department of Chemistry, University of Tirana, St. Bulevardi "Zogu I", 1001, Tirana, Albania
2Professor at Department of Chemistry, University of Tirana, St. Bulevardi "Zogu I", 1001, Tirana, Albania
3Associate Professor at Department of Chemistry, University of Tirana, St. Bulevardi "Zogu I", 1001, Tirana, Albania

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ABSTRACT

One of the major environmental problems today is hydrocarbon contamination related to the petrochemical industry. This study investigated the spatial distribution of 13 polycyclic aromatic hydrocarbons (PAHs) and 10 aliphatic hydrocarbons in soil and surface water nearby a petrochemical industrial region in Albania. All analyze were performed by gas chromatography/flame ionization detection. The sum of PAHs'concentrations ranged from 5.73ng g^{-1} dry weight to 198.57 ng g^{-1} dry weight and from 44.43 mg L^{-1} to 466.95mg L^{-1} in soils and surface waters, respectively. The results showed that total aliphatic hydrocarbons concentrations varied from0.19ng g^{-1} dry weight to 79.73 ng g^{-1} dry weight in soils and 2.32mg $L^{-1}$to 25.25mg L^{-1}in surface waters. The composition pattern of PAHs by ring size was surveyed, as well. 4- and 5- rings PAH were dominated in soils and surface waters. The levels of PAHs in the petrochemical area of Ballsh were relatively higher in water in comparison with those reported around the world for similar studies. Likewise, the aliphatic hydrocarbons profile was predominated mainly from heavier n-alkanes in all sampling station. The origin of hydrocarbon contamination of the analyzed samples of Ballsh industrial area is related to the industrial activity and discharges.

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INTRODUCTION

Petroleum oil industries have been identified as important emissions sources of a wide variety of chemical substances (Chen, Lin and Chan, 2014), among which can be mention petroleum hydrocarbons.On the basis of chemical structure and physico-chemical properties, petroleum hydrocarbons are divided into two main classes: aliphatic and polycyclic aromatic. Petroleum hydrocarbons in soil and water pose serious risks to the environment and human health. They can affect the physio-ecology of soil and water flora and microorganisms. The toxic components can migrate from soil to groundwater and crops, as a result will endanger human health (Zhang et al. 2012). Aliphatic and polycyclic aromatic hydrocarbons (PAHs) have a high persistence in the environment, low biodegradability, highlipophility and some of them can be highly toxic (Moreda et al. 1998).

These organic micro pollutants are widespread distributed in the environment (atmosphere, water and aquatic systems, soils, sediments and biota (Berset and Holzer, 1995;Martinez et al. 2004;Li et al. 2010;Adeniyi and Afolabi,2002;Wu et al. 2007). PAHs are ubiquitous environmental pollutants generated primarily during the incomplete combustion of organic materials like coal, oil, petrol, and wood. Some PAHs present in the environment originates from natural sources like volcanoes and forest fires,but emissions from anthropogenic activities, such aspyrolytic processes (especially the incomplete combustion of organic materials), residential heating, power generation, incineration, and vehicle emissions predominate(Martinez et al. 2004;Bozlaker, Muezzinoglu and Odabasi,2008;Kim, Oh and Chang,2003).The US EPA has classified 16 PAHs as priority pollutants. These PAHs are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo [*a*] anthracene, chrysene, benzo [*b*] fluoranthene, benzo [*k*] fluoranthene, benzo[*a*]pyrene, dibenz [*a,h*] anthracene, benzo [*g,h,i*] perylene, and indeno [1,2,3-*cd*] pyrene (Ramesh et al.,

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***Corresponding author:* Morsina Çipa,**
1PhD student at the program of Chemical Analysis of Matter and Environment, Department of Chemistry, University of Tirana, St. Bulevardi "Zogu I", 1001, Tirana, Albania.

