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Levels of BTEX and Chlorobenzenes in water samples of White Drin River, Kosovo

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Abstract

In this paper, the concentrations of some volatile organic compounds (VOC) in water samples from the White Drin River (Kosovo) are presented. The White Drin River is one of the largest river in Kosovo and one of the largest in the Balkans. Water of the river could be affected by anthropogenic pollutions that comes mainly by directly discharges of urban wastewaters. The volatile organic pollutants that were analyzed were chlorobenzenes (mono-, di-, tri-, tetra-, penta- and hexachlorobenzene) and BTEX (Benzene, Toluene, Ethylbenzene, ortho-, meta- and para-Xylenes). Water samples were taken in February 2023, at 15 different stations from Drini Waterfall (near Peja to Albanian border). The head space solid phase micro-extraction (HS/SPME) method was used for the extraction and quantitative analysis of chlorobenzenes and BTEX followed by gas chromatography (GC) techniques. This method presents advantages for the analysis of volatile pollutants because it eliminates the use of organic solvents and different sample treatment steps that often lead to erroneous results. The sensitivity and reproducibility of HS is favorable for volatile organic pollutants. The adsorption of organic pollutants was carried out on a polydimethylsiloxane (PS) fiber at a temperature of 50^{o}C for 30 minutes. Desorption process was carried out in the injector of the gas chromatograph at high temperature (250 °C for 10 seconds). The qualitative and quantitative analysis of chlorobenzenes (mono-, di-, three-, tetra-, penta- and hexachlorobenzene) was realized in the GC/ECD apparatus, while the analysis of BTEX was carried out in the GC/FID apparatus. VOC were present almost in all analyzed samples. BTEX presence is related to the high intensity of transport near the river. The presence of chlorobenzenes can be a consequence of urban spills, of cleaning/sanitization processes, as degradation products of other compounds (pesticides, PCBs, etc).

1. Introduction

The aim of this study was determination of some volatile organic pollutants in the White Drin River (Kosovo part) which is one of the largest river in Kosovo. BTEX and chlorobenzene compounds could be present in the river because of transport emission, industrial activity, urban waste and agriculture activity. These compounds were determined by using HS/SPME technique following by GC/FID/ECD analyse. White Drin River flows in the semi-karst part of Kosovo (122 km), in an arc-shaped course before it arrived in Albanian border. The river originates in the southern slopes of the Zhleb Mountain, in the north of Peja city. The river springs near the Radavc Cave. The cave is multi-levelled, not much explored and has a lake inside. The stream is originally a sinking river which eventually springs out from the strong well and falls down as a 25 m high waterfall named the White Drin Waterfall near the village of Radac, (8 km from Peja). The river water in the first part of it is used for drinking and on brewery industry. Generally, the largest cities are distant from the river (Peja, Gjakova, Prizren) whilst some smaller towns (Klina) and large villages (Krusha e Madhe, Gjonaj) are closer to it. The White Drin also creates the small White Drin Canyon. The White Drin River is affected mostly by the agriculture and some industrial activities.

Urban wastes are discharged directly to the river in some part of it. The river is used for irrigation of agricultural crops in the areas near the river.

BTEX refers to the chemicals benzene, toluene, ethylbenzene and xylene. These compounds occur naturally in crude oil and can be found in the natural gas and petroleum deposits. Other natural sources of BTEX compounds include gas emissions from volcanoes and forest fires. The primary man-made releases of BTEX compounds are through emissions from motor vehicles and aircrafts. Also, it can be found from coal mine, termocentrals, in many industrial processes, to the cigarette smoke [1]. BTEX compounds are created and used during the processing of petroleum products and during the production of consumer goods such as paints and lacquers, thinners, rubber products, adhesives, inks, cosmetics and pharmaceutical products. BTEX compounds are among the most abundantly produced chemicals in the world. The most common sources of exposure to BTEX compounds are from breathing contaminated air, particularly in areas of heavy motor vehicle traffic and petrol stations, and through cigarette smoke. Exposure to BTEX from water contributes only a small percentage of the total daily intake, compared with inhaled air and dietary sources. Benzene is a known carcinogen (cancer causing). Note that it should not be detected in drinking water at more than 1 part per billion (ppb). The remaining chemicals (toluene, ethylbenzene and xylenes) are not recognized as carcinogenic and their drinking water health guidelines are much higher—between 300 and 800 ppb [2-4].

