Quantification of uncontrolled oil pollution of the East Jiu

Lautaru Vlad[1]*, *Kovacs Izabella*[1]

1 National Institute for Research and Development in Mine Safety and Protection to Explosion – INSEMEX Petroșani

Abstract. In the current global context, where drinking water sources are constantly diminishing, surface water pollution has become an environmental problem that requires rapid action to conserve drinking water sources and protect aquatic biodiversity. Water pollution has many causes and can be caused by nitrates, detergents, pesticides, heavy metals, petroleum products and many other harmful substances that come from different sources. In this paper we analyzed the pollution of surface waters, respectively of the water course - Jiul de Est, with petroleum products, considering that in its immediate vicinity there are several points of sale and storage of motor fuels, but also pollution with petroleum products that come from cars that transit the roads in the vicinity of East Jiu.In order to be able to quantify the degree of oil pollution of the Eastern Jiu, water samples were taken in order to analyze them with the Fourier Transform Infrared Spectrometer determination method. The purpose of the work is to determine whether the degree of oil pollution of the Eastern Jiu is an environmental problem that requires the intervention of the competent authorities in order to reduce the effects that this type of pollution can have.

1. INTRODUCTION

In the process of sustainable development, both at national and international level, the problem of managing water resources occupies a major place, taking into account that water, considered for a long time as an inexhaustible and renewable resource, has become and is proving increasingly obvious one among the limiting factors in socio-economic development. As the main environmental factor and major vector for the propagation of pollution at local and cross-border level, as a vital resource for life support, water has gone through a series of stages from the point of view of organizing its own management. [1]
The main dimension of water is quality, which is currently a major objective in water management, in which the monitoring activity has a determining role, representing the basic tool in the development of water policies, ensuring related management.
The input of pollutants into aquatic ecosystems can occur unintentionally (most natural sources), accidental/episodic (from natural or authorized sources) and continuously (from authorized sources). [2]

According to the manner of discharge into the receiving body of water, the sources are classified into point and diffuse, and understanding the differences between them is necessary to be able to exercise an effective control of the pollution processes.

Among the main surface water pollutants such as suspended solids; acids and bases; fertilizers (nitrates and phosphates); cyanides; sulfites; phosphorus; metals and metalloids; organic compounds (petrochemical products and plastics); organic effluents; pesticides; PCBs; various metallic compounds; radionuclides; detergents; microorganisms, we will focus on organic compounds, respectively petroleum products, on the East Jiu river, downstream of certain economic operators whose main object of activity is the sale of fuels, in the immediate vicinity of the water course.
From the point of view of approaching water quality as a resource and implications for human health, water quality is, as a rule, defined by legal regulations based on the comparison of individual indicators with the values prescribed by the standards. The methods of analysis and interpretation of the data related to the chemical pollution of the water courses are mainly based on the comparison of the measured values with the standard limit values.
Starting from the need to ensure a volume of data as rich as possible and with a high level of confidence, the activity of knowledge of water quality has an important role in water quality management.

In order to quantify the analytical results and the effects produced by petroleum hydrocarbons on water and the environment, they have been regulated as quality indicators of TPH (Total Petroleum Hydrocarbons) methods in European and national legislation. Total petroleum hydrocarbons is a general term that includes several hundred chemical compounds derived from crude oil, consisting of carbon and hydrogen, i.e. benzene, toluene, xylene, hexane, naphthalene, fluorene, fuels, mineral oils and so on. From an environmental point of view, the total content

* Corresponding author: vlad.lautaru@insemex.ro

of petroleum hydrocarbons can seep into the environment through accidents, from industrial emissions or as by-products of commercial or private uses, can be released directly into water through leaks, can form films on the surface, can sink in bottom sediments or decompose due to bacterial activity in the aquatic environment.
The population is exposed to moderate levels of TPH as a result of handling substances with a high TPH content, consuming TPH-contaminated water, touching contaminated soil, living near an oil spill, inhaling VOC vapors at gas stations, using chemicals at home or at work or the use of certain pesticides. [3]

Figure 1 - Course of water polluted with petroleum products[9]

High levels of TPH can affect the central nervous system and as a cumulative effect at high concentrations in the air one compound can cause headaches and dizziness and another compound can cause a nerve disorder called "peripheral neuropathy" or cause effects on the blood , the immune system. system, lungs, skin and eyes [2, 3]. In this case, the precise analysis of the total content of petroleum products is an important step in estimating the environmental impact for a given site.