2012). Chronic exposures to even low concentrations of these chemicals cause long-lastings damage such as cancer, infertility and neurotoxicity to humans and wildlife (Neal, Zhu and Foster, 2008; Brandt and Watson, 2003; Menzie, Potocki and Joseph,1992). The lower molecular weight PAHs (LMW-PAHs) are acutely toxic but non-carcinogenic, whereas the high molecular weight PAHs (HMW-PAHs) are strongly carcinogenic and mutagenic (Karlsson and Viklander,2008;Hu et al. 2008). Aliphatic hydrocarbons show risks to human health and commonly attract the attention of scientific researchers. These compounds are more likely to be isolated from the epidermis than are aromatic hydrocarbons (Baynes, Brooks and Riviere, 2000). Alkanes are responsible for pneumonia caused by inhalation of oil paraffin, folliculitis by skin contact with oil, paraffinoma or oleogranuloma by subcutaneous injection of oil, follicular lipidosis by chronic ingestion, and the accumulation of long-chain in viscera (Salvayre et al. 1988). Moreover low levels of n-alkanes can cause inflammation in an in vitro model (Zhang et al. 2014). Aliphatic hydrocarbons are photo catalytically organic compounds and constitute the bulk of crude oil, for this reason, they can be used to evaluate petroleum contamination (Zhang et al. 2012).

The oil refinery in Ballsh city is the largest refinery in Albania and produces up to one million ton of oil per year, it is located along Gjanica River in the southern part of Albania. In recent year the growth of this industry and the marketing of the petroleum products have resulted in the pollution of the environment by oil spills involving leakages from tanks and dumping of waste petroleum products. As a result, serious contamination from petroleum hydrocarbons is reported from local community for Gjanica River, water reservoir and the soil around refinery industry. The objective of the present study wasthe investigation of the hydrocarbons' presenceand distribution in the soils and surface waters nearby Ballsh petroleum refinery in Albania. Another important goal of this investigation was the creation of the first complete scientific database for the levels and health effect of these compounds in this area, to be used for comparisons in the future surveys.

MATERIALS AND METHODS

Study area and sample collection

The petroleum industry area chosen for conducting this field study is located in the city of Ballsh, southern Albania. This refinery has been in operation since 1973.The soil and water sampling sites are shown in Figure1, while their exact position was recorded using the Global Positioning System. Sampling was performed in April 2016. Ten soil samples were collected at depths ranging from 0-15 cm and composited from an average of three sub-samples at each location. However, five surface water samples (0-10 cm) were gathered from Gjanica river and water reservoir near the petroleum industry. Soil and water samples were collected and stored in pre-washed in the dark amber glass bottles. Samples were transported to the laboratory in ice cool boxes and stored at 4^{o}C before processing.

Sample treatment

Prior to GC-FID analysis, PAHs and aliphatic hydrocarbons in soil and water samples were extracted by separate methods. A portion of 1 g homogenized soil sample was weighted and extracted with 20 mL hexane: dichloromethane mixture3:1 (v/v) and sonicated for 30 minutes at 40 ^{o}C in an ultrasonic bath. Further clean-up was done on silica gel columns pre-eluted with hexane. After addition of the samples, the column was eluted with 20 mL hexane: dichloromethane 4:1 (v/v)and the eluate was evaporated to1 mL in Kuderna-Darnish concentrators for qualitative and quantitative analyses.An aliquot of water samples (50 mL) was extracted for 10 minutes in a separatory funnel with 40 mL hexane. The clear supernatant was transferred to glass tube and sodium sulfate anhydrous was added, to dry the organic phase from water. The Cleanup procedure was similar as soil samples.

Instrumental analysis

The identification and quantification of the target hydrocarbons was performed with a GC 450 Varian gas chromatograph equipped with flame ionization detector and PTV injector. The separation was achieved with a VF-1ms capillary column (30 m x 0.33 mm i.d. 0.25 µm). The injection volume consisted of 2µL; the injector block operated on 280 ^{o}C. The oven programme was set at 60 ^{o}C for 2 min, increased by 10 ^{o}C /min to 180 ^{o}C, then at 5 ^{o}C /min to 280 ^{o}C, followed by temperature ramp at 8 ^{o}C /min to 300 ^{o}C and maintained for 7 min. The temperature of the detector was 300 ^{o}C.