The major use of chlorobenzene is as an intermediate in the production of herbicides, dyestuffs, and rubber. Chlorobenzene is also used as a high-boiling solvent in industrial applications as well as in the laboratory. Chlorobenzene is nitrated on a large scale to produce 2-nitrophenol, 2-nitroanisole, bis(2-nitrophenyl) disulfide, and 2-nitroaniline by nucleophilic displacement of the chloride, with respectively sodium hydroxide, sodium methoxide, sodium disulfide, and ammonia. The conversions of the 4-nitro derivative are similar. The major use of chlorobenzene is as an intermediate in the production of herbicides, dyestuffs, and rubber. Chlorobenzene is also used as a high-boiling solvent in industrial applications as well as in the laboratory. Chlorobenzene is nitrated on a large scale to give a mixture of 2-nitrochlorobenzene and 4-nitrochlorobenzene, which are separated. These mononitro chlorobenzenes are converted to related 2-nitrophenol, 2-nitroanisole, bis(2-nitrophenyl) disulfide, and 2-nitroaniline by nucleophilic displacement of the chloride, with respectively sodium hydroxide, sodium methoxide, sodium disulfide, and ammonia. The conversions of the 4-nitro derivative are similar [5-8].

Head-space (HS) technique is commonly used mainly for the concentration (extraction) and analysis of volatile organic compounds. In this technique the sample first establishes a balance between the gas phase (above in the head-space) and the sample which may be liquid or solid. This balance is established using moderate temperatures (30 - 70^{o}C) to create the opportunity for volatile compounds to pass into the gas phase. After that, a polymer fiber which has high adsorption capabilities (Solid Phase Micro-Extraction or SPME) is used to fix homogeneous gas sample and pass it directly to the injector of the gas chromatograph (GC). The injector carries out the passage of the sample from the polymer fiber to the column of the apparatus through the desorption process at high temperature (220 - 280°C). Chromatographic columns enable the separation of all volatile compounds found in the sample. The head-space technique can be used in static and/or dynamic mode, Today, HS technique is fully automated. The advantage of HS technique is operation without the use of solvents and in a single step the extraction and analysis of the sample compounds is performed. HS/SPME analysis followed by GC analysis consists of two steps: Adsorption of the compound from the sample and transfer of the sample directly to the gas chromatograph by desorption process. The amount of analyte transferred to the instrument is proportional to the volume of the gas phase, and to the concentration of the analyte, accepting that the space above the sample is in equilibrium with the sample [3-4; 8-10].

2. Material and Method

2.1. Water sampling in Drini Bardhe River

Water samples were taken in 15 different stations of the White Drin River (Figure 1). Water samples were sampled and analyzed in February 2023. A quantity of 2.5 litre of water from each station in Teflon bottles. The sampling method was based on ISO 5667-3: 2018. Water samples were tranported and conserved at +4 °C prior to their analyze.

2.2. Analyzes of BTEX in water samples

For the determination of BTEX, 5 ml of water samples were taken from the stations of the White Drin River in SPME bottles with a volume of 10 ml. The bottles were equipped with Teflon stoppers suitable for their analysis by Head-space technique. The manual SPME syringe equipped with a 100 um PDMS (Polydimethylsiloxane) fiber was inserted through the Teflon stopper into the top of the sample. The bottle was placed at a temperature of 50^{o}C for 30 minutes. PDMS fiber was transferred to the gas chromatograph injector where desorption process was carried out at 250^{o}C for 10 seconds. For the qualitative and quantitative determination of BTEX, the Varian GC 450 apparatus equipped with a flame ionization detector (FID) and a PTV injector was used. The separation of BTEX was performed in VF-1ms (30m length x 0.33mm internal diameter x 0.25μm film), suitable for their separation [2, 3, 8, 10].

Figure 1. Sampling sttaion at Drini River.

2.3. Analyzes of chlorobenzenes in water samples

For the chlorobenzenes analyze, 5 ml of water samples were taken in SPME bottles with a volume of 10 ml. The bottles were equipped with Teflon stoppers suitable for their analysis by Head-space technique. The manual SPME syringe equipped with a 100 um PDMS (Polydimethylsiloxane) fiber was inserted through the Teflon stopper into the top of the sample. The bottle was placed at a temperature of 50°C for 30 minutes. The process of desorption for the chlorobenzenes was realized to the gas chromatograph injector at 260°C for 10 seconds. Qualitative and quantitative determination of chlorobenzenes was realized in a Varian GC 450 apparatus equipped with electron capture detector (ECD). The separation of chlorinated benzene derivates was performed by using a RTX-5 capillary column (30m length x 0.25mm internal diameter x 0.25μm film), suitable for their separation [4, 9].

3. Results

In this study, water samples from the White Drin River, which is one of the largest river in Kosovo, were analyzed. The water samples were taken in February 2023. The analysis of volatile organic compounds was carried out using the HS/SPME technique followed by gas chromatography technique. The qualitative and quantitative analysis of BTEX was realized by means of GC/FID, while the analysis of chlorobenzenes was realized by means of GC/ECD. The processed data for BTEX and chlorobenzenes in the water of the river are shown in respectively in Table 1 and 2. The analysis of volatile compounds (BTEX and Chlorobenzenes) was performed by done three injections for each sample. The data obtained are averaged for each station separately and for all water samples taken in the White Drin River. The data were obtained using the external standard method using standard solutions of BTEX and chlorobenzenes from 0.5 to 50 ppb (6 calibration points). The data for these compounds are given in ppb level. For the data obtained, statistical processing was done using Excel to calculate the mean value, standard deviation, median value, minimum and maximum values.

