

PRELIMINARY DATA REGARDING THE CONTENT OF PETROLEUM PRODUCTS IN WATER AND SOIL SAMPLES FROM SUPLACU DE BARCĂU AREA, ROMANIA

Dan COSTIN^{1*}, Carmen ROBA¹, Nicoleta BRIȘAN¹, Ovidiu TANASĂ¹

¹ Faculty of Environmental Science and Engineering, Babeș-Bolyai University,
Cluj-Napoca, Romania

* Corresponding author: dan.costin@ubbcluj.ro

ABSTRACT. The main objective of the present study was to perform a general screening study regarding the quality of surface water, underground water and soil in Suplacu de Barcău area. In some of the investigated sampling points, the concentration of the analyzed parameters reflects the impact of the anthropic activities carried out in the area. Based on petroleum hydrocarbons content, the surface waters can be classified as 1st and 2nd quality class. For some of the analyzed underground water and soil samples, the petroleum hydrocarbons content exceeded the intervention level, while the majority of the analyzed underground waters had the petroleum hydrocarbons content below the alert level.

Key words: *oilfield, in-situ combustion, petroleum hydrocarbon, water, soil*

INTRODUCTION

Rapid economic development of modern society and dramatic population growth is accompanied by a continued high demand of energy sources, especially hydrocarbons. Simultaneously, the conventional oil reserves have recorded a constant decline due to the problems in locating new oil fields. Therefore, oil industry started to focus on the remaining oil recovering in old reservoirs and the unconventional oil resources, such as heavy oil, extra heavy oil, oil sand, tar sands, oil shale and bitumen. These unconventional resources are equivalent to about 70% of all fossil fuels resources in the world.

The main characteristics of unconventional oil are: high viscosity, high density, high content of nitrogen, oxygen, sulfur and heavy metals and increased quantity of heavier oil fractions (Santos et al., 2014). In order to recover this unconventional oil, as well as to recover the remaining oil in conventional reservoir after primary operation, different enhanced oil recovery (EOR) can be applied: thermal methods, chemical methods and gas methods (Manrique et al., 2010). In the case of thermal methods, the heavy oil production is accomplished by viscosity reduction with the aid of a heat source. The local raising of the reservoir temperature is made by either injection of hot water, hot steam, or in-situ (Butler, 1991).

In the case of in-situ combustion (ISC), also known as fire-flooding, the thermal energy necessary for viscosity reduction is achieved by chemical reaction between the heavy fraction of the crude oil and injected oxygen. The compressed air at the surface is the most common way to introduce oxygen in the reservoir. In addition to oil viscosity decreasing, gas drive and thermal expansion maintain the production. The combustion front propagates through the reservoir, with the reaction components displacing vapors and liquids ahead toward production wells (Sarathi, 1999).

Haynes et al. (1979) based on the environmental assessments for EOR pilot projects implemented in USA, have revealed a number of potentially important environmental impacts on land, vegetation, surface water, groundwater and air. More specifically for ISC operation, the water quality problems could be associated with:

- formation of water-soluble, secondary chemical compounds (e.g., metals and metal oxides) in the reservoir during the high temperature combustion process;
- corrosion and erosion of well casings, particularly by hot sand, resulting in fluid leaks;
- improper disposal of low pH produced water containing small amounts of oil and residues of metallic substances from the crude oil.

The combustion of large quantities of oil during the development of ISC process potentially can release SO₂, NO_x, hydrocarbons, CO, CO₂, and other combustion products as fugitive or uncontrolled emissions (Zoveidavianpoor and Jalilavi, 2014). Subsidence can also occur as a result of the oil extraction from sandy reservoirs.

Petroleum hydrocarbons represent a common environment contaminant class, being in some cases regulated as hazardous wastes. It is a complex mixture of hundreds of compounds, ranging from light to heavy volatile hydrocarbons, with very different physico-chemical and toxicological properties. The total petroleum hydrocarbons (TPH) parameter generally includes hazardous substances from C10 to C40 (ISO, 2004).

There are a variety of spectroscopic and nonspectroscopic techniques used to analyze the presence of petroleum hydrocarbons in environmental samples. The most frequently used methods include immunoassay, general gravimetry, gas chromatography with flame ionization detection or mass spectrometry, infrared spectroscopy, Raman spectroscopy, and fluorescence spectroscopy (Okparanma and Mouazen, 2013). In the present study the presence of petroleum hydrocarbons in water and soil samples was analyzed by fluorescence spectroscopy.

STUDY AREA

Suplacu de Barcău geologic structure is situated in the northeastern part of Bihor County, at about 75 km northeast of Oradea town, under the village of the same name. Studied area, with a hilly terrain features (maximum altitude of 570 m), belongs to the north-eastern part of Pannonian Basin, bordered by Plopiș Mountains on the south, Șimleu Basin on the southeast and Barcău River (a left tributary of Crișul Repede

River) on the north and east (Fazecaş et al., 2011). Suplacu de Barcău village has an area of 2.735 ha and a population of 2.554 inhabitants.

The geology of Suplacu de Barcău area is represented by a Precambrian metamorphic basement (mica schists and gneiss) covