

Oil Pollution Analysis of Gjanica River from Petroleum Refinery and Production Industry in Albania

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

Aim: Oil industry has its effect in environmental. For this reason we evaluated oil pollution from oil extraction processes, and petroleum refinery in Gjanica River.

Study Design: Analysis of hydrocarbon content for river bed pollution from oil industry are evaluated. This is made by comparing gas chromatogram with the model.

Place and Duration of the Study: University of Vlora and ex Oil and gas Institute Fier between August 2016 and March, 2017.

Methodology: Sediment samples were collected in the Gjanica River. Extracts were prepared and taken using Soxhlet apparatus in ex Oil and Gas Institute in Fier. And hydrocarbons contents were evaluated using Hewlett Packard 5890 series II gas chromatography.

Results: Based on the results of oxygen indicators in the Gjanica River COD = 559mg/l and BOD₅ = 102.5 mg/l, we conclude that there are no living beings in this area. And based on six sediment samples analysed we see old and new hydrocarbon compounds in bed River.

Conclusion: High levels of oil products discharges have damaged the living life of the river water for, more than fifty year. This quantity has contaminated sediments of the bed and/or river banks that need to be removed.

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1. INTRODUCTION

Gjanica river is branch of Seman river in Albania. The environmental monitoring programs, pollution level and pollutant sources of the zone were evaluated. River starts from the eastern side of Ballshi refinery. It continues through Visoka oilfield and then flows through Fieri city, and join the Seman river in Mujalli. Gjanica River transports two types of oils: Large amounts of oil that floats on the surface of the water almost all along its flow. Moreover, thin oil sheets can be seen even at the Semani river water surface causing big concern to the livings and humans; Dissolved oil in water, which are calculated total quantities [1].

Gjanica river accumulates the waste water of petroleum refinery Ballsh, the waste water of oil decantation station of Visoka, and industrial waste water of Fieri city, sewage of residential areas, as well as urban waste, up to its confluence with the river Seman [2]. In their flow towards the Seman river (northward), pollutant values decrease as a result of freshwater input, while floating oil patches reach the Adriatic sea, causing its pollution.

The indicators for the pollution estimation are: the total quantity of technological waters discharging in the river ; the oil content diluted in the discharging waters (taking into consideration the total quantity of discharging oil); phenols content; the chemical oxygen demand (COD); the biological oxygen demand (BOD₅); hydrocarbon river bed pollution analysis [3].

In this study from the measurements and analyzes performed, which are taken, it is clear that with passing towards Fier city (inhabited area) the percentage of pollution is increasing. The increase in pollution is clearly shown by the graphs obtained from the gas – chromatogram, which show high level of hydrocarbon compounds.

Therefore, the treatment of the waters and the restoration of the whole zone are quite imperative. The life quality for the biota and humans in the zone will be improved and, moreover, its touristic values will be increased.

2. MATERIALS AND METHODS

In this study we took in consideration the long time discharges in aquatic environment of river. The best way to describe it is throughout the sediments, which shows the history and intensity of discharges [4]. In those sediments (in bed River) samples are evaluated hydrocarbons contents using Hewlett Packard 5890 series II gas chromatography.

2.1 Study Area

Gjanica river emanate from Shpiragu mountain and has a longitudinal extension at 66.7 km, with a catchment basin area around 234.1 km² (Fig. 1). This flow changes during seasons and has a range from 0.146 – 124m³/sec [5]. The area we take into consideration regarding the oil industry pollution activity includes interval from Aranitasi to the Ballsh area, in the direction of the city of Fier through which this river passes. It joins with the river Seman 3 km north of the city in the Mujalli village.

This pollution includes surface leaks of by-products of KPTHN in Gjanica river, resulting in increased content of hydrocarbons, nitrates, ammonia and phenols at levels higher than the allowed norms. The Gjanica River is polluted by the waters of the industrial zone of the city of Fier, the sewage of the inhabited areas, as well as the urban waste, up to its union with the Seman River.

In the Gjanica river have been systematically performed a series of analyses to assess the degree of water pollution.

The main objects of the study are:

1. The amount of technological discharges of decanting stations, oil refineries.
2. The waters of the Gjanica River after the discharges of the oil industry and the urban ones.
3. Assessment of riverbed pollution.

2.2 Sample Collection and Preparation

Specifically, on the Gjanica River three water sampling stations were identified:

- After the discharges of the town of Ballsh (including the discharges of the oil refinery, the Usojë decantation and the urban ones). This is the southernmost station.
- After discharges of Visoka decanting station.
- After discharges of the oil refinery and the urban ones of the city of Fier. This is the northernmost station.
- National Hydrocarbons Scientific Centre, Fier.
- Chemistry-Processing Centre, Kuçova, subordinated to the company "Armo".
- Institute of Public Health, Tirana.
- Veterinary Research Institute, Tirana.
- Definitions by foreign companies those are active in oil exploration and production in Albania.

