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An overview on persistent organic pollutants levels in the White Drin River, Kosovo

Afërdita Camaj Isa
PhD Candidate in Organic Chemistry
University of Prishtina
10000, 31 George Bush Str., Prishtine, Republic of Kosovo
https://orcid.org/0000-0001-7044-8810

Arben Haziri*
PhD in Chemistry, Full Professor
University of Prishtina
10000, 31 George Bush Str., Prishtine, Republic of Kosovo
https://orcid.org/0000-0002-0779-390X

Aurel Nuro
PhD in Chemistry, Full Professor
University of Tirana
1010, 4 Mother Teresa Sq., Tirana, Albania
https://orcid.org/0000-0003-1875-2430

Arieta Camaj Ibrahimi
PhD in Food Science and Technology, Associate Professor
University Haxhi Zeka
30000, "UÇK" Str., Pejë, Republic of Kosovo
https://orcid.org/0000-0002-3560-3704

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Abstract. The purpose of this study was to assess the concentrations of persistent organic pollutants in the White Drin River, Kosovo region. The study focused on organochlorine pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and benzene, toluene, ethylbenzene, and xylenes. The White Drin River originates from Peja, Kosovo, and extends to the Albanian border near Kukesi, making it a significant water body. It is potentially affected by anthropogenic pollution due to its passage through Kosovo's urban areas, villages, farms, and industries. Sampling was conducted at 15 stations along the river, from the river waterfall to the Albanian border, during two distinct periods in 2023 (January – February and August – September). Organochlorine pollutants were concurrently extracted using liquid-liquid extraction followed by analysis using capillary gas chromatography equipped with an electron capture detector. Polycyclic aromatic hydrocarbons were isolated through a two-step liquid-liquid extraction, with

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*Corresponding author

dichloromethane and hexane. Benzene, toluene, ethylbenzene, and xylenes were isolated using headspace solid – phase microextraction assisted by polydimethylsiloxane fibre. Qualitative and quantitative analyses of polycyclic aromatic hydrocarbons, and benzene, toluene, ethylbenzene, and xylenes, were conducted via gas chromatography with a flame ionization detector. The analyses showed the presence of persistent organic pollutants in the river water samples during both sampling periods. Elevated concentrations of volatile polychlorinated biphenyls, benzene, toluene, ethylbenzene, and xylenes, and polycyclic aromatic hydrocarbons, were observed in the water samples during both periods. This study underscores the significance of investigating organic pollutants in Kosovo's water systems, considering both local geographic concerns and the broader global issue of environmental pollution

Keywords: organochlorine pesticides; polychlorinated biphenyls; polycyclic aromatic hydrocarbons; benzene, toluene, ethylbenzene, xylenes, water analyses; gas chromatography; electron capture detector; flame ionization detector

INTRODUCTION

In recent decades, environmental pollution has emerged as a global concern. A variety of contaminants, including pesticides, pharmaceuticals, and industrial residues, are infiltrating water bodies through sewage systems, agricultural runoff, and atmospheric deposition. Persistent organic pollutants (POPs) have been detected in water bodies, highlighting their persistence and bioaccumulation tendencies. The easy accumulation of persistent organic compounds in the food chain can be mainly because of their hydrophobic properties and bio-magnification process (Nuro *et al.*, 2018). The presence of polycyclic aromatic hydrocarbons (PAHs) and BTEX compounds in surface water bodies can be mainly because of industrial and automobile transport, as well as mechanical activity, mechanical businesses, fuel stations, forest burning, etc.

The purpose of this study was to determine POP concentrations in water samples from the White Drin River in Kosovo. It is a vital resource for local communities and a valuable ecosystem of Kosovo. As the river flows towards the Albanian border, it merges with the Black Drin River to form the Drin River before flowing into the Adriatic Sea. It is crucial to evaluate pollution levels in its water, especially regarding POPs because it passes near urban, industrial, and agricultural areas. This transboundary river system, significant for its ecological importance and potential environmental impact, has not been investigated before for the presence of these organic pollutants. The river is under threat from unchecked urbanisation, agricultural practices, and industrial outputs leading to untreated waste discharge due to rapid population growth and socio-economic development, thereby jeopardising water quality and environmental sustainability, as concluded recently by S. Laha *et al.* (2022). Organochlorine pesticides have been extensively used in Kosovo for over half a century. Polychlorinated biphenyls (PCBs), although not used in Kosovo until the 1990s, were found in some electrical transformers from that period and were subsequently detected in various water ecosystems due to atmospheric deposition. PAHs and BTEX, primarily generated through vehicular transportation, coal mining, and other industries, are also influenced by forest fires and natural background. These pollutants exhibit high stability, significant bioaccumulation potential, and the ability to spread over long distances from their sources, persisting in the environment for many years (Nuro *et al.*, 2019).

Previous studies by E. Ferreira da Silva *et al.* (2024) have underscored the impact of land-use/land-cover dynamics and climate change on river water quality, reinforcing the significance of our research on the White Drin River. Pollutants like PAHs and BTEX compounds have been linked to adverse effects on water quality and human health according to a review by T. Olasehinde and A. Olaniran (2022). The increasing prevalence of Persistent Organic Pollutants (POPs) in various environmental compartments has been a subject of global concern due to their notorious effects on both human health and the environment (Adeniji *et al.*, 2022). In recent years, A. Mandal *et al.* (2024) have proven that the list of POPs keeps increasing, and their concentrations levels are widely varied region-wise. Y. Bununu *et al.* (2023) discussed the intricate relationships between land cover and land use change and climate change. They highlighted how these dynamics can affect food security, which could be linked to the health of river ecosystems. H. Zhang *et al.* (2023) further underscored the importance of understanding the unhindered connections and overlaps in aquatic ecosystems. They pointed out that microplastics, one of the most representative emerging contaminants, are carriers of other pollutants due to their strong adsorption capacity. This is particularly relevant to the present study as it highlights the potential for pollutants to be transmitted to aquatic organisms and humans through the extended food chain, thereby increasing the concentration of pollutants. W. Zhou *et al.* (2022) assessed the impact of urbanisation on river water quality. They found that the contents of pollutants such as nitrogen, trace metals, and organic pollutants were significantly accumulated in the lower reaches of cities, suggesting life-type pollution characteristics in urban rivers. This aligns with our observations of the unchecked discharge of untreated waste into the White Drin River due to urbanisation.

The present study underscores the urgent need to examine the water quality dynamics of the White Drin River and uncover the prevalence of persistent organic pollutants within its aquatic environment. By elucidating the origins and magnitudes of POP contamination, this study aims to provide valuable insights into the river ecosystem's ecological health and offer a roadmap for evidence-based conservation efforts.