RESULTS AND DISSCUSION

Polycyclic aromatic hydrocarbons

The levels of the 13individual PAHs analyzed in soil and water, as well their sums of total and 8 carcinogenic PAHs are summarized in Table1. Mean PAHs values in soil samples ranged between 0.01ng g^{-1} dry weight for acenaphthylene and 60.99 ng g^{-1} dry weight for benzo [α] anthracene. Mean PAHs values in water samples ranged from 0.01mg $L^{-1}$for acenaphthylene to 90.94 mg $L^{-1}$for benzo [α] anthracene. The Σ total PAH in soils varies from 5.73 to 198.57 ng g^{-1} dry weight with a mean value of 90 ng g^{-1} dry weight. On the other hand, the Σ total PAH in water ranged from 44.43 mg L^{-1} to 466.95 mg L^{-1} with a mean value 137.48 mg L^{-1}. The detected concentrations for 8 carcinogenic PAHs were ranged from 5.73ng g^{-1} dry weight to 198.57 ng g^{-1} dry weight and 43.34mg L^{-1} to 466.95mg L^{-1} in soil and water samples, respectively. The mean concentration for Σ 8 carcinogenic PAHs was 90ng g^{-1} dry weight in soil and 43.34 mg L^{-1} in water samples. It is clearly observed that the HMW-PAHs are the most widespread compounds on studied samples. The higher contents of HMW-PAHs in water and soil indicates that the contamination might be caused by fresh entrance of PAHs into the water via wastewater discharge of the oil refinery and atmospheric way.
For the composition study, 13 PAH compounds were divided into four groups according to their number of aromatic rings. Figure 2., Shows the 3-, 4-, 5- and 6-ring PAHdistribution for soil sampling site.

According to the obtained results, 3-ring PAHs (acenaphthylene, fluorene, anthracene and phenanthrene) weren't detected in any of the sample stations. It is clear that 4-ring PAHs (benzo[α] anthracene, chrysene and pyrene) and 5-ring PAHs (perylene, benzo [b] fluoranthene, benzo [k] fluoranthene and dibenzo [α,b] anthracene) were abundant at most sampling site, such as S-1, S-3, S-5 and S-10. 6-ring PAHs (indeno [1,2,3-cd]pyrene and benzo [g,h,i] perylene) had the lowest concentrations in all soil samples, and in some of them were not detected.

