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Research Article

Monitoring Pollution of Undergraund Water Caused by the Oil Industry, Area Patos – Marinz

Ecology and Environmental Biology

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Abstract

Soil, water, air and underground water pollution by the Oil Extraction Industry, i.e. crude oil and oil-water mixture is present in most of the oil fields installations. With 2000 wells covering about 200 km2, the Patos-Marinza oil field is one of the largest oil fields in Albania, but also one of the sources with the greatest contamination potential for soil, groundwater, water and air pollution from different sources of the industrial activity in this region. Oil leakages and discharges on land are transported by filtration waters or rinsing waters, contaminating both groundwater (springs, watersheds) and surface waters (streams, reservoirs, rivers, lakes). These contaminated groundwater and surface waters are used and continue to be used for irrigation, and in some cases as potable water for humans and animals. Knowing that hydrocarbons bring many effects with carcinogenic effects to humans, it is necessary to këp under monitoring all the sources that are used as drinking water for the residents.The purpose of this paper is to monitor and evaluate the Bacteriological, Physico-Chemical, Havy Metals, Pesticides, Aromatic Polycyclic Hydrocarbons (PAHs); Vajra & Graso (HEM); all thrë of the main wells in the Patos -Marinza area. Two drilling wells in Marinza and drilling well Qafë Stefan (Kuman).

Introduction

In oil field there is a significant pollution on the ground not only from accidental oil discharges. From this pollution the flora and fauna of the water network in the oil field has been and is the most influenced and the most endangered.

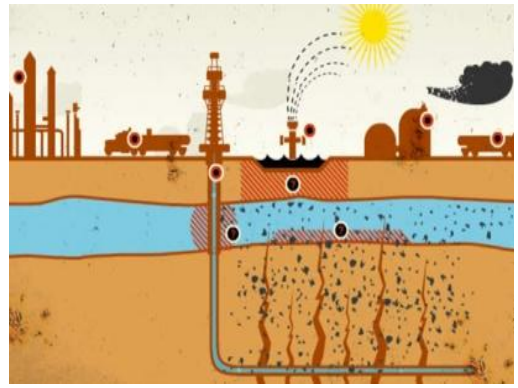
The large amount of liquid discharges in the hydric network and their physico-chemical characteristics have adversely affected the development of flora and fauna. This contamination is a situation inherited from long-term activity in the oil field. More problematic this situation is around oil extraction wells.

The most important reasons for land contamination are as follows:

- Damage to equipment and technological connections in the well's head. In some cases there is damage to the gaskets of the wells and consequently there are oil leaks. It is necessary that the wells to be under a systematic control and intervene in time to eliminate the various breakdowns and defects.
- Subterranean cleaning of wells and replacement of equipment.

- Replacement of oil pipelines and main oil pipelines. In many low points of these pipelines is a significant amount of oil that must be carefully managed during this process.
- Interruption of power supply. The amount of oil found in the heating furnaces in the decanter, in the moment of power interruption, should be immediately discharged to avoid coke. Oil is stored in oven in the quantity, up to 5 m^3. This process should also be carefully managed to prevent soil and water contamination.

An ever-present danger, is the landslide in areas where it can be favored by broken relieves. Experience so far has shown that the land slide has bën associated with fracturing oil pipelines and consequently there has bën soil and groundwater contamination on large surfaces. In some cases, landslide can cause damage to wells column pipe that may lead to uncontrolled fountains.



In such cases, preventive measures should be taken wherever possible.
Highly hazardous, for the soil, is pollution from the diluents (solar oil) where it is applied. Its low viscosity favors the rapid spreading of the surface to the surface of the soil and undergruound water.
Soil polluted from the hydrocarbons has direct negative consequences on the structure of the soil, groundwater and vegetation. Evaporation of light petroleum fractions is an additional factor in air pollution. Soil polluted from oil, greatly reduces the productivity of cultivated crops or spontaneous vegetation.

The high presence of hydrocarbons in the soil is associated with a decrease in the amount of nutrients in the soil and especially nitrite. This is accompanied by the yellowing of plant leaves or the complete failure of agricultural crops.
Waters that are separated from oil after the decontamination process. These discharges are the inseparable part of the oil production process. From the calculations it turns out that the amount of water discharged during the decanting of oil at the decanting stations, in the area we are monitoring, is as in the table:

Table 1. The amount of water discharged from the decanter stations

Decanting Stations	Quantity (m^3/year)
Sheqishte Decanting	133069
Marinza Decanting	291028

Figure 4. Sheqishte channel near the inhabited area, polluted by oil

These contaminated groundwater and surface waters are used and continue to be used for irrigation, and in some cases as potable water for humans and animals. Knowing that hydrocarbons bring many effects with carcinogenic effects to humans, it is necessary to keep under monitoring all the sources that are used as drinking water for the residents.