MATERIALS AND METHODS

Water sampling in The White Drin River. The sampling was performed at 15 different stations along the White Drin River in February and September 2023. Sampling sites are presented in Figure 1. These time periods were chosen because February corresponds to the peak flow of the river, and the impact of nearby agricultural activities is at its minimum during this period while September corresponds to the minimum flow and agricultural and transportation activity is higher compared to other periods. For each station, a volume of 2.5 litres of water was collected in amber glass bottles with Teflon screw caps. The sampling procedure followed the guidelines specified in ISO 5667-3:2024 (2024). After collection, the water samples were preserved and transported at +4°C before undergoing analysis.

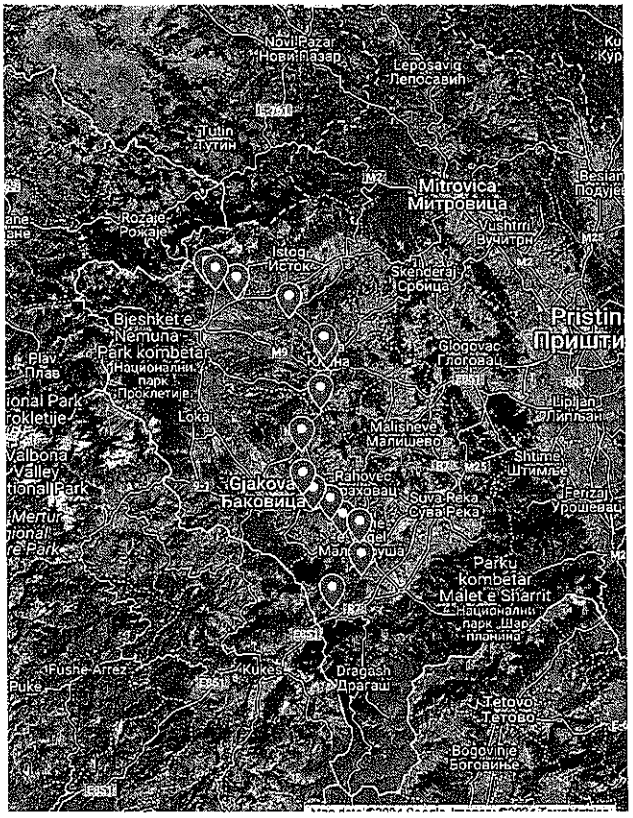

***Figure 1**. Sampling stations on the White Drin River, February and September 2023*
***Source:** Google Maps*

Treatment of water samples for pesticide and PCB analyses. Liquid-liquid extraction was used for extraction of organochlorine pesticide and polychlorinated biphenyls from water samples. One litre of water and 2×40 ml n-hexane were added in a separatory funnel as extracting solvent. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removal. 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 hexane, the samples were injected in GC/ECD (Nuro *et al.*, 2018).

Gas chromatography analysis of pesticides and PCBs. Gas chromatography technique was used to determine the concentrations of various organochlorine pesticides and polychlorinated biphenyls from liquid matrices, using fused silica capillary column with electron capture detector (diphenyl dimethyl polysiloxane Rtx-5, 30 m×0.25 mm i.d.×0.25 μm). Prior to analysis, liquid-liquid extraction was used to extract chlorinated organic pollutants. n-Hexane was used as organic solvent for extractions. After the extraction, the organic layer passed through Na_2SO_4 anhydrous to remove the remaining water. The sample clean-up was performed in florisil column, n-Hexane/Dichloromethane (4/1) was used for elution. After clean-up and concentration procedures for all samples, organochlorine pesticides and polychlorinated biphenyls were analysed on a gas chromatograph Varian 450 GC analytical system completed with split/splitless injector with electron capture detector. Helium was used as a carrier gas with flow rate at 1 ml/min, while nitrogen was used as makeup gas (24 ml/min). Quantification of organochlorine pesticides and polychlorinated biphenyls was based on external standard method for lindane and its isomers, heptachlors, aldrins, chlordanes, DDTs, endosulfanes, and 7 PCB markers (Method 505..., n.d.).

Treatment of water samples for PAH and n-alkanes analyses. Two steps liquid-liquid extraction (LLE) was used for extracting PAHs from river water samples. One litre of water with firstly 40 ml dichloromethane (first step of LLE) and next 40 ml hexane (second step of LLE) as extracting solvent were added in a separator funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removal. Extracts were concentrated to 1 ml hexane using Kuderna-Danish concentrator and then injected in GC/FID for qualification/quantification of PAHs (Nuro *et al.*, 2019).

GC/FID determination of PAH in water samples. Two-step LLE was used for extracting Polycyclic aromatic hydrocarbons from water samples. The sample was first extracted with dichloromethane (first step of LLE) and after that with n-hexane (second step of LLE) as extracting solvent in a separating funnel. After extraction, the organic layer passed through 5 g of Na_2SO_4 anhydrous to remove the remaining water. Extracts were concentrated using Kuderna-Danish

concentrator to 2 ml final volume. Polycyclic aromatic hydrocarbons in water samples were quantified with a Varian 450 GC instrument equipped with a flame ionisation detector and programmable temperature vaporiser injector. 100% dimethylpolysiloxane phase column VF-1 ms capillary column (30 m×0.33 mm×0.25 μm). Helium was used as carrier gas at 1 ml/min. Detector temperature was 280°C. Nitrogen was used as the makeup gas. Hydrogen and synthetic air were used as flame detector gases at 30 ml/min and 300 ml/min, respectively. Environmental Protection Agency EPA 525 Standard Mixture was used for qualitative and quantitative analyse of polycyclic aromatic hydrocarbons. Quantification of polycyclic aromatic hydrocarbons was based on external standard method (EPA Method 610-Polynuclear Aromatic Hydrocarbons).

HS-SPME technique for determination of BTEX in water samples. BTEX was determined in water samples 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 um PDMS fibre was used to extract BTEX from water samples. Adsorption process was conducted at 50 °C (using a water bath) for 45 minutes. The sample injection was performed manually at 280°C in a programmable temperature vaporiser injector (headspace mode was selected) of a Varian 450 Gas Chromatography instrument. Fused silica capillary column with dimensions of 30 m×0.33 mm×0.25 μm RTx, was used as a stationary phase. Helium was used as carrier gas at 1 ml/min, and nitrogen as a makeup gas. Detector temperature was maintained at 280°C. A mixture of known concentrations of benzene, toluene, ethylbenzene, and xylenes was used for qualitative and quantitative analyses based on external standard method according to (Method 8015d..., n.d.).