Table 1. BTEX data in water samples of White Drin River, February 2023.

BTEX	Mean	STDEV	Median	Min	Max
Benzene	0.256	0.052	0.223	N.D.	1.187
Toluene	0.141	0.047	0.135	N.D.	1.583
m-Xylene	0.026	0.011	0.028	N.D.	0.186
p-Xylene	0.105	0.028	0.103	N.D.	0.748
o-Xylene	0.039	0.586	0.038	N.D.	0.102
Ethylbenzene	0.089	0.009	0.086	N.D.	0.211

Table 2. Data of chlorobenzenes in water samples of White Drin River, February 2023.

Chlorobenzene	Mean	STDEV	Median	Min	Max
Chlorobenzene	0.428	0.103	0.418	N.D.	2.158
1,2-Dichlorobenzene	0.075	0.026	0.069	N.D.	0.126
1,3-Dichlorobenzene	0.052	0.013	0.055	N.D.	0.284
1,4-Dichlorobenzene	0.036	0.017	0.038	N.D.	0.206
1.3.5-Trichlorobenzene	0.129	0.029	0.131	N.D.	0.245
1.2.3-Trichlorobenzene	0.068	0.016	0.057	N.D.	0.355
1.2.4-Trichlorobenzene	0.227	0.047	0.225	N.D.	0.954
Tetrachlorobenzene	0.124	0.049	0.128	N.D.	0.850
Pentachlorobenzene	0.210	0.058	0.223	N.D.	1.147
Hexaclorbenzene	0.364	0.086	0.354	N.D.	2.352

N.D. – Not Detected or lower than Limit of detection (LOD)

4. Discussion

BTEX were detected almost in all analyzed samples (Figure 2). The highest level was found for station WDR3 and the stations near the border to Albania (station 12 - 15) and the minimum near Drini Waterfall (station 1). Presence of BTEX in the water of the river could be related to the automobilist transport, the spilling/accidents of hydrocarbon near the river and beyond, and the impact created by mechanical businesses (car service) in the area of river. Waste from other businesses operating in this area is also not excluded. The distribution of BTEX in the Drin river stations shows that there are several main groups that have a similarity level greater than 75% (Figure 3). Only station WDR3 has a similarity lower than 20% with other stations. This fact shows that the origin and level of pollution are the same in all the samples taken in analyze. For station WDR3 it can be note that there is a punctual source that affects the value found and/or it can represent a momentum value.

It was noted presence of Benzene in higher quantities than other volatile compounds (Figure 4). Its presence is a consequence of its identification in high quantity at some stations. The Benzene presence was noted in three stations near Kosovo-Albania border. The source of it could be mainly because of transport emissions, mechanical businesses, and petroleum distributors. The level of similarity between Xylenes and Ethylbenzene was around 60% (Figure 5). The level of similarity for the main group with benzene was around 40% and the lower similarity was for Toluene with around 35%. This profile shows that the main factor for the presence of BTEX in water samples was because of transport emission. This could also be the value of the moment of this compound or spillage of hydrocarbon waste from any vessel. Benzene levels in water samples, for each station do not exceed the permitted levels of it for surface waters according to EU 2008/105.

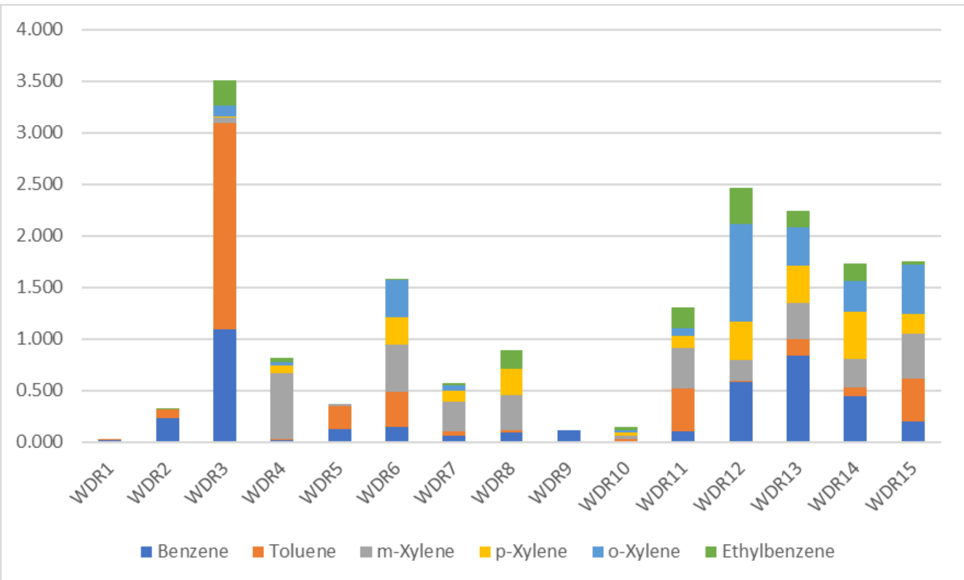

Figure 2. Total of BTEX in water samples of Drini River, Kosovo.