Also, five riverbed sampling stations were identified (Fig. 2):

- bridge before entrance to the town of Ballsh (northern most station);
- in the Ofiçinë before the Visoka decanting plant;
- after Visoka decanting plant;
- before the bridge at the entrance of Fier's city (Gjanica river),
- at the bridge in the centre of Fier,
- Overpass of Hoxhara canal.

The sampling procedures were carried out respecting the requirements of environmental monitoring methodologies and rules. These methods are in accordance with the Albanian state standard based on the European standard (ISO) and the American one (ASTM).

Analytical determination of pollution indicators are performed by these institutions:

Defined indicators are: Amount of emissions, pH, Suspended substances, Oxygen, Amount of water (m), Dissolved oil, Phenols, H₂S gas, Nitrite, Nitrate, Phosphate, Iron, NKO, NBO₅, Boron, Ammonium, Aromatic hydrocarbons of benzene series (benzene-Toluene, E.Benzene, P.Xylene, M.Xylene, O.Xylene) [1], chromatograms of river bed pollution with oil.

From the measurements and analyses performed, as well as the assessments with gas chromatographic (GC), it is clear that with the passage towards the city of Fier (inhabited area) pollution of water and riverbed increase. This pollution includes surface runoff of by-products of KPTHN in Gjanica, bringing increase content of hydrocarbons, nitrates, ammonia and phenols at levels higher than the allowed concentrations. The Gjanica River is also polluted by the waters of the industrial zone of the city of Fier, the sewage of the inhabited areas, as well as the urban waste, up to its union with the Seman River.

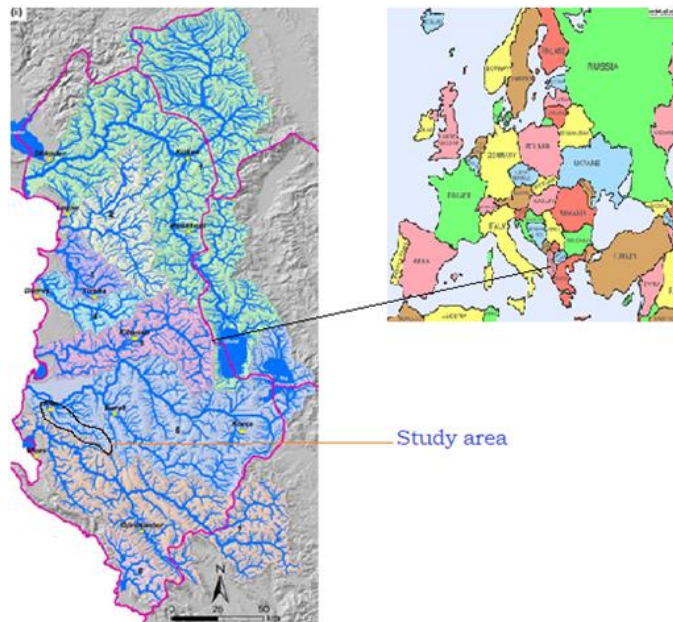


Fig. 1. Study river Gjanica zone

We have divided the polluting potential of the Gjanica River into four categories:

- Layered water discharged after the oil separation process at the Usojë (when water is injected into wells) and Visoka decanting plants.
- Technological waters discharged from Ballsh and Fier oil refineries,
- Uncontrolled polluting waters,
- Industrial discharges of food industry, hospitals and urban areas of Fier and Ballsh [1].

- Has increased the amount of oil extracted, and
- Has increased the water content of crude oil.

In oil wells the fluid comes out as of water-oil emulsions. Oil decanting plants have been set up to separate water from oil. The decanting technology in these plants is old. The water treatment process is performed only in the gravimetric separation of oil, through horizontal concrete separators, which have emerged from the technological scheme of oil preparation.

These waters were not treated prior to discharge.

This increases the amount of oil discharged into the Gjanica River.

Discharge waters quantities from decanting plants in resents year has increased for two reasons:

From the observations it is noticed that, the river Gjanica is polluted to a considerable extent due to the discharge from waters of these plants.