RESULTS AND DISCUSSION

This preliminary study showed the first data on organochlorinated pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbon and volatile organic hydrocarbons benzene, toluene, ethylbenzene, and xylenes in water samples of the White Drin River, Kosovo. Table 1 presents statistical data about analysed organochlorine pesticides (as individuals, their total and grouped in their classes) for both periods.

Table 1. *OCP data in water samples of the White Drin River (February and September 2023)*

OCPs	Drin Bardhe River, February 2023					Drin Bardhe River, September 2023				
	Mean	Min	Max	Median	STDEV	Mean	Min	Max	Median	STDEV
a-HCH	0.216	0.000	1.269	0.092	0.345	0.721	0.000	7.676	0.104	1.951
b-HCH	0.133	0.015	0.381	0.050	0.137	0.188	0.007	1.251	0.031	0.342
Lindane	0.383	0.000	3.087	0.039	0.817	0.032	0.000	0.318	0.000	0.086
d-HCH	0.564	0.000	5.209	0.101	1.325	0.464	0.004	4.619	0.084	1.173
Heptachlor	0.322	0.000	1.534	0.062	0.474	0.064	0.000	0.598	0.000	0.159
Aldrine	0.138	0.000	1.010	0.041	0.266	0.099	0.000	0.570	0.023	0.154
Heptachlor epoxide	0.107	0.000	0.511	0.040	0.150	0.051	0.000	0.325	0.000	0.106
g-Chlordane	0.268	0.000	1.135	0.101	0.329	0.466	0.000	5.155	0.000	1.338
Endosulfan I	0.103	0.000	0.701	0.041	0.186	0.038	0.000	0.274	0.000	0.086
a-Chlordane	0.287	0.000	2.053	0.061	0.532	0.023	0.000	0.145	0.000	0.044
44-DDE	0.058	0.000	0.321	0.015	0.094	0.054	0.000	0.294	0.008	0.092
Dieldrin	2.087	0.000	9.350	0.245	3.039	0.304	0.000	0.924	0.218	0.342
Endrin	0.176	0.000	1.373	0.000	0.357	0.672	0.000	7.676	0.076	1.960
Endosulfan II	0.089	0.000	0.876	0.021	0.225	0.182	0.000	1.251	0.031	0.345
44-DDD	0.294	0.000	2.053	0.016	0.633	0.022	0.000	0.318	0.000	0.082
Endrin aldehyde	0.172	0.000	1.912	0.024	0.486	0.191	0.000	1.252	0.024	0.344
44-DDT	0.111	0.000	1.071	0.017	0.271	0.041	0.000	0.598	0.000	0.154
Endosulfan sulphate	1.883	0.000	6.890	0.196	2.540	0.074	0.000	0.570	0.013	0.151
Methoxychlor	0.118	0.000	1.104	0.028	0.278	0.104	0.000	0.606	0.009	0.168
Endrin ketone	0.974	0.000	2.480	0.082	1.184	0.105	0.000	1.227	0.000	0.315
Mirex	0.022	0.000	0.159	0.000	0.044	0.000	0.000	0.000	0.000	0.000
∑ OCPs	8.504	1.679	18.306	6.734	5.742	3.895	0.261	20.585	1.456	5.997
∑ HCHs	1.296	0.090	5.654	0.699	1.507	1.405	0.018	13.546	0.219	3.418
∑ Heptachlors	0.429	0.000	1.719	0.204	0.531	0.115	0.000	0.877	0.017	0.231
∑ Chlordanes	0.554	0.000	2.324	0.327	0.655	0.489	0.000	5.155	0.021	1.333
∑ Aldrins	3.547	0.082	9.478	2.826	3.212	1.371	0.030	9.052	0.676	2.280
∑ Aldrins	0.581	0.000	3.708	0.198	1.018	0.221	0.000	1.816	0.058	0.455
∑ Endosulfanes	1.883	0.000	6.890	0.196	2.540	0.294	0.000	1.623	0.092	0.435

Source: *developed by the authors of this study*

The presence of Organochlorine Pesticides was observed in all analysed water samples collected from the White Drin River for both periods. Their presence in the White Drin River can be attributed to their prior use in nearby agricultural areas, recent arrivals due to soil runoff, water currents, and punctual sources within its watershed. The highest level of pollution was found on February with 8.51 ng/l while in September the average concentration was two times lower (3.90 ng/l). This difference should be mainly explained by the larger amounts of rainfall which affect the washing of agricultural lands, directly affecting their water levels. The levels of organochlorine pesticides in the White Drin River water samples were within the permissible limits set by European Union regulations (Directive 2013/39/EU, n.d.), where the total concentration of organochlorine pesticides should not exceed 50 ng/l for surface waters. Notably, the most polluted stations for both periods were found near Peja city, indicative of local agricultural activity (Fig. 2). This difference should be mainly explained by the larger amounts of rainfall that affect the washing of agricultural lands, directly affecting their water levels. Notably, the most polluted stations for both periods were found near Peja (WDB7 and WDB8 stations), indicative of local agricultural activity (Fig. 2).

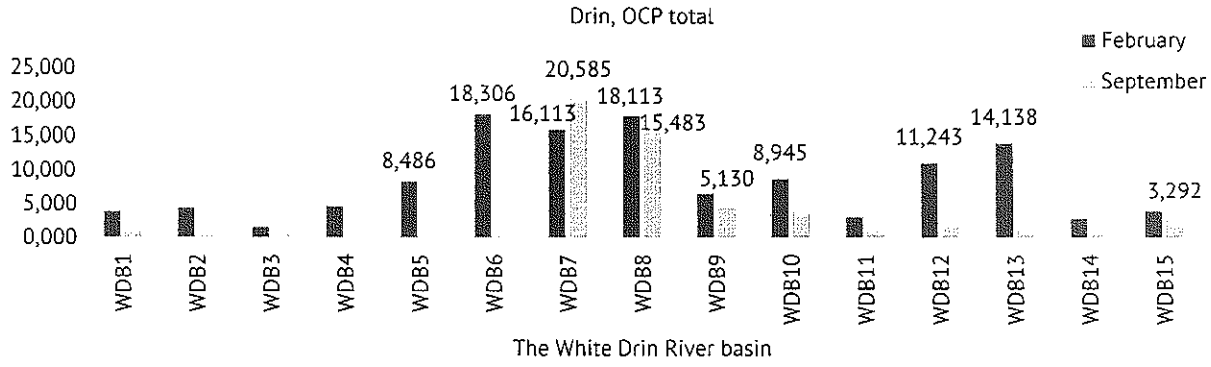

Figure 2. *Total of OCPs in water samples of the White Drin River (February and September 2023)*
Source: *developed by the authors of this study*