2. Methods and materials

The objectives of the work are to characterize the quality conditions of the Jiul de Est course from the point of view of oil pollution, as well as their trends, to assess the water and pollutant flows, to compare the measured values with the admissible values and to issue warnings in emergency situations.[10]
In the context where in the immediate vicinity of the course of the river studied in this paper, there are several economic operators whose object of activity is the sale of petroleum products, respectively car fuel, and the area of the Jiului Valley transited by the East Jiul is an area with the mining industry, which can also pollute surface waters with petroleum hydrocarbons, we have placed the sampling points in such a way that they are as representative as possible for the research that is the basis of this work.[9]
The mining industry, with its exploitation and preparation branches, is a large consumer of industrial water, contributing to a very large extent to the pollution of natural receptors in the area. The natural watercourses in the mining regions have waters whose composition changes along the way, depending on the quantity and quality of received groundwater, meteoric waters and residual waters discharged into them. [4]

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- Sample 1 – The blank sample, upstream from the gas stations located in the immediate vicinity of Jiului de Est - coordinates: 45,37824ºN, 23,37154ºE
- Sample 2 – Downstream from gas station 1 - coordinates: 45,39205ºN, 23,37212ºE
- Sample 3 – Downstream from gas station 2 - coordinates: 45,39373ºN, 23,37221ºE
- Sample 4 – Within the Petrila locality - coordinates: 45,44312ºN, 23,38371ºN

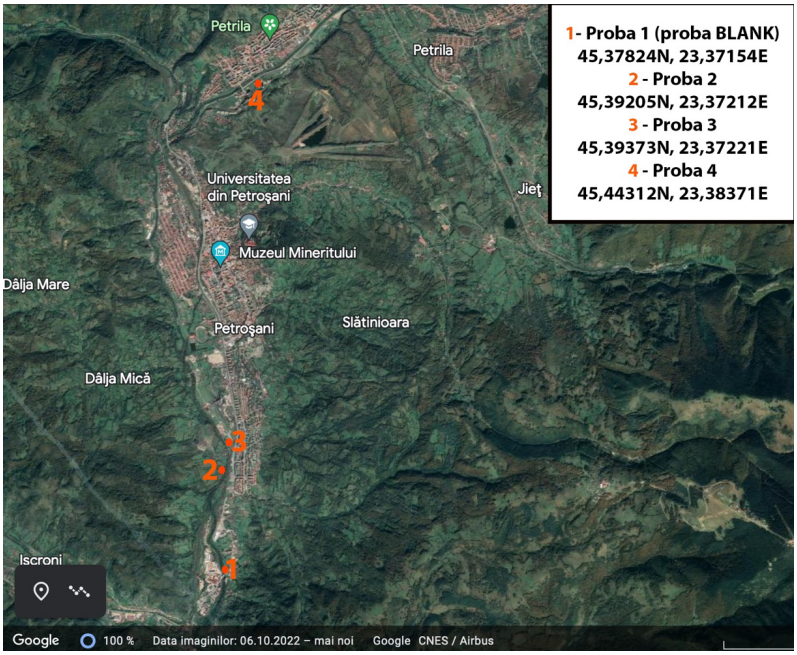

Figure 2 – Graphic representation on map of sampling points – map imported from Google Earth

The places where the water samples were taken are represented graphically in figure 2, and the images from the moments of the on-site determinations can be found in figure 3. The determinations were carried out by the staff of the Environmental Protection Laboratory within the INSEMEX Petrosani INCD, according to the sampling standards water in force.

Figure 3. – Sampling of water samples from the Jiul de Est river – own source

The pictures used for figure 3 were selected from the pictures taken when taking water samples in the field.
The laboratory analyzes were carried out by INCD INSEMEX Petrosani qualified staff, from the Environmental Protection Laboratory, with the help of the determination equipment provided by INSEMEX INCD - Fourier-transform infrared spectroscopy FTIR.
The Fourier-transform infrared spectrophotometer measures an infrared spectrum by the Fourier transform of an interferogram obtained by using an optical system based on the use of a Michelson interferometer in which light, after passing through aperture, is transformed into a parallel beam by the collimator mirror and enters the light beam splitter [7]. A germanium film, deposited on a substrate of potassium bromide by evaporation, comprises the light beam splitter and divides the single beam into two beams, reflecting one towards the fixed mirror and transmitting the other towards the moving mirror.[8]
The operating principle graphically represented in figure 4 helps us to understand the determination principle that we used to determine the content of petroleum products in the samples taken.