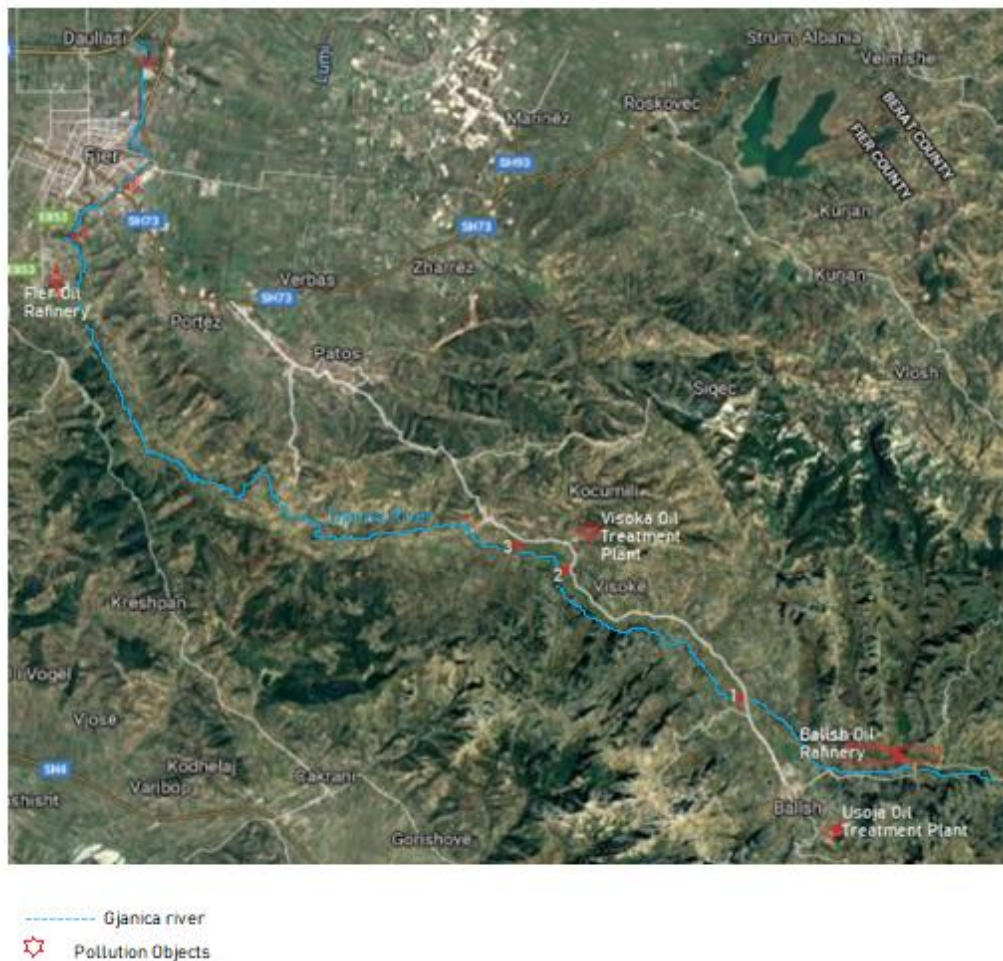


Fig. 2. Sampling points on Gjanica riverbed (sole)

2.3 Analytical Procedures

Sediment samples were taken at the bottom of the Gjanica River. To perform the analyzes for each of the samples, 50 g of sample was weighed after drying it in a thermostat at a temperature of 60 - 65 °C for a period of three hours. In each case the purification of the sample was carried out in the Soxhlet apparatus and chloroform was used as a solvent, which is a strong solvent, no residue remained on the filter paper [6].

The fractions obtained from the solution were analyzed to determine the individual hydrocarbon composition of the aromatic fraction, where the evaluation methodology is the same as in the case of the saturated fraction. The working conditions are the same. In this case it is difficult to identify aromatic samples, such as phenanthrene, dimethyl-phenanthrene, naphthalene, etc., as well as the rapports between them. Under these conditions, are required longer analytical procedures, so, we do only the gas-chromatograph comparison of a crude oil with the profiles obtained for each sample.

Their extracts have undergone gas chromatographic analysis. Hydrocarbons contents were evaluated using Hewlett Packard 5890 series II gas chromatography. Important conclusions are reached, by looking at the distribution of hydrocarbon compounds, based on the number of Carbons. For illustration we are presenting the distribution of normal paraffin of brut oil in Albanide.

3. RESULTS AND DISCUSSION

In Gjanica river discharges of stratified water from oil wells are on average 36,459 m³ per month or 437,517 m³ per year and from refineries 2,102,259 m³/year.

These waters contain in the dissolved state, apart mineral salts, petroleum hydrocarbons with toxic properties, tension-active substances, which serve as demulsifies. These substances have the ability to create foams, which become obstacles in the process of river self-cleaning.

During periods of rainfall, the amount of oil discharged into the river increases as a result of rinsing contaminated surfaces.

Large quantities of oil have been discharged with technological waters, as a result of old oil industry technology (Table 1).

Currently data on oil discharges with water are controversial because they do not include floating slicks, submersible and sliding oil ports in aquatic environments. In my opinion the total oil content in the discharged waters should be higher.

It is clear that the water discharged from the decanting stations is highly polluted. Their discharge into the Gjanica River causes its pollution.

The oil refinery of Ballsh is located in the upper sector of the Gjanica River. This refinery is built on alluvial river deposits. It has an extension of 2 km along the river. Technological waste resulting from the technological process is discharged into the Gjanica river. This refinery discharge technological waste through two main channels. In addition there are also some secondary discharges in river.

In the discharge waters are analysed the contents of dissolved oil for 5 years, this indicator takes the value up to 96mgr./l. Thus, in 5 years into the Gjanica River has been discharged 482.43 tons of oil, which has crossed the Adriatic Sea [1].

Table 1. The amount of technological water discharged into the Gjanica River and dissolved oil in them [1]

Nr.	Discharge objects	Polluted water m ³	Dissolved oil in discharge waters
1	KPTHN Ballsh (Oil Refinery)	1 416 000	60-153 mgr./l
2.	Power plant Ballsh	189 800	
3.	Decantation plant Usojë	44 118	50-76 mgr./l
4.	Decantation plant Visokë	112 495	20.8 - 29mgr/l
5.	Oil Refinery Fier	689 259	90-96 mgr./l
6.	Urban water of Ballsh city	1 152 000	
7.	Urban water of Fier city	8 030 000	
	Total	11 633 972	

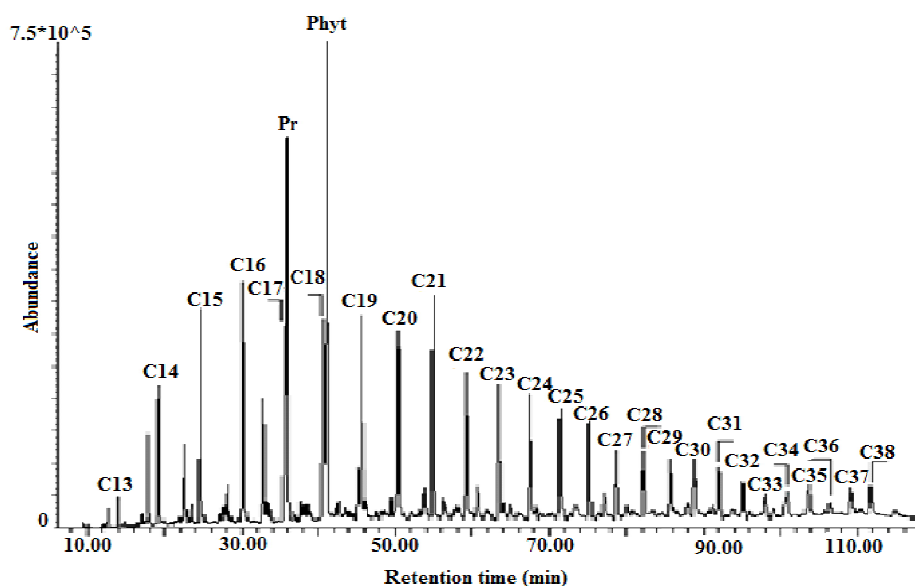


Fig. 3. Chromatogram of a brut oil in Albania

Table 2. Average results of discharge water analysis from decanting plants (mg/l) [3]

Parameter	Diapason
pH	6.35
Total dissolved solids	67.5-76
Oxygen	1.9-2.1
Ammonium	32-41
Oil	165-500
Phenol	46-96.5
Gas H ₂ S	6-6.15
Nitrite	0.36-1.67
Nitrate	2.6-3.65
Phosphate	1.12-1.3
Iron	0.16-0.21
COD	417-750
BOD ₅	64.15-68.25
Bore	45-78.7

From the above estimations the refinery discharges have polluted Gjanica river and has reached the shoreline of the Adriatic Sea.

The water purification unit of this plant did not work from the beginning and the efforts to restore this unit to work have been non-persistent and ineffective.

So, as shown in the Table 1, in recent years, from this refinery flows into the river Gjanica not less than 100 tons of oil, which ends at the river Seman [7].

The results of the analysis of benzene and its counterparts in the water of the river Gjanica, as

influence of discharges from plants and uncontrolled waters is high. Aromatic hydrocarbon content is lower in the river due to natural flow. However, the water of this river is polluted.