Some other stations (WDB6, WDB13, and WDB12) were found to have higher level in February. The maximum level of pollution for February was 18.31 ng/l at WDB6 station and the maximum level for September was 20.59 ng/l at WDB7 station. Stations with lesser pollution for both periods were form WDB1 to WDB4 stations located in the first part of the river. These stations have no agricultural activity developed on a high scale due to the characteristics of the mountainous terrain. In addition, this topography affects the higher velocity of water flow in the first segment of the river. The greater amount of water in February and the greater slope are factors that affect the reduction of pollution for these stations. Figure 3 shows the profile of the classes of pesticides included in the analysis. Their profile in February was: aldrins > endosulfanes > HCHs > chlordanes > DDTs > heptachlors. Their profile in September was: HCHs > aldrins > chlordanes > endosulfanes > DDTs > heptachlors.

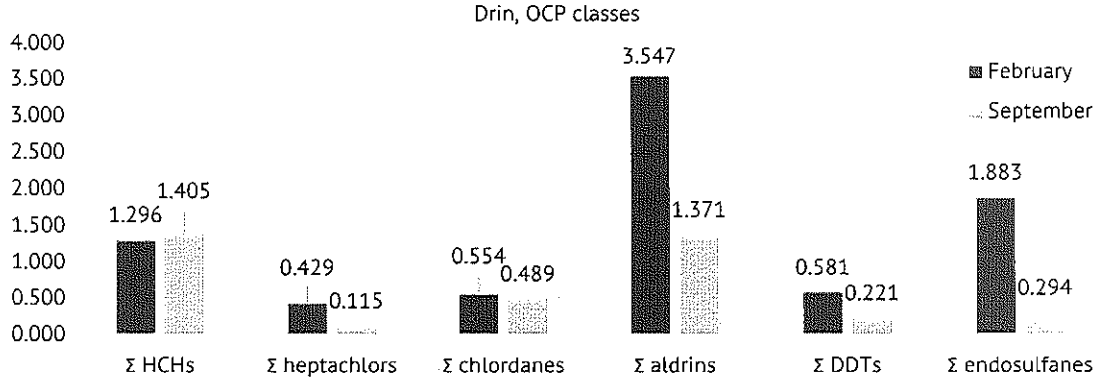

Figure 3. *Organochlorine pesticides classes in water samples of The White Drin River*
Source: *developed by the authors of this study*

The total of pesticide classes in no case exceeds the allowed rate for surface waters according to Directive 2013/39/EU (n.d.). A different profile of pesticide classes is observed for both periods. This should be related to dissimilar sources of pollution for different periods, e.g., in one period the biggest factor is the washing of the lands, while in another period the use of pesticides or their point sources near the White Drin River has a greater impact. Profile of individual pesticides in water samples of the White Drin River for both periods is presented in Figure 4.

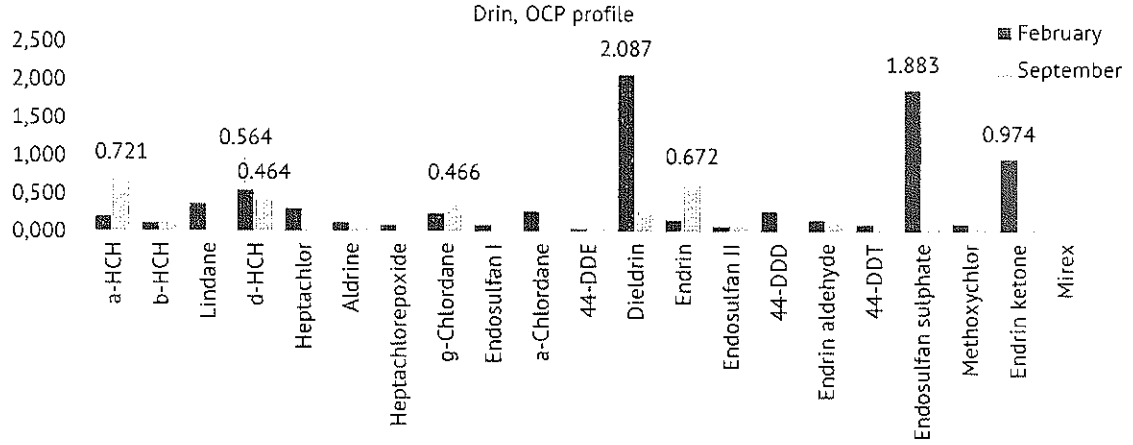

Figure 4. *Profile of OCPs in water samples of The White Drin River, February and September 2023*
Source: *developed by the authors of this study*

Some of the most frequently detected pesticides were, respectively, as follows: dieldrin > endosulfan sulphate > endrin ketone > d-HCH > g-chlordane (in February) and a-HCH > endrin > d-HCH > g-chlordane (in September). The active substances used as pesticides have not been identified in any case, but mostly their degradation products have been detected. This is related to the fact that these pesticides have not been used recently in the areas near the Drin River but are new arrivals from specific sources or from areas where these pesticides were used earlier. Some of these pesticides or their degradation products have been found as impurities in pesticides that are allowed to be used in agricultural areas near the river. Table 2 shows statistical data for PCB markers for both periods of sampling, February and September 2023. In addition, these chlorinated pollutants were identified in all analysed water samples.

Table 2. *PCB data in water samples of the White Drin River (February and September 2023)*

PCBs	Drin Bardhe River, February 2023					Drin Bardhe River, September 2023				
	Mean	Min	Max	Median	STDEV	Mean	Min	Max	Median	STDEV
PCB 28	2.239	0.005	8.290	0.954	2.763	0.307	0.002	0.924	0.218	0.339
PCB 52	3.765	0.022	25.360	0.876	6.788	0.279	0.007	1.252	0.208	0.356
PCB 101	0.164	0.000	1.533	0.062	0.382	0.067	0.000	0.606	0.007	0.155
PCB 118	1.317	0.000	13.591	0.113	3.516	0.385	0.000	4.619	0.022	1.181
PCB 153	0.285	0.000	2.580	0.017	0.692	0.216	0.000	1.913	0.010	0.513
PCB 138	0.212	0.000	1.591	0.027	0.423	0.241	0.000	2.010	0.000	0.589
PCB 180	0.086	0.000	1.104	0.000	0.283	0.000	0.000	0.000	0.000	0.000
Total	8.067	0.243	38.890	3.423	10.491	1.495	0.066	5.719	0.943	1.704