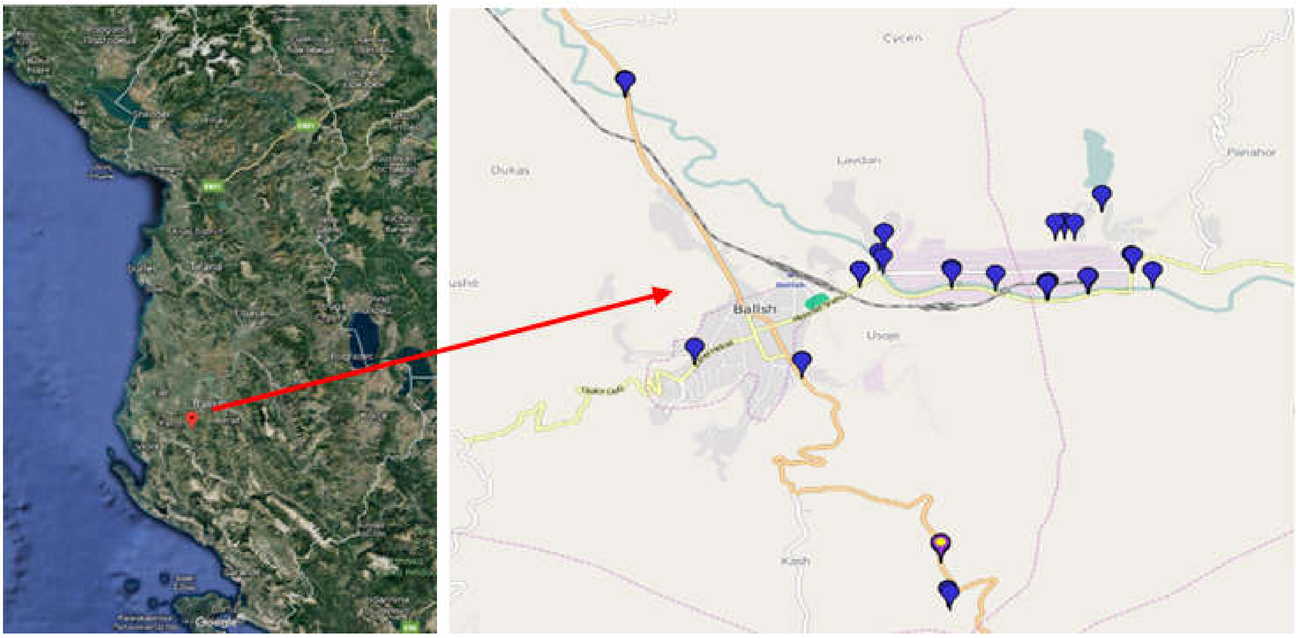

Figure1. Location of Ballsh city on the map of Albania (on the left) and sampling station of soils and surface water nearby the petroleum industry (on the right)

Table 1. PAHs concentration on soil and water samples from Ballsh petroleum industry, Albania.

Analyte	Soil Samples (ng g^{-1} dry weight) n=10			Water Samples (mg L^{-1}) n=5		
	Mean	Min	Max	Mean	Min	Max
Acenaphthylene	0.01	0.01	0.01	0.01	0.01	0.01
Fluorene	-	-	-	-	-	-
Phenanthrene	-	-	-	-	-	-
Anthracene	-	-	-	30.40	30.40	30.40
Pyrene	-	-	-	-	-	-
Benzo[a]anthracene	60.99	2.78	161.62	90.94	18.85	342.17
Chrysene	-	1.88	1.88	41.54	10.45	72.63
Perylene	2.13	1.87	2.38	1.74	0.58	2.89
Benzo[b]fluoranthene	12.13	0.41	23.85	13.10	5.10	26.67
Benzo[k]fluoranthene	28.39	1.06	55.72	14.86	5.98	23.73
Indeno[1,2,3-cd]pyrene	24.99	10.72	39.27	12.41	3.36	21.46
Dibenzo[a,b]anthracene	7.75	7.75	7.75	3.04	2.31	3.77
Benzo[g,h,i]perylene	0.10	0.10	0.10	0.98	0.98	0.98
Σ 13 Total PAHs	90.00	5.73	198.57	137.48	44.43	466.95
Σ 8 carcinogenic PAHs	90.00	5.73	198.57	131.40	43.34	466.95

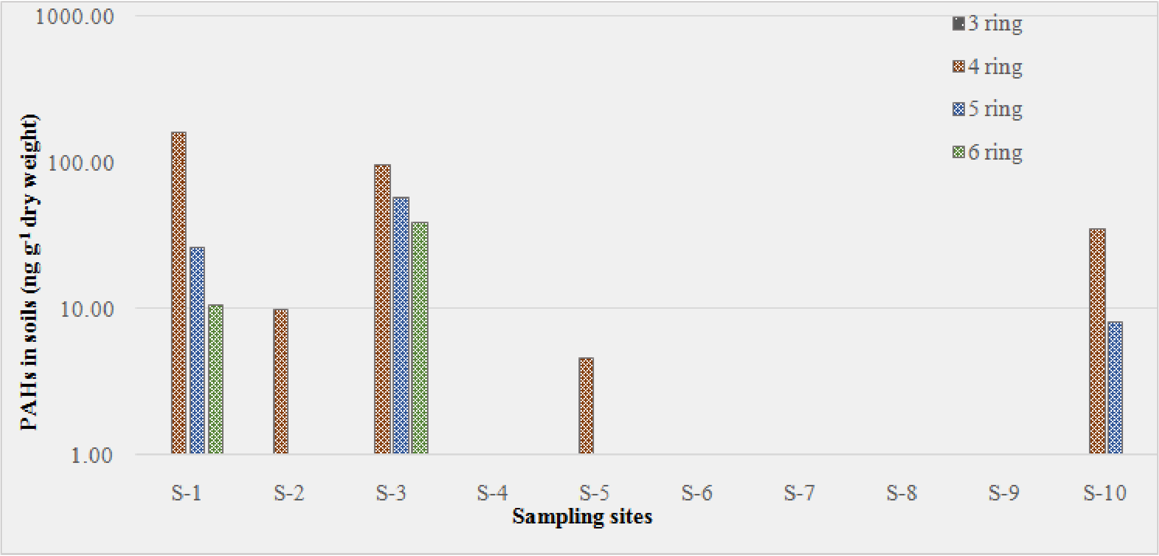

Figure 2.Concentration of 3-, 4-, 5-, 6-ring in soil nearby petroleum refinery in Ballsh, Albania.