The maximum value of benzene reaches 1.39 mg/l and toluene 2.4 mg/l, while the values of other counterparts decrease. However, the presence of these hydrocarbons in the aquatic environment must always be controlled as they are classified as carcinogenic.

As a result of these discharges, the pollution of Gjanica has been so high that it is considered lifeless from an ecological point of view and can be classified as a dead river.

In terms of fauna and flora, we can say that for some time, they have been reduced to a minimum or do even not exist.

Analyzes performed show the high level of pollution throughout the period of the year and in particular, when the oil refineries and oil decantation plants Usojë, Visokë were in operation. The water analyzes of the Gjanica River are given in Table 3 [8].

Based on the results of oxygen indicators in the Gjanica River (COD = 559mg/l and BOD₅ = 102.5 mg/l), we conclude that there are no living beings in this area.

Table 3. Results of Gjanica river water analysis from Ballshi after industrial complex in Fier city

Chemical indicator	Between Usojë and Visoka			Between Visoka and Fier			After industrial complex Fier		
	Minimum value (mg/l)	Maximum value (mg/l)	Medium value (mg/l)	Minimum value (mg/l)	Maximum value(mg/l)	Medium value (mg/l)	Minimum value (mg/l)	Maximum value (mg/l)	Medium value (mg/l)
pH	6.5	7.4	6.8	6.3	6.8	6.5	7.3	9	7.9
Nitrite	0.20	0.36	0.33	0.25	0.37	0.35			
Nitrate	2.6	3.32	3.3	3.05	4.5	4.3	4.15	55	29.5
Ammonium	1.23	8.36	8.3	6.9	10.0	9	44.5	177	110.7
Iron	0.18	0.77	0.73	0.14	0.25	0.22			
Phosphate	0.69	1.20	1.18	0.75	1.45	1.43			
Phenol	2.62	3.64	3.60	2.6	3.7	3.4	1.44	3.0	2.22
Total dissolved solid	71.0	110	108	64	91	89	53	120	86.5
COD	131	157	150	109	157	154	204.5	914	559
BOD ₅	42.4	58.2	58	38.7	54.5	50.5	55	150	102.5
H ₂ S				1.3	2.5	2.3	2.7	3.2	2.95
Oil products				61.0	363	360	27	80	53.5

From what we reflected above regarding the amount and polluting elements of the river Gjanica, the soil samples taken at the bottom of the river were analyzed. These samples were taken at the following points: the bridge before the entrance to the town of Ballsh; in the Ofiçina before Visoka decanting plant; after Visoka decanting plant; before the bridge at the entrance of the city of Fier (of the river Gjanica), at the bridge in the centre of Fier; before the confluence of the Gjanica River with the Seman River.

Based on the following graph that shows the distribution of carbon content (in the model Fig. 3) we will make the interpretation of chromatograms obtained from the analysis performed by gas-chromatograph, in order to assess the degree of pollution of the Gjanica riverbed, which is very variable in its longitudinal extent.

Chromatogram 1.1 (Fig. 4) is the graph obtained from the analysis of the sample taken at the bridge before entering the town of Ballsh.

Based on the comparison between the model and chromatogram 1.1 we see that, the hydrocarbon content at this point is negligible. This is seen in chromatograms, and where the content of carbon molecules is very low. This is due to the high speed of the river in this area and

where it is seen that in the river bed is found gravel, sand and clay deposits.

Fig. 5 shows the chromatogram obtained from the analysis of sample 2.2 taken in the North of the Ofiçina area before Visoka decanting plant, where the pollutant layers are three. Here we see hydrocarbons with low carbon contents, as well as a significant amount of hydrocarbons with high carbon. This is explained by the fact that, in this area in which the sample was taken, the river widens and is accompanied by meanders, as well as by significant oil spills and oil fractions in the period when the river inflows have been high.

The rapid decline of inflows has been accompanied by oil sedimentation on the river bank. The time of oil sediments in contact with the atmosphere has led to the evaporation of light oil fractions and on the shore has remained the heavier oil fractions.

In chromatogram 3.1 (Fig. 6) we see an increase of all hydrocarbon compounds. In the sample taken after the Visoka decanting plant we have several layers of hydrocarbons in the sediment. The pollution of the river bank behind the decanting station can also be seen with the naked eye. During the sampling process, the discharges from this plant were negligible, but from the analysis of this sample we see that we have old and new sediments, which is reflected in the content of these hydrocarbons.

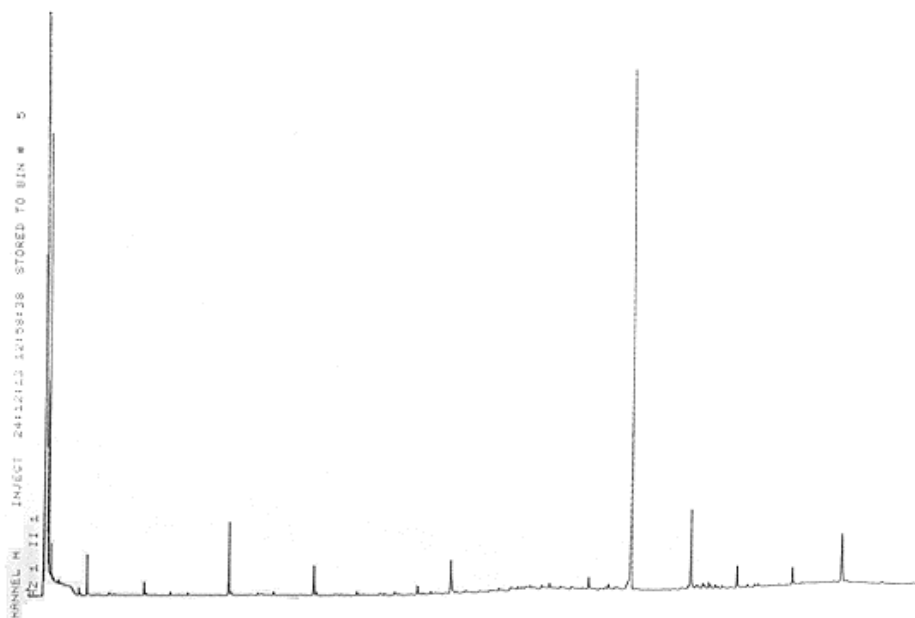


Fig. 4. Chromatogram according to the sample 1.1 (see Fig. 3).

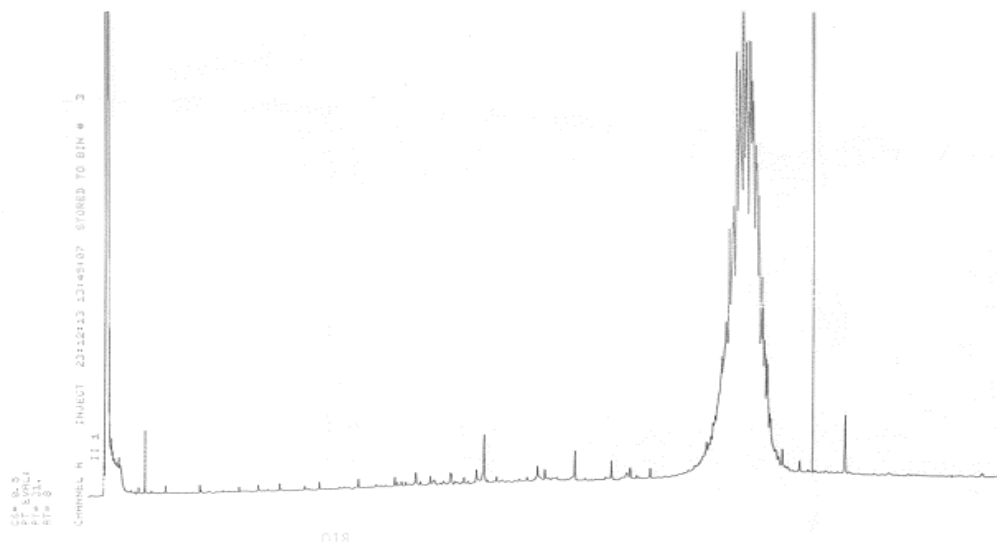


Fig. 5. Chromatogram according to the sample 2.2 (see Fig. 3).

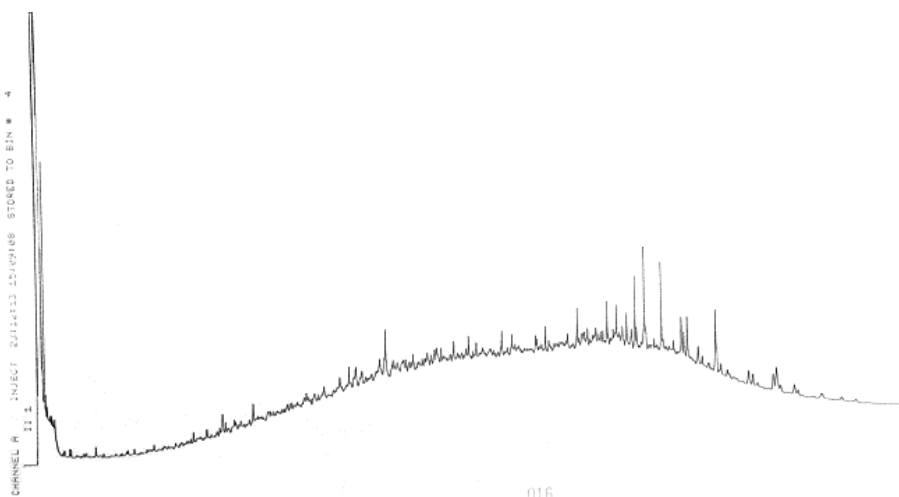


Fig. 6. Chromatogram according to the sample 3.1 (see Fig. 3)