Source: *developed by the authors of this study*

Their presence could be mainly explained by the atmospheric deposition and industrial activity. The maximum level for PCB markers was found in February with 38.89 ng/l. The average level of PCB markers was 8.07 ng/l in February and 1.50 ng/l in September, respectively. This difference is also related to the amount of precipitation and the amount of water in the river; in February, this indicator is much higher than in September. The total PCB marker for each station in each period is presented in Figure 5. For February, the highest levels were found at stations WBD7 (38.09 ng/l), WDB11 (11.45 ng/l), WDB6 (17.34 ng/l), WDB5 (9.97 ng/l), WDB13 (9.46 ng/l), WDB8 (9.12 ng/l), and WDB10 (8.32 ng/l); for September, the highest levels were at stations WDB8 (5.72 ng/l), WDB10 (4.28 ng/l), and WDB9 (3.72 ng/l). The most polluted stations are near the areas where the industrial activity is higher. In addition, the amount of their deposits

increases due to the discharge of some of its important effluents in this part of the river. Urban spills and industrial waste also affect the increase of their level in these stations.

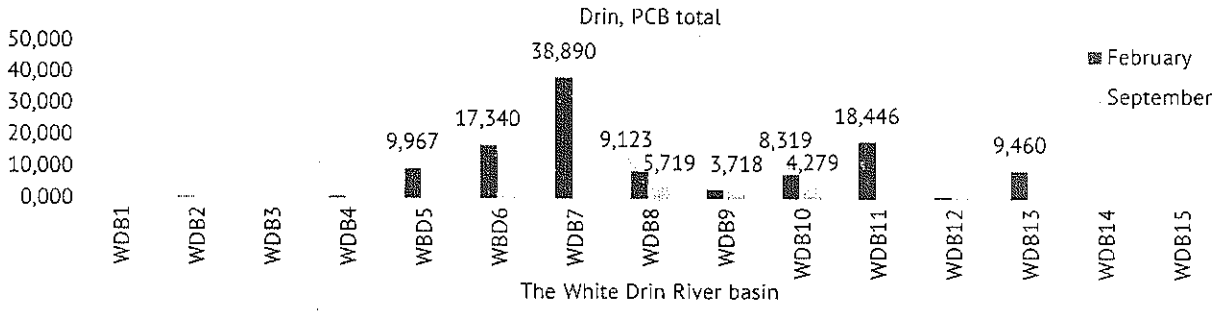

Figure 5. *PCB markers in water samples of the White Drin River (February and September 2023)*
Source: *developed by the authors of this study*

The profile of the marking PCBs is presented in Figure 6. Their profile for February was: PCB 52 > PCB 28 > PCB 118 > PCB 153 > PCB 138 while their profile for September was: PCB 118 > PCB 28 > PCB 52 > PCB 138 > PCB 153. In both periods, their profile is built according to the high presence of volatile PCBs because their main origin must be atmospheric deposits. The presence of heavier PCBs should be linked to their point sources. The PCB levels in the water samples from the White Drin River were comparable with those reported in earlier studies in Albanian water ecosystems (Nuro *et al.*, 2019).

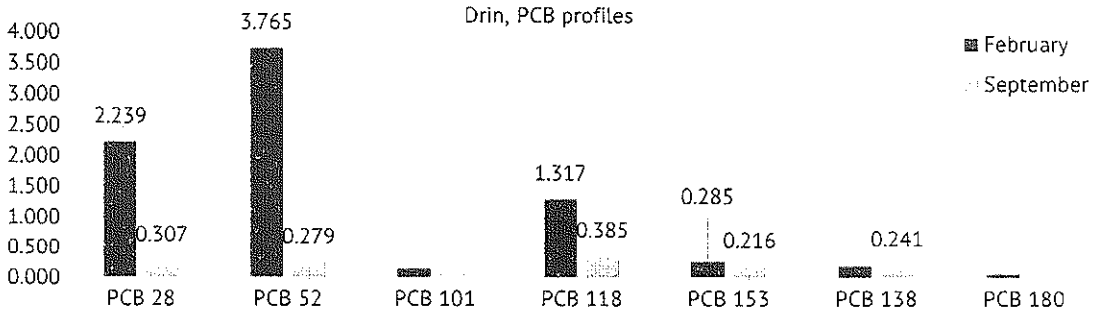

Figure 6. *Profile of PCB s in water samples of The White Drin River*
Source: *developed by the authors of this study*

Table 3 shows statistical data for polycyclic aromatic hydrocarbons in both periods of sampling, February and September 2023. PAHs were identified in about 75% of the samples in February and in about 30% of the samples in September. The presence of PAH in water samples must be a consequence of industrial activity, mining, road transport, urban spills, fires, etc. In February, the average level of PAH was 2.22 μg/l, and their maximum was 5.33 μg/l (WDB11) while in the month of September the average level was 3.43 μg/l, and the maximum was 46.44 μg/l (WDB15).

Table 3. *PAH data in water samples of the White Drin River (February and September 2023)*

PAHs	White Drin River, February 2023					White Drin River, September 2023				
	Mean	Min	Max	Median	STDEV	Mean	Min	Max	Median	STDEV
Acenaftilene	0.231	0.000	2.040	0.000	0.561	0.033	0.000	0.263	0.000	0.077
Fluorene	0.185	0.000	0.970	0.000	0.337	2.575	0.000	38.621	0.000	9.972
Fenantrene	0.091	0.000	0.702	0.000	0.189	0.037	0.000	0.360	0.000	0.102
Antracene	0.146	0.000	0.718	0.000	0.233	0.009	0.000	0.130	0.000	0.034
Piren	0.379	0.000	1.645	0.224	0.480	0.368	0.000	5.291	0.000	1.363

Table 3. Continued

PAHs	White Drin River, February 2023					White Drin River, September 2023				
	Mean	Min	Max	Median	STDEV	Mean	Min	Max	Median	STDEV
Benzo[a]antracene	0.316	0.000	1.333	0.184	0.401	0.144	0.000	1.517	0.015	0.390
Krizene	0.212	0.000	1.125	0.000	0.377	0.037	0.000	0.276	0.000	0.091
Perilene	0.190	0.000	0.913	0.000	0.306	0.191	0.000	1.913	0.000	0.518
Benzo[b]fluorantrene	0.182	0.000	0.959	0.000	0.325	0.034	0.000	0.516	0.000	0.133
Benzo[k]fluorantrene	0.291	0.000	0.919	0.000	0.359	0.000	0.000	0.000	0.000	0.000
Indeo[123cd]Pirene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dibenzo[ab]Antracene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Benzo[ghi]Perilene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total	2.224	0.000	5.325	2.130	1.570	3.427	0.000	46.435	0.100	11.912

Source: *developed by the authors of this study*

Figure 7 shows the total PAH in the water samples of the White Drin River for the two periods. There is a different distribution of PAH for the two periods: in February, there were low levels of PAHs at many stations, while in September, PAH were identified in a large number in the station near the border with Albania. This may be related to the different origin of PAH for both periods and to the current values of these pollutants. During both periods, the starting stations were not contaminated with PAH.