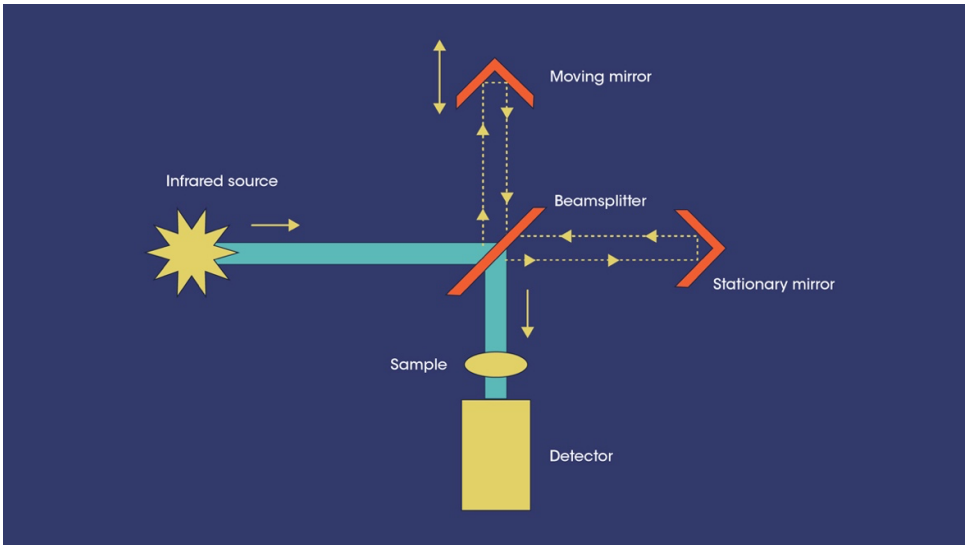

Figure 4 – How FTIR Spectometer works [3]

Both mirrors reflect their rays back to the beam splitter and part of each returning beam is reflected and transmitted. Using the principle of overlap, the light transmitted from the fixed mirror and the light reflected from the moving mirror recombine and interfere with each other as they move towards the collector mirror [1].
The values determined with the help of the FTIR equipment will be compared with the maximum allowed value of total petroleum hydrocarbons according to Order 161/2006, namely 200 µg/l.[6]

3. Results and discussion

The presence and concentration of the total content of petroleum products in water is a public concern due to the harmful effect and impact on aquatic life and public health. Currently, regulations and standards have been established that require the monitoring of the total content of petroleum products in water, so for the analytical analysis of TPH in water using Mid-IR laser spectroscopy, it is necessary to use a Fourier transform infrared spectrometer that can provide a resolution high.
Quantification of the total content of petroleum products in water using FTIR spectroscopy involves plotting the calibration curve against the absorbance value measured at a specific wavelength for a specific certified reference material or standard calibrator prepared in the laboratory.
The four samples taken were analyzed with the help of FTIR according to the internally validated method within the Environmental Protection Laboratory - Insemex Petrosani, and the values found in table 1 were obtained.
The measurements were made by measuring the substance's absorbance intensity at a single point, with autozero spectrum processing according to each baseline interferogram that was predetermined before each measurement. A peak's elevation or descent within an absorbance spectrum is directly proportional to the concentration of the analyte in the infrared region. No tools like spectrum slicing, spectral derivatives, peak deconvolution, netezing, or curve adjusting were used for each specific IR radiation spectrum to improve the spectral aspect and extract more information from the spectrum.

Table 1 – Results of determination

Nr Crt	The name of the sample	Determined value of TPH [μg/l]	Maximum value allowed for TPH according to ORD. 161/2006	Exceeding the maximum allowed value
1.	**Sample 1**	**12**	200 μg/l	**NO**
2.	**Sample 2**	**23**		**NO**
3.	**Sample 3**	**23**		**NO**
4.	**Sample 4**	**9**		**NO**

Following the obtained values, we observe according to table 1 that there are no exceedances of the concentration of petroleum hydrocarbons for the samples taken.

Conclusions

1. 1. Following the results obtained, we note that in none of the sampling points established for this research are there any excesses of the values of total petroleum hydrocarbons established by ORD. 161/2006.
2. 2. We note after the analysis of the obtained results that for samples 2 and 3, the total oil hydrocarbon values measured, although they do not exceed the legal limit, are higher than in the case of samples 1 and 4, respectively sample 1 – fur sample, and sample 4 – sample taken from the radius of the city of Petrila, which indicates a possible uncontrolled pollution in that area.
3. The samples with the highest determined concentrations, respectively samples 2 and 3, are located in the immediate vicinity of the two economic operators whose main activity is the sale of automotive fuel, in both sampling points the value of the concentration of total petroleum hydrocarbons is 23 µg/l.
4. Although in the sampling sites chosen for this research the values of petroleum hydrocarbons of the samples taken do not exceed the limit value established by law, we observe the presence of petroleum hydrocarbons in the water course of the Jiul de Est river, a fact that must be monitored by the competent authorities in this sense.

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