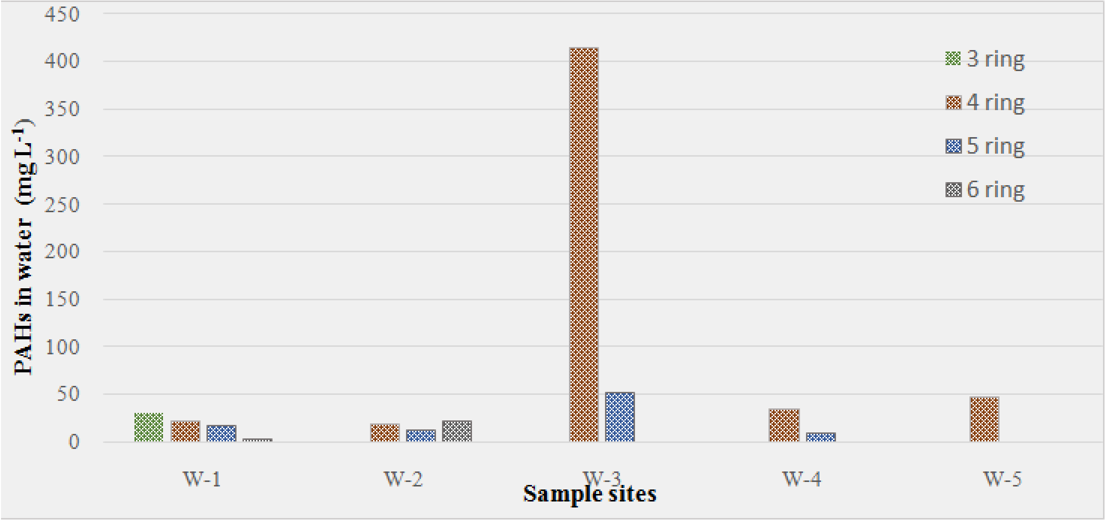

Figure 3.Concentration of 3-, 4-, 5-, 6-ring in surface water nearby petroleum refinery in Ballsh, Albania

Table 2. Concentration of aliphatic hydrocarbons found in soil (ng g^{-1} dry weight) and water (mg L^{-1}) samples from Ballsh petroleum industry, Albania

Analyte	Soil Samples (ngg^{-1} dry weight) n=10			Water Samples (mgL^{-1}) n=5		
	Mean	Min	Max	Mean	Min	Max
nC_{10}	-	-	-	-	-	-
nC_{12}	-	-	-	-	-	-
nC_{14}	-	-	-	-	-	-
nC_{16}	-	-	-	-	-	-
nC_{18}	0.65	0.65	0.65	0.84	0.78	0.89
nC_{20}	4.01	3.16	4.86	7.51	7.51	7.51
nC_{20x}	-	-	-	-	-	-
nC_{22}	24.19	3.97	69.97	5.13	0.55	15.47
nC_{24}	2.78	0.19	6.70	0.86	0.16	2.27
nC_{26}	25.91	9.06	42.75	4.63	4.63	4.63
Σ10 TAHs[a]	29.45	0.19	79.73	9.44	2.32	25.25

[a]TAH: Total aliphatic hydrocarbons

Moreover, in some sampling site such as S-4, S-6, S-7, S-8 and S-9 weren't identified any of the target compounds. The relatively high contaminated soils are mainly located in the area around oil well (S-1) and oil refinery (S-3, S-5). The high magnitude of HMW-PAHs, could be explained due to the fact that LMW-PAHs were gradually decreased by dilution owing to relatively high-water solubility and more easily degradation. Therefore HMW-PAHs could easily survive to reach the soils due to their low vapor pressure, low water solubility and more resistant to degradation (Sun et al. 2009). The concentration of 3-ring, 4-ring, 5-ring and 6-ring PAH in surface waters at different sampling site were illustrated in Figure 3. In terms of individual PAH composition in water, most of the target compounds were detected at all sampling sites.