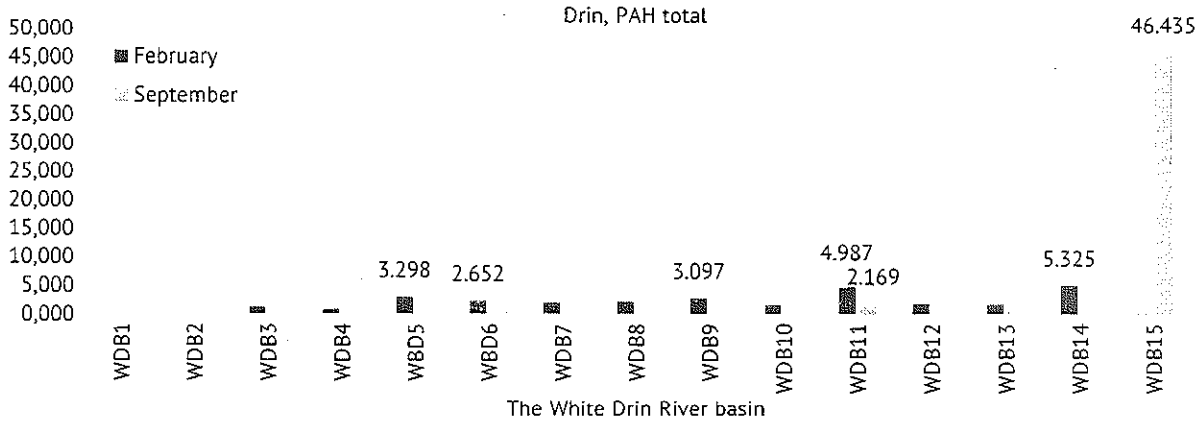

Figure 7*. PAHs in water samples of The White Drin River (February and September 2023)*
Source: *developed by the authors of this study*

Figure 8 shows PAH profiles in the water samples for the two periods. In February, the PAH profile was: pyrene > benzo[a]anthracene > benzo[k]fluoranthene > acenaphthylene > chrysene, while in September, the profile was: fluorene > pyrene > perylene. These PAHs indicate that their origin is mainly from urban or industrial discharges, mining, or other point sources. Only a small part of them come from thermal treatments such as industrial processes and transport emissions. The PAH levels in the water samples from the White Drin River were comparable or higher than the reported levels for Balkan area rivers. However, the concentration of PAH individuals, such as Fluorene, exceeded the permissible levels set by European Union regulations (Directive 2013/39/EU, n.d.).

Table 4 shows statistical data about BTEX in water samples of the White Drin River for both periods. Furthermore, benzene, toluene, ethylbenzene, and xylenes were detected almost for all water samples in February and 75% of samples in September. The origin of BTEX contamination could be similar, involving automobile transportation, industrial activity, and hydrocarbon spills, but temporal factors and momentum values may affect their levels. The average level of BTEX was 4.27 µg/l for February and 2.78 µg/l for September.

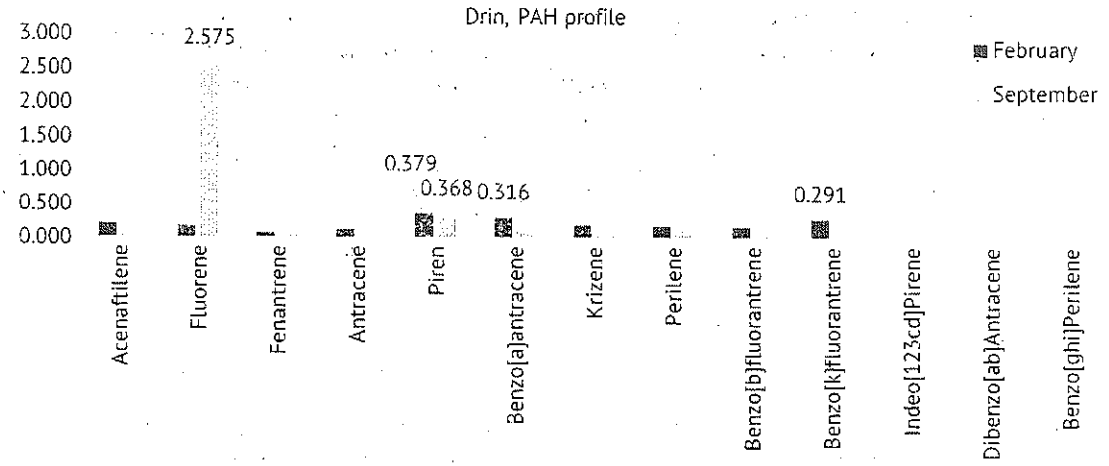

Figure 8. *Profile of PAHs in water samples of The White Drin River*
Source: *developed by the authors of this study*

Table 4. *BTEX data in water samples of the White Drin River, February and September 2023*

BTEX	White Drin River, February 2023					White Drin River, September 2023				
	Mean	Min	Max	Median	STDEV	Mean	Min	Max	Median	STDEV
Benzene	2.074	0.026	11.250	0.782	3.062	0.295	0.000	2.450	0.046	0.669
Toluene	0.936	0.000	4.580	0.578	1.267	1.608	0.000	15.539	0.079	4.173
m-Xylene	0.489	0.022	1.277	0.514	0.345	0.057	0.000	0.640	0.000	0.166
p-Xylene	0.293	0.000	0.743	0.224	0.283	0.065	0.000	0.949	0.000	0.245
o-Xylene	0.332	0.000	1.910	0.053	0.548	0.698	0.000	6.457	0.000	1.801
Ethylbenzene	0.147	0.000	0.706	0.016	0.229	0.051	0.000	0.771	0.000	0.199
Total	4.271	0.738	12.707	2.868	3.585	2.774	0.000	17.989	0.175	5.278

Source: *developed by the authors of this study*

Figure 9 shows the total BTEX for each station in both periods. Notably, BTEX has the same distribution as PAH for February. They are identified in all stations. The highest levels for February were the stations: WDB9 (12.71 μg/l), WDB6 (10.92 μg/l), WDB7 (7.88 μg/l) and WDB8 (4.13 μg/l). For September, there was a smaller number of stations where BTEX was detected, but in some of them the levels were significantly high, specifically, at stations WDB6 (17.99 μg/l), WDB15 (9.96 μg/l), and WDB14 (8.83 μg/l). This should be related to the origin of river water pollution with these pollutants.