From the chromatogram in Fig. 7 taken from the analysis of sample 4.1, sample which was taken before the bridge at the entrance of the city of Fier, we see a series of hydrocarbon deposits (Fig. 10), where the thicknesses of these sections are from 0-15 mm. In this zone we have high deposits of clays and silk.

Even in this chromatogram we see that the heavy fractions of hydrocarbons are in high content because of the degradation process that these hydrocarbons undergo over time.

From the following chromatogram (Fig. 8), which is obtained from the analysis of sample 5.1,

taken at the bridge in centre of Fier city we see a high content of hydrocarbon. This type of graph is explained by the fact that in river waters come discharges from the oil industry, as well as from urban area.

The chromatogram recorded from the analysis of the sample 6.1 (Fig. 9) taken at the Hoxhara overpass reveals the hydrocarbon pollution of this river. The first layer of oil is found almost on the surface in 1 cm of river deposits (mainly clay), with thickness 1cm. After second deposits of 3cm thick there is a second layer with a thickness of 2cm. The third layer with a thickness of 2.5-3cm

variable is found after 20 to 25 cm. This clearly reflects the high level of pollution which comes from the discharges of the oil industry, as well as urban discharges, as well as plastic waste or other waste coming from car washes, etc.

This deposition is caused due to the reduction of the river flow velocity (topography) and its numerous branches (the sample was

taken in July 2016 before clearing the river bed).

The Fig. 10 taken in river banks sediments eroded by water flow shows the history and intensity of discharges, and the amount of sediments that the river Gjanica has brought over the years. This is like a picture of the history of sediment and hydrocarbon pollution transport process.

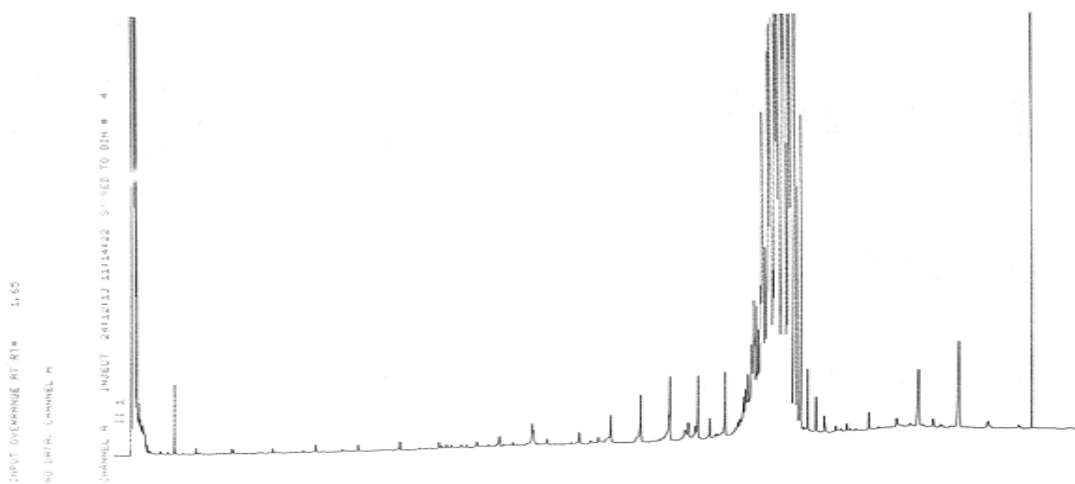


Fig. 7. Chromatogram according to the sample 4.3 (see Fig.3).