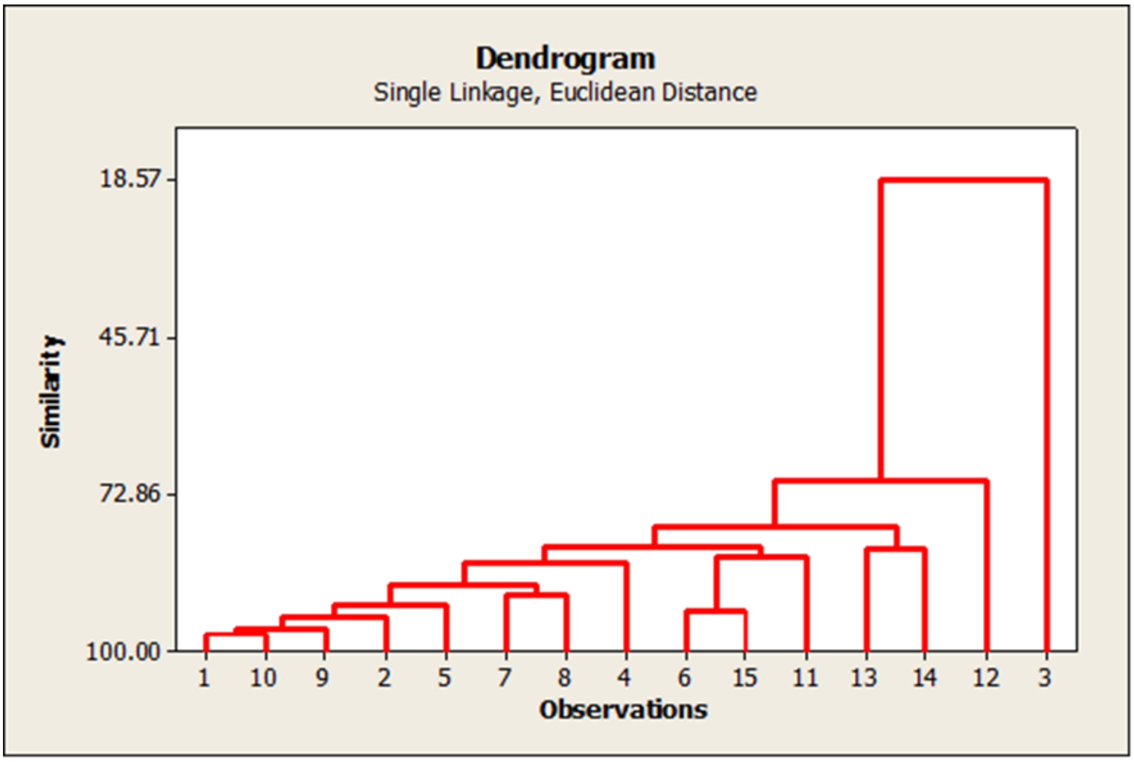

Figure 3. Dendogram of BTEX in stations of White Drin River (Kosovo part).