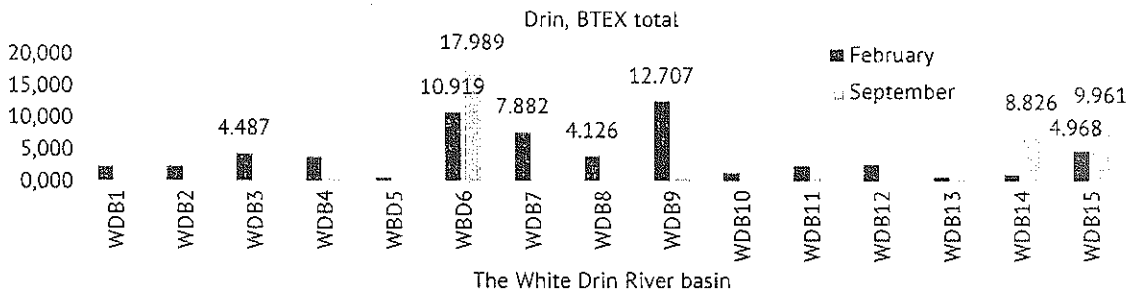

Figure 9. *BTEX in water samples of The White Drin River, February and September 2023*
Source: *developed by the authors of this study*

Figure 10 shows the profile of BTEX in water samples for both periods. BTEX profile in February was: benzene > toluene > m-xylenes > p-xylenes > o-xylenes > ethylbenzene while their profile in September was: toluene > o-xylene > benzene. In September, there appears to be a stronger influence of point sources or momentary values of water, while for February, it is a more constant source that may come from transport or industry emissions. Benzene and toluene were more abundant in the White Drin River. Notably, benzene concentrations exceeded the permissible levels according to European Union EU regulations (Directive

2013/39/EU, n.d.) at two stations (WDB6 and WDB9) in the White Drin River basin. BTEX levels in the water samples from the White Drin River were higher than the reported levels for Balkan area rivers.

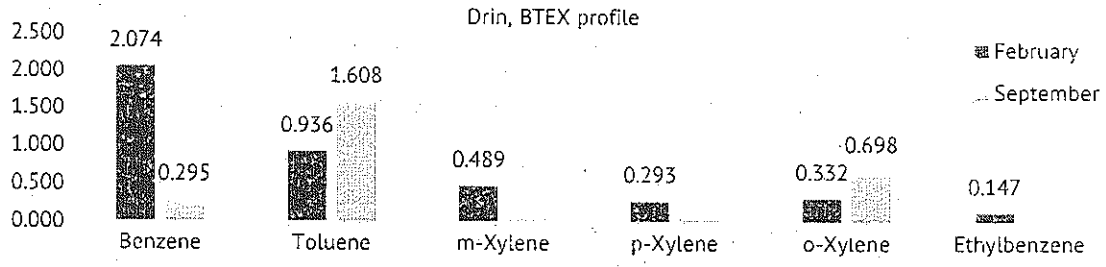

Figure 10. *Profile of BTEX in water samples of The White Drin River for both periods*
Source: *developed by the authors of this study*

According to the results presented above, a high-precision analysis of these parameters was conducted during two periods of the year. This led to the first-time discovery of different POPs in the White Drin River basin. Additionally, knowledge was gained about their mobility and persistence in this particulate river system. The concentrations of organochlorine pesticides in water samples collected from the White Drin River were evaluated according to the permissible limits established by European Union regulations, specifically Directive 2013/39/EU (n.d.), which mandates that the total concentration of OCPs in surface waters should not exceed 50 ng/L. Analysis revealed that the levels of both total OCPs and individual pesticides in the samples did not surpass the regulatory thresholds outlined in the Directive. However, isolated instances of excess were observed for specific compounds such as hexachlorocyclohexanes at station WDB7 (February 2023), endosulfan at station WDB10 (September 2023), and DDTs at station WDB5 (September 2023).

The heightened presence of these substances is attributed primarily to localised point sources proximal to the study areas. The concentrations of OCPs detected in the White Drin River water samples align with findings reported by various researchers across the Balkans regarding the levels of these contaminants in surface waters. Notably, recent studies conducted in Albania by A. Tafa (2022), C. Lancioni *et al.* (2022) indicated elevated levels of Polychlorinated Biphenyls (PCBs) in the Vjosa (Aoös) River, exceeding recommended standards, particularly following winter flood events, signifying substantial pollution within the river system. In a comprehensive review by C. Chițescu *et al.* (2021), focusing on emerging and persistent pollutants in the aquatic ecosystems of the Lower Danube basin and northwest Black Sea region, the assessment encompassed seven studies pertaining to pesticides in surface water and sediment samples within the designated area. Selection of target compounds was based on literature documenting their occurrence as contaminants and their classification as priority substances under the Water Framework Directive.

Additionally, the review emphasised the significance of considering abiotic transformation products of these compounds, which may exhibit heightened toxicity, persistence, and bioaccumulation compared to their parent compounds. The prevalence of volatile PCBs in the study area is believed to stem predominantly from atmospheric deposition, while the presence of heavier PCBs is linked to identifiable point sources. Comparative analysis with previous studies conducted in Albanian water ecosystems, such as the study by A. Nuro *et al.* (2019), indicates that PCB levels in the White Drin River water samples, particularly during February, were comparable to or higher than those reported elsewhere. Moreover, investigations into organochlorine pesticides in Porto-Romano revealed elevated concentrations in both water and sediment samples, with mean concentrations of PCB markers exceeding levels observed in the White Drin River.

Similarly, the levels of polycyclic aromatic hydrocarbons (PAHs) detected in the White Drin River water samples were comparable to or exceeded reported levels in rivers across the Balkan region. Notably, concentrations of individual PAHs, such as Fluorene, surpassed the permissible limits stipulated by European Union regulations (Directive 2013/39/EU, n.d.). Investigations conducted by A. Nuro *et al.* (2019) in the Port of Durres and Porto-Romano identified volatile PAH compounds in water samples, attributing their presence to various anthropogenic activities including shipping, automotive emissions, and industrial operations. Moreover, C. Grigoriou *et al.* (2021) conducted a study on the monitoring of polycyclic aromatic hydrocarbon levels in mussels (Mytilus galloprovincialis) from aquaculture farms in the Central Macedonia region, Greece, using gas chromatography – tandem mass spectrometry. Their findings indicated moderate to low concentrations of PAHs at all sampling sites, with seasonal variations observed, particularly higher values during the winter period.