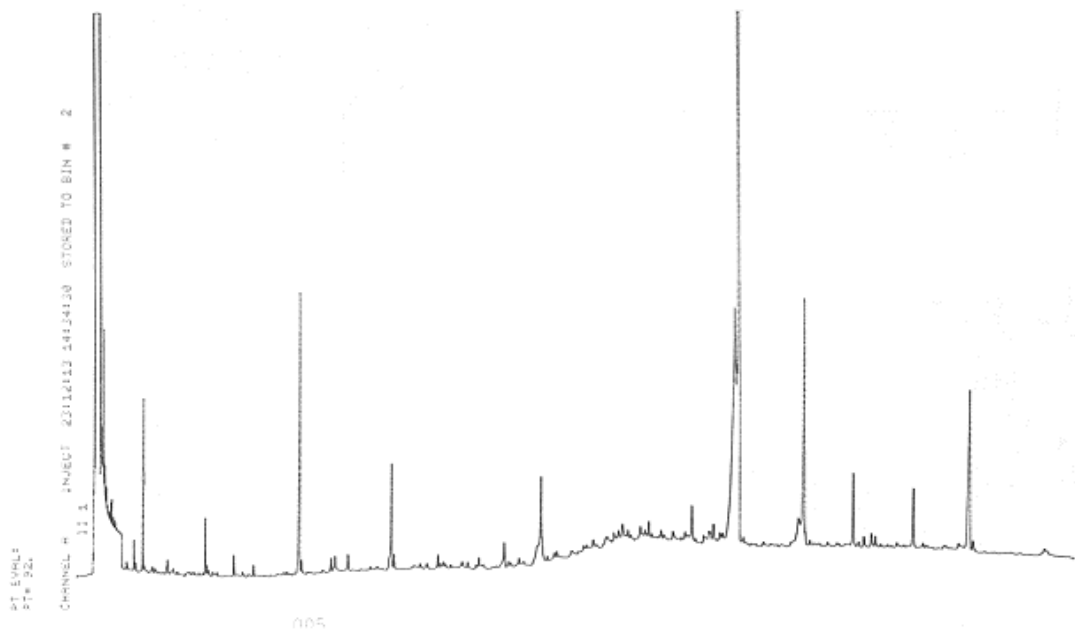


Fig. 8. Chromatogram according to the sample 5.1 (see fig.3).

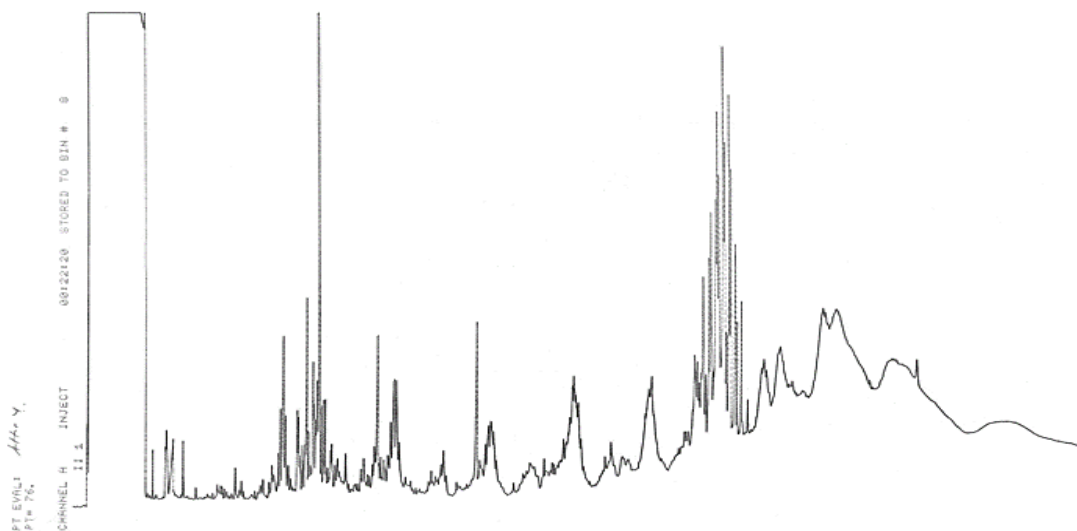


Fig. 9. Chromatogram according to the sample 6.1 (see Fig.3).



Fig. 10. River sediments on the bank of the river Gjanica (before the bridge at the entrance of Fier)

4. CONCLUSION

The impact of the oil industry on the riverbed gives us a clearer picture from the consequences that this industry has brought to the water pollution of the Gjanica River, and consequently to the aquatic life.

We must prevent the discharge of hydrocarbon polluted water into the river flow, and any other surface flow.

Three phenomena have been recorded in the sediments of the Gjanica River: the number of

discharges, the amount of discharges and the amount of sediments that the Gjanica River has transported.

Due to the preservation of hydrocarbon pollutants in the riverbed, it is generally more interesting to remove contaminated sediments from the bed and/or river banks, due to the high level of toxicity they have in the living life of the river water.

Removal of polluted sediments of Gjanica should be carried out from Visoka decanting plant to the confluence of it with the river Seman.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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