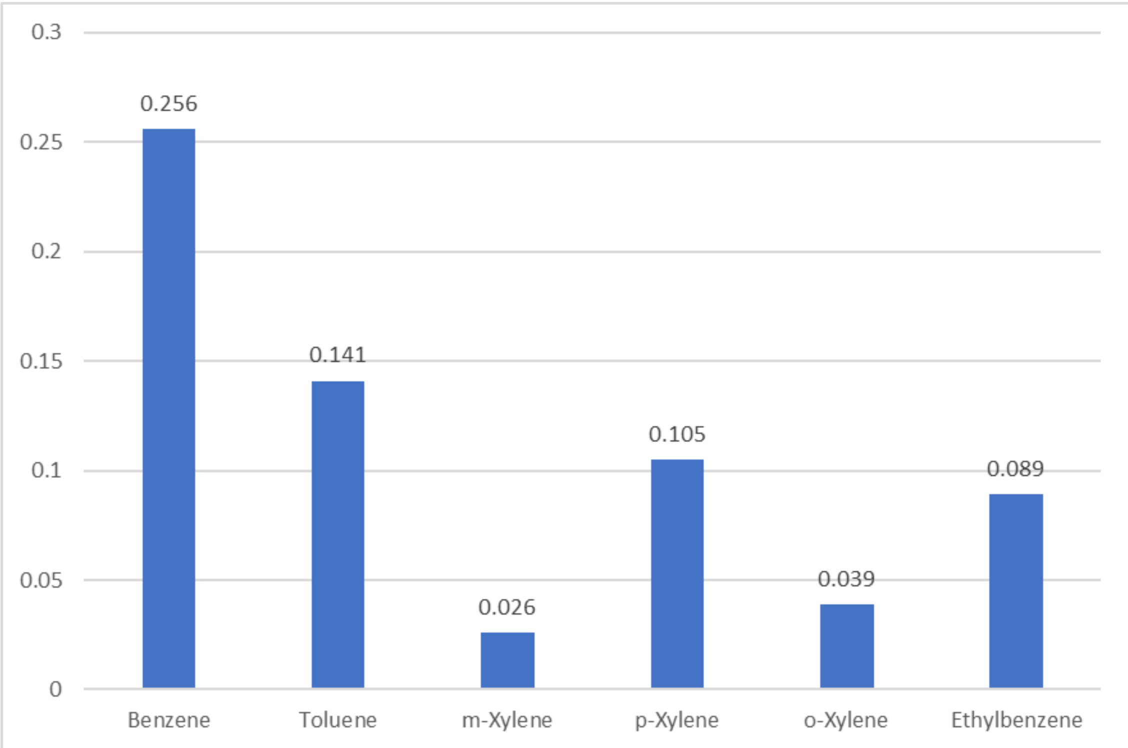

Figure 4. Profile of BTEX in water samples of Drini River, Kosovo.

The presence of chlorobenzenes was noted almost in all analyzed water samples (Figure 6). Their maximum was noted in several stations located near cities or villages while the minimum in waterfall of White Drin station. Their presence may be a consequence of direct discharges of liquid urban waste from houses and/or businesses, due to hygiene/cleaning products, as a consequence of the degradation of large organic molecules with chlorine (pesticides, PCBs, etc.). The dendogram of chlorobenzenes in stations of White Drin River (Figure 7) shown four main groups with a similarity level more than 78%. Stations 3, 4, 12 and 15 have lower similarity. Different origin of chlorobenzenes can be in stations of the river. At a higher level were found chlorobenzene, pentachlorobenzene and hexachlorobenzene, whose presence was identified at a higher level at several stations near of urban centers or agricultural areas (Figure 8). The presence of these compounds may be mainly by wastewater discharges or degradation products of pesticides and other molecules. The dendogram of chlorobenzenes in water samples shown a high level of similarity for the chlororbenzenes except chlorobenzene, 1,2,3-trichlorobenzene and pentachlorobenzene which have a lower level of similarity (Figure 9). Their origin could be different. The levels of volatile organic pollutants in the water of the White Drin River were similar to the levels reported in previous works for Balkan area [8-11].