The use of diagnostic ratios suggested a mixture of petrogenic and pyrolytic sources for the PAHs detected. As for benzene, toluene, ethylbenzene, and xylenes (BTEX) levels in the White Drin River water samples,

concentrations exceeded reported levels for rivers in the Balkan region. Notably, Benzene concentrations surpassed the permissible limits set by the European Union regulations (Directive 2013/39/EU, n.d.) at two stations (WDB6 and WDB15) along the White Drin River. This elevation in BTEX levels is likely attributable to local pollution sources affecting the river, particularly considering station WDB1 as a reference point. Comparative analysis with the study by A. Nuro *et al.* (2019) regarding BTEX levels in water samples from Porto-Romano indicates either comparable or lower concentrations, with Benzene concentrations remaining below the permitted level of 10 ng/L.

CONCLUSIONS

Organic pollutants, including pesticides, PCBs (polychlorinated biphenyls), PAHs (polycyclic aromatic hydrocarbons), and BTEX (benzene, toluene, ethylbenzene, and xylene) were detected in water samples collected from the White Drin River during the analysis conducted in February and September 2023. The concentration levels of organochlorine pollutants (OCPs and PCBs) were notably higher in samples near Klina (WDB 6 to WDB9) and near Prizreni and Albanian border (WDB14 and WDB15). It is worth noting that degradation products of pesticides were observed at higher levels than their active counterparts, which is indicative of the historical use of pesticides in Kosovo and the subsequent degradation processes. PCBs in their volatile form were found to be present at elevated concentrations in all water samples, potentially due to atmospheric deposition.

Some water samples also contained heavy PCBs, which could be linked to terrestrial sources. Momentum values might contribute to these findings. The presence of PAHs and BTEX in the water samples may be attributed to vehicle transportation and potential accidental spills of hydrocarbons from gas stations or mechanical businesses in the vicinity of both rivers. Certain individual pollutants, such as endrin ketone, endosulfan I, endosulfan sulphate, PCB52, PCB 118, acenaphthylene, and benzene were detected at relatively higher concentrations compared to other compounds. The presence of punctual sources and water currents could influence these variations. Overall, the concentrations of priority substances in the water of the White Drin River were generally below the permissible levels set for surface waters according to EU Directive 2013/39 EU. However, some individual pollutants, notably acenaphthylene and benzene, exceeded the permitted levels. It is crucial to emphasise the need for continuous monitoring of organic pollutants in Kosovo's rivers due to their persistent presence and potential environmental and health implications.

This study examined the presence of organic pollutants in water samples collected from the White Drin River in Kosovo, highlighting the significance of ongoing monitoring efforts in this critical water ecosystem. The findings of this study serve as a reference point for future analyses and studies not only in other water systems within Kosovo but also in the broader context of science and the food chain. By providing scientific information on pesticide application and management, this review underscores the importance of continued vigilance and proactive measures to safeguard water quality and environmental health.

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CONFLICT OF INTEREST

The authors of this study declare no conflict of interest.

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Огляд рівнів стійких органічних забруднювачів у річці Біла Дрінi, Косово

Афердіта Камай Іса
Кандидат наук в галузі органічної хімії
Приштинський університет
10000, вул. Джорджа Буша, 31, м. Приштина, Республіка Косово
https://orcid.org/0000-0001-7044-8810
Арбен Хазірі
Кандидат хімічних наук, професор
Приштинський університет
10000, вул. Джорджа Буша, 31, м. Приштина, Республіка Косово
https://orcid.org/0000-0002-0779-390X
Аурел Нуро
Кандидат хімічних наук, професор
Тиранський університет
1010, пл. Матері Терези, 4, м. Тирана, Албанія
https://orcid.org/0000-0003-1875-2430
Арієта Камай Ібрагімі
Кандидат харчових наук і технологій, доцент
Університет Хаджі Зека
30000, вул. «UÇK», м. Печ, Республіка Косово
https://orcid.org/0000-0002-3560-3704

Анотація. Метою цього дослідження було оцінити концентрації стійких органічних забруднювачів у річці Білий Дрин у Косовському регіоні. Дослідження було зосереджено на хлорорганічних пестицидах, поліхлорованих біфенілах, поліциклічних ароматичних вуглеводнях, а також бензолі, толуолі, етилбензолі та ксилолах. Річка Білий Дрин бере свій початок у Печі, Косово, і простягається до албанського кордону біля Кукесі, що робить її важливим водним об'єктом. Вона потенційно зазнає антропогенного забруднення через те, що протікає через міські райони, села, ферми та промислові підприємства Косова. Відбір проб проводився на 15 станціях вздовж річки, від водосховища до албанського кордону, протягом двох різних періодів у 2023 році (січень-лютий та серпень-вересень). Хлорорганічні забруднювачі одночасно вилучали методом екстракції рідина-рідина з подальшим аналізом за допомогою капілярної газової хроматографії, оснащеної детектором електронного захоплення. Поліциклічні ароматичні вуглеводні були виділені за допомогою двоступеневої екстракції рідина-рідина з дихлорметаном і гексаном. Бензол, толуол, етилбензол і ксилоли виділяли за допомогою твердофазної мікроекстракції з насадкою з полідиметилсилоксанового волокна. Якісний та кількісний аналіз поліциклічних ароматичних вуглеводнів, а також бензолу, толуолу, етилбензолу та ксилолів проводили за допомогою газової хроматографії з полум'яно-іонізаційним детектором. Аналізи показали наявність стійких органічних забруднювачів у пробах річкової води протягом обох періодів відбору проб. Підвищені концентрації летких поліхлорованих біфенілів, бензолу, толуолу, етилбензолу та ксилолів, а також поліциклічних ароматичних вуглеводнів спостерігалися у пробах води протягом обох періодів. Це дослідження підкреслює важливість вивчення органічних забруднювачів у водних системах Косова, враховуючи як місцеві географічні проблеми, так і ширшу глобальну проблему забруднення навколишнього середовища

Ключові слова: хлорорганічні пестициди; поліхлоровані біфеніли; поліциклічні ароматичні вуглеводні; бензол, толуол, етилбензол і ксилоли; аналіз води; газова хроматографія; детектор захоплення електронів; полум'яний іонізаційний детектор