Material and Method

Method of sampling and preservation, method of their prior treatment are strictly followed. Sampling is carried out through the pumps installed inside the wells. Initially the water was left to flow for a few minutes and then collected in a PET bottle with a volume of 2 liters. Water samples are stored at -20 ° C for freezing and for some chemical analysis by acidification, according to the methods.

Turbidity. Turbidity is a parameter that quantitatively characterizes the level of algae, microorganisms and solid particles that scatter and absorb light. The turbulence measurements were performed with the TURB 430 IR apparatus, with the nefelometric method.

Determination of sulphates. Sulfates in water are usually analyzed by adding an excess of barium chloride that give the barium sulfate precipitate, which can be determined by the turbidimetric method.

Determination of chlorides in the waters. Determination of the chloride ion content in the waters was accomplished by silver titration with silver nitrite by titration Mohr, in which for the determination of the last titration point, is used as a marker the potassium chromate.

The determination of reactive phosphorus in the water is done according to the standard method ISO 6878-1998.

Determination of nitrites. Nitrite is determined by the formation of a pink compound formed at pH 2.5 by the sulphanilic acid diazotization with N (1-naphthyl) ethylenediamine dihydrochloride NED.

Concentration of the Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} main elements concentration in the waters. Determination of the concentration of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} was carried out in the filtered water fraction after filtration with a glass filter of 1μm size and acidified with nitric acid up to pH = 2. The measurements were performed using the atomic absorption spectrometer.

Determination of heavy metals in water. Water samples were submitted to the filtration process as soon as they arrived in the lab by filtration with 0.45µm glass filter to determine the content of the filtrate of heavy metal (EPA, No. 1637 and 200.12), acidified to pH < 2 with nitric acid, HNO_3cc, and stored in the refrigerator at 4^{OC} temperature until the day of analysis. Determination of this heavy metal fraction present in water samples is important because metal toxicity is related to the form of heavy metal ions in the solution. The metals studied were: Pb, Cd, Cr, Fe, Ni, Mn. Determination of the content of each metal in the water samples was accomplished by atomic abrasion technique with graphite oven, SAA / AET, using the NOVAA / AAS spectrometer.

Gas Chromatography – Flame Ionization Detector or GC-FID is a very common analytical technique that is widely used in the petrochemical, pharmaceutical and natural gas markets.

An FID typically uses a Hydrogen/Air flame into which the sample is passed to oxidise organic molecules and produces electrically charged particles (ions). The ions are collected and produce an electrical signal which is then measured. As common with other GC techniques, a carrier gas is required with low Water and Oxygen impurities since Water and Oxygen can interact with the stationary phase and cause significant problems such as high baseline noise and column blëd in the output gas chromatogram which both reduces the analyser sensitivity and decreases column lifetime. The FID is also extremely sensitive to Hydrocarbon impurities in the Hydrogen and Air supply for the flame. Hydrocarbon impurities can cause increased baseline noise and reduce the detector sensitivity.

Results and Discussions

We analise the samples and evaluate Bacteriological, Physico-Chemical, Havy Metals, Pesticides; Vajra & Graso (HEM); all three of the main wells in the Patos -Marinza area. Two drilling wells in Marinza and drilling well Qafë Stefan (Kuman). Here are the result:

a. Biological evaluation;

Nr.	Microbiological index	Drilling well Nr. 1 Marinzë	Drilling well Nr. 2 Marinzë	Drilling well “Qafa e Stefanit”, Kuman,	Standard
1	Total Coliform	**60**	**760**	**86**	0/100 ml water
2	Fecal Coliform (E. Coli)	**12**	**22**	**16**	0/100 ml water
3	Streptococcal Fecal	0	**51**	0	0/100 ml water

b. Physico-Chemical evaluation:

Nr.	Chemical Indicators	Drilling well Nr. 1 Marinzë	Drilling well Nr. 2 Marinzë	Drilling well “Qafa e Stefanit”, Kuman	Standard	Max. permissible
1	Taste and odor (dilution number)	No normal (taste and strong odor of H_2S)	No normal (taste and odor of H_2S)	normal	0	2 ballë në 12^0 C, 3 ballë në 25^0 C
2	Color and appearance(mg/l shkalla Pt/Co)	normal	normal	normal	1	20
3	pH (unit pH)	7.35	7.27	7.2	6.5-8.5	9.5
4	Electrical Conductivity (µS/cm)	500	500	1000	400	
5	Calcium (mg/l)	44.08	45.09	115.23	75	200
6	Suspended solids (mg/l)	0	0	0	Not permited	
7	Turbidity (unit FTU)	0	0	0	0.4	4
8	Total Alkalinity (mg ekv/l)	7	6.1	9.2		
9	Carbonate (mg/l)	0	0	0		
10	Bicarbonate (si HCO_3^-) (mg/l)	427	372.1	561.2	water should not be aggressive for $CaCO_3$	
11	Ammoniac (mg/l)	0.41	0.16	0.24	0	0.05
12	Nitrites (mg/l)	0	0	0.0099	0	0.05
13	Nitrate (mg/l)	0.44	0.44	6.6	25	50
14	Total Hardness (^{0}gjermane)	15.4	17.08	30.1	10-15	20
15	TDS (mg/l)				500	
16	Phosphate (mg/l)	0.6	0.72	0.86	0.4	2.5
17	Organic matter(mg/l)	1.37	1.02	1.04	1	3
18	Chlorides (mg/l)	135.4	28.3	117.01	25	200
19	Sulphates (mg/l)	15	9	110	25	250
20	Magnesium (mg/l)	40.1	46.8	60.8	20	50

c. Havy metal evaluation:

Nr.	Element	Drilling well Nr. 1 Marinzë	Drilling well Nr. 2 Marinzë	Drilling well"Qafa e Stefanit", Kuman	Standars (μg/l)	Max. permissible (μg/l)	The detection limit of the appliance
1	Leaden (Pb)	n.d.	n.d.	**8.3**	0	10	0.06 μg/l
2	Cadmium (Cd)	n.d.	n.d.	n.d.	3	5	0.006 μg/l
3	Chrome (Cr)	n.d.	n.d.	6.6	0	50	0.05 μg/l
4	Copper (Cu)	n.d.	n.d.	92	100	1000	0.04 μg/l
5	Nickel (Ni)	n.d.	n.d.	n.d.	20	50	0.2 μg/l
6	Zinc (Zn)	n.d.	n.d.	8	100	3000	0.004 μg/l
7	Mangan (Mn)	**18**	**10**	**20**	20	50	0.014 μg/l
8	Iron (Fe)	n.d.	n.d	n.d.	50	300	0.06 μg/l

d. Oil and grease evaluation (HEM)

Nr.	Oil and grease	Result (mg/l)	The detection limit of the appliance	Method of analysis
1	Drilling well Nr. 1 Marinzë	1.2	1.4 mg/l	EPA – 1664 Rev. A
2	Drilling well Nr. 2 Marinzë	0.8	1.4 mg/l	EPA – 1664 Rev. A
3	Drilling well "Qafa e Stefanit", Kuman	1.4	1.4 mg/l	EPA – 1664 Rev. A

Note: The standard presented in the tables above refer to the current Albanian drinking water standard

Note: n.d. – non deducted;

Analytical Conclusions:

Microbiological Aspects: In both water samples obtained in Drilling well no. 1 Marinzë and drilling well No. 2 Marinza, for the microbiological aspect, results as follows: both analyzed water samples result in high bacterial contamination of fecal origin with high fecal coliforms, while wells no. 2 in Marinza results in very high bacterial contamination of fecal origin with the presence of fecal coliform and Str. Fecal. Drilling well Nr. 2 results many times more polluted than well. 1. 52/100 ml water

The total coliforms in the two wells result high, in the well no. 2 many times higher than the well no. 1; 760/100 ml water towards 60/100 ml water

In the sample of water obtained at the "Qafe Stefan" drilling well, analyzed for the microbiological aspect, results as follows: The presence of bacterial contamination of fecal origin is noted with the presence of high fecal coliforms. Total coliforms are also found in high values compared to the standard.

This result show us that oil contamination is not the only contamination problem in this area, but the septic tanks and the fracturing of waste water pipe are transferd in the groundwater.

Physico-chemical aspect: Even for physico-chemical aspects, the water samples analyzed for physico-chemical indicators result as follows:

Drilling well no. 1 and Nr. 2 Marinz results organoleptically with high odor and taste H_2S, resulting in max. Acceptable.

Chloride (Cl-): Chloride is the major ion associated with Individual Septic Disposal. It is found in all natural waters with relatively small amounts. It can also be derived from human sources. Chloride can affect the food taste. However, it does not cause any health hazard. Chlorides in the drilling well n.1 result high compared to the standard, 135.4 mg/l towards 25mg/l of the standard but in the values of max. Permissible 200 mg/l. For drilling well Qafa e Stefanit too 117.01 mg/l Other indicators result in respect to the standard.

Even for the physic-chemical aspect, the analysis of the drilling well Qafa Stefan results organoleptically with the smell and taste,

Indicators such as electrical conductivity

Electrical conductivity (EC): Electrical conductivity measures the water ability to conduct an electric current. It signifies the amount of total dissolved salts and is very useful for assessing the purity of water. It is generally used to estimate the amount of total dissolved solids and minerals. It increases with the reaching of dissolved minerals. The value of "Qafë Stefan" drilling well is 1000 µS/cm, the standard is 400 µS/cm

Sulphate (SO_4^{2-}): Sulphate occurs in groundwater in the form of inorganic sulphate and dissolved gas (H_2S). It is not a harmful substance, although high values of sulphate in groundwater may have laxative consequence concentration of sulphate in the samples was 110 mg/l for drilling well Qafa Stefanit higher than standart 25 mg/l

Total strength result higher, 30.1 ^{0}german, above the max. permissible 20^0 german,

Toxicological aspect; Heavy metals:

Drilling well no. 1 and no. 2 Marinz, resulting in the presence of manganese, at well No.1 this indicator results in the max standard values for manganese 20 µg/l. For other indicators it is not found the presence of heavy metals in the water.

The "Qafe Stefan" drilling well, results in the presence of lead 8.3 µg/l and manganese 20 µg/l in water at high values above the permissible norms for lead and at the maximum acceptable limits for manganese.

The presence of Cadmium, Nickel and Iron is not ascertained, while Chromium and Zinc result in low values. Copper results readily above the norm.

Toxicological aspect: Oils & Grass (HEM):

In all analyzed samples it was found the presence of oils and greases in water. Drilling well no. 1 and no.2 are under the detection limit of appliance for drilling well Qafë Stefan the presence is higher.

Toxicological aspects: Chlororganic pesticides:
In all the water samples analyzed for pesticide indicators, indicate that their presence in the water was not found.

Toxicological aspect: Aromatic Polycyclic Hydrocarbons (PAHs); In both samples analyzed according to EPA 525 (L-L extraction) with GC/FID, no aromatic polycyclic hydrocarbons were found, but the presence of some aliphatic hydrocarbons and volatile compounds, such as benzene, was found. In the chromatogram of water samples, benzene occupies most of its surface, namely:
In the analytical chromatogram of well-drilling no. 1 Marinze - benzene is 51.28% of the total amount of aliphatic hydrocarbons and other volatile compounds, resulting during the analytical process.

In the analytical chromatogram of well-drilling no. 2 Marinze - benzene is 99.18% of the total amount of aliphatic hydrocarbons and other volatile compounds, resulting during the analytical process.

In the analytical chromatographic column of the well-drilling at Qafë Stefan, Kuman-benzene accounts for 95.85% of the total amount of aliphatic hydrocarbons and other volatile compounds, resulting during the analytical process.

We point out that the analytical technique used in GC/FID is less sensible analytical technique than GC / MS technique.

Conclusion and Recomandation

- Referring to contemporary world literature and the classification of carcinogenic substances, we emphasize that benzene is classified in the first group - A- of substances with the highest carcinogenicity.
- On the other hand, by evaluating the analytical results of the well-drilled water, for all of the indicators shown in the tables above results: Currently, well-drilling does not present hygienic safety for the safe and cleaner hygienic drinking water supply population.
- Currently, the well-drilling water analyzed does not meet the requirements of the Albanian standard for drinking water quality, currently in force, in microbiological, physico-chemical and toxicological aspects.
- For water to be used for public supply, it must mët the requirements of the Albanian standard for drinking water quality for all parameters, values of which that are above the standards.
- Under these conditions, all well-drilling can not be used for public drinking water supply, as it does not meet the standards for its quality.
- A more detailed analysis of water with a GC/MS device is recommended, which is the most sensitive analytical technique and enables quantitative analysis (in μg / l) for aliphatic

hydrocarbon and other volatile compounds, as required by standard. The GC/FID technique, for water analysis can not identify the quantitative side of these elements, but their quality side.

- We think that the well- drilling water should be monitored for a long period for the analytical parameters presented above, while the authority considers the possibility of finding alternative water resources alternatives, which provide good quality water and within Albanian standards and the Directives of EU for water.

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