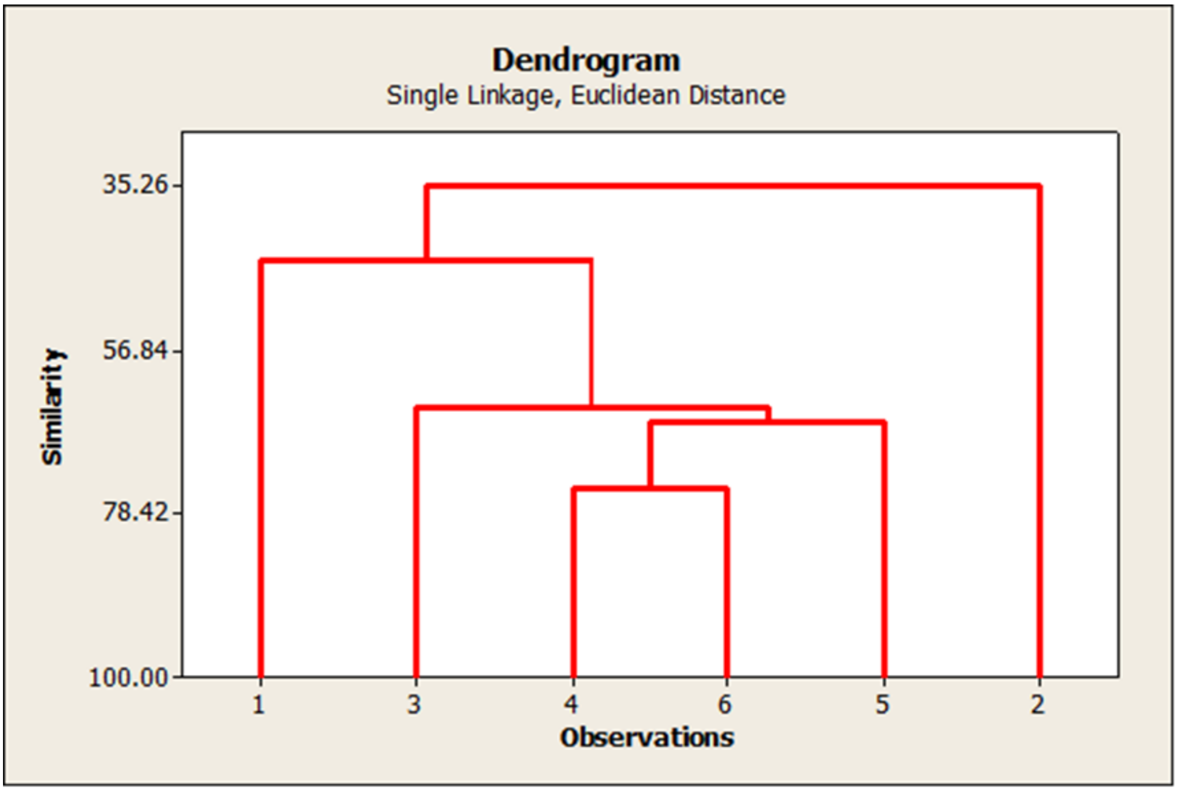

Figure 5. Dendogram of BTEX compounds in water samples.

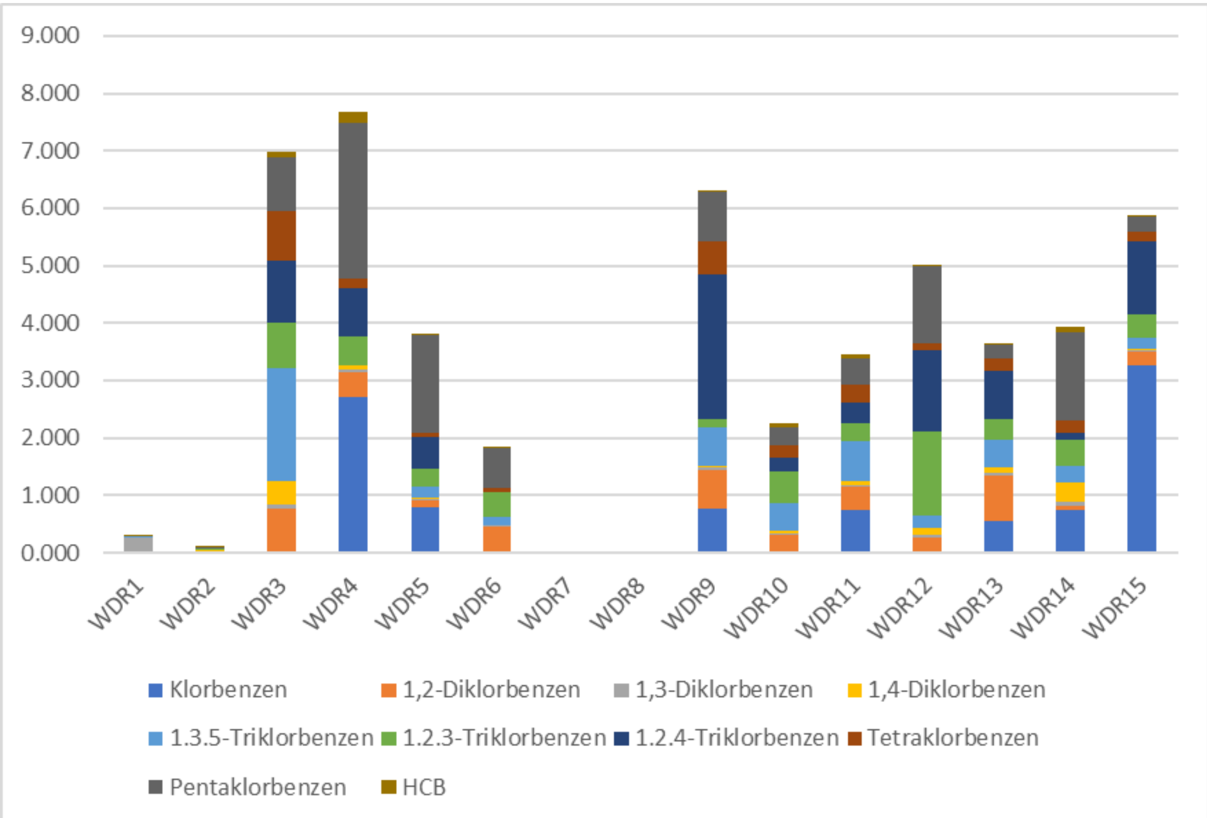

Figure 6. Total of chlorobenzenes in water samples of Drini River, Kosovo.