The PAHs concentrations of waters are mostly dominated by 4-ring PAHs followed by 5-ring PAHs. In addition, 3-ring PAHs also show slightly dominance at W-1 sample site, which is a reservoir near an oil well, otherwise, 3-ring PAHs were not quantify in any other station. 6-ring PAHs are not determined in most of the water samples except W-1 and W-2, where the sampling was taken 300 m in the river flow after the refinery spills. The similarity pattern of PAHs contaminant abundance in surface waters and soils was contributed to the fact that petroleum products contain mainly 2-, 3- to 3-ring PAHs. 5- and 6-ring PAHs are minor constituents in crude oil and its refined products (Stogiannidis and Laane, 2015).

HMW-PAHs (4-5-ring) predominated in water could be explained with fresh inflow PAHs contamination. Apart from highly industrially polluted rivers, the concentration of individual PAHs in surface and coastal waters are generally 50 ng L^{-1}(or 0.00005 mg L^{-1}) (WHO, 1998). Concertation about this level (sometimes into the 10 μg L^{-1} range) indicate contamination by PAHs mainly industrial point and atmospheric deposition and urban runoff. The concentrations of PAHs in water exceeded 10 μg L^{-1}, suggesting that the water was heavily contaminated by PAHs. The total PAHs concentrations found in water in Ballsh are several orders of magnitude higher than those detected in some European river water (Sorell, Brass and Reding, 1980].

Aliphatic hydrocarbons

The levels of the 10 individual aliphatic hydrocarbons identified and quantified in soil and water samples are illustrated in Table1. Mean n-alkanes values in soil ranged between 0.65 ng g^{-1} dry weight for $nC_{18}$to 24.19 ng g^{-1} dry weight for nC_{22}, while the mean value in water samples varied from 0.78 mg L^{-1} for $nC_{18}$to 7.51 mg L^{-1} for nC_{20}.

The sum of total TAHs were ranged from 0.19 ng g^{-1} dry weight to 79.73 ng g^{-1} dry weight (mean: 29.45ng g^{-1}) and from 2.32 mg L^{-1}to 25.25 mg L^{-1} (mean: 9.44mg L^{-1}) in soil and water samples, respectively. To conclude, the most abundant constituents in soils and waters were the heavier aliphatic hydrocarbons.

Meanwhile the lighter n-alkanes were not detected in any sampling station. Aliphatic hydrocarbons distribution profile in soil and water samples is presented in Figure 4 and Figure 5, respectively. It was observed that in soil samples nC_{18} had lower concentration levels (0.65 ng g^{-1} dry weight) than nC_{24} (0.19–6.70ng g^{-1} dry weight), nC_{20} (3.16–4.86ng g^{-1} dry weight), nC_{22} (3.97–69.97ng g^{-1} dry weight) winding up with the nC_{26}(9.06 - 69.97ng g^{-1} dry weight). The prominent analytes in water were approximately similar with soil. The concentration levels for waters were 0.78mg L^{-1} - 0.89 mg $L^{-1}$for nC_{18}, 0.16mg L^{-1}- 2.27 mg $L^{-1}$for C_{24}, 4.63mg L^{-1} fornC_{26}, 7.51mg L^{-1}fornC_{20}, and thereafter with 0.55mg L^{-1} - 15.47mg L^{-1} fornC_{22}. It was observed that in both types of samples, the nC_{22} was found as the major compound. The heavier n-alkanes constitute the group of compounds which are present in the higher concentrations. Most probably this is because of fresh oil entering the topsoil and surface waters.

Conclusion

This study documents the first comprehensive analysis of PAH and aliphatic hydrocarbons in soil and surface water samples near petroleum industry located in Ballsh, Albania. The PAHs group profile reveals that the high molecular weight compounds (4- and 5-rings) dominated in soil and water samples. Because of the fact that some of them are carcinogenic, there is a concern regarding the risk their present for the environment and human health in Ballsh area. The results manifested that the levels of PAHs were relatively high in Gjanica river waters compared with other rivers in the world. The dominant sources of PAH appear to be the oil spills and wastewater discharge. The aliphatic hydrocarbons profile was similar between soil and water samples, heavier n-alkanes predominate in all samples. Moreover, the most abundant analyte was nC_{22} in both type samples. Information from this study could be useful in designing future strategies for environmental protection and management of the petroleum industry in Ballsh.

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