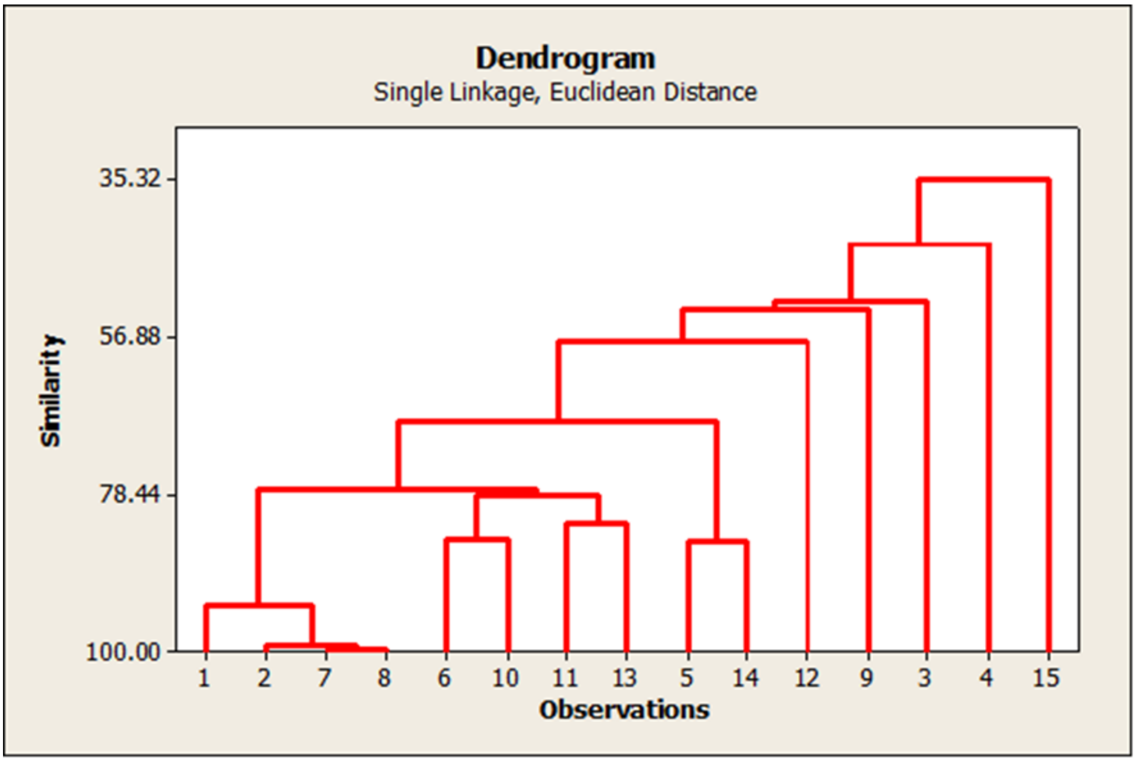

Figure 7. Dendogram of chlorobenzenes in water samples of White Drin River, Kosovo.

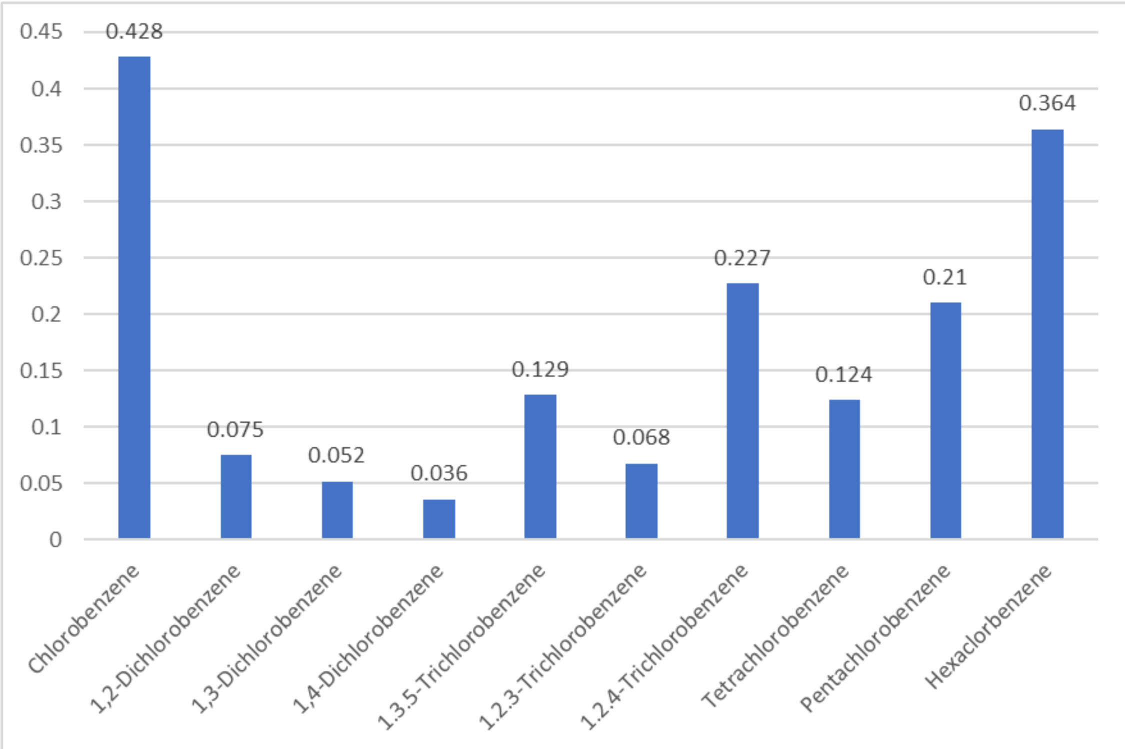

Figure 8. Profile of chlorobenzenes in water samples of Drini River, Kosovo.

5. Conclusion

In this study, water samples from the White Drin River, which is one of the largest river in Kosovo, were analyzed. The analysis of chlorobenzenes and BTEX was carried out by HS/SPME technique followed by GC/FID/ECD technique. Volatile organic pollutants were present in almost all analyzed water samples. BTEX presence is related mainly to the intensity of automobilist transport near the river. Spills of hydrocarbon by gas stations, agro-mechanicals or mechanical businesses operating in this area are not excluded. Momentum values and the influence of water flow are not excluded. Benzene was the compound that was most frequently identified in the highest quantity for all samples. Chlorobenzenes were also detected for most of the samples analyzed.

Chlorobenzene, pentachloro benzene and HCB were identified at higher level in several stations of the river. The presence of chlorobenzenes can be a consequence of urban spills, of cleaning/sanitization in houses and businesses, as degradation products of other compounds (pesticides, PCBs, etc). The levels of VOC in the water of White Drin River were similar to the levels reported in previous works for the water of some Albanian rivers. The presence of BTEX and chlorobenzenes in the water samples of the White Drin River shows that the monitoring of this area should be continuous.

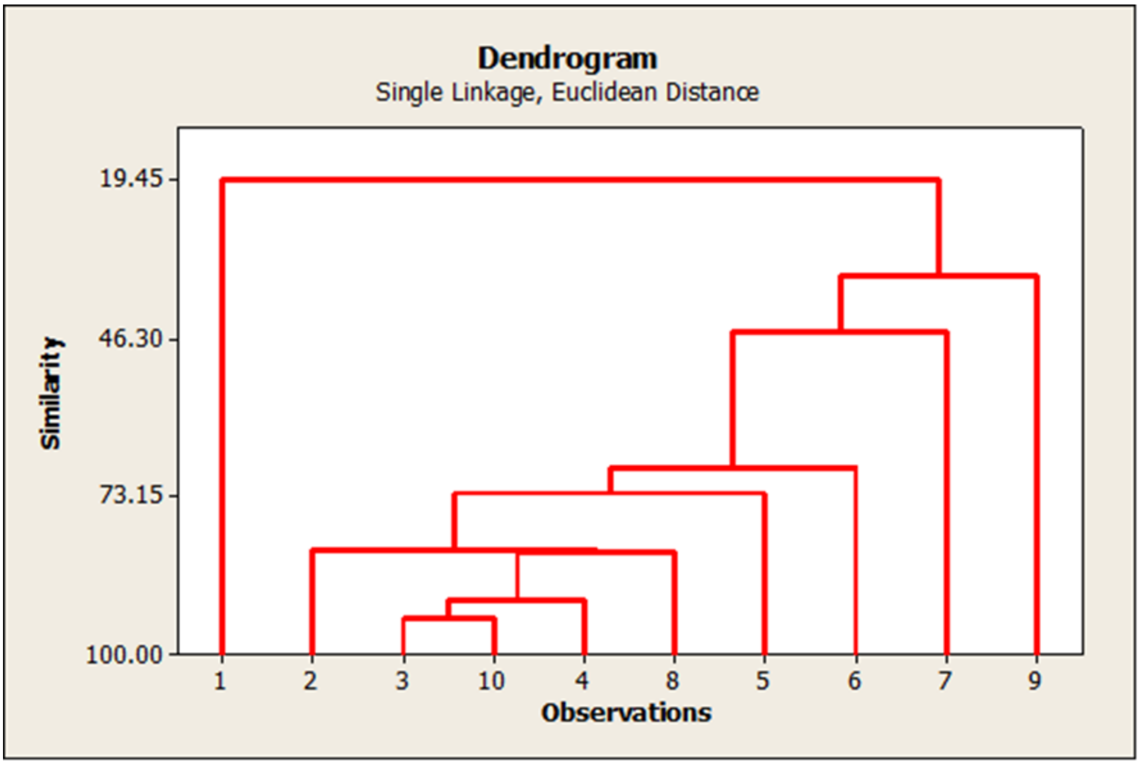

Figure 9. Dendogram of chlorobenzenes in water samples of White Drin River.

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Author contributions

Aferdita Camaj: Idea of this work, sampling of water in White Drin River, sampling treatment, data collection, processing data, paper writing **Arben Haziri:** Idea of this work, sampling of water in White Drin River, chromatography analyze, data collection, processing data, paper writing and correcting **Aurel Nuro:** Idea of this work, sampling treatment, chromatography analyze, data collection, processing data, paper writing and correcting **Arjeta Camaj Ibrahimi:** Idea of this work, sampling of water in White Drin River, sampling treatment, processing data

Conflicts of interest

The authors declare no conflicts of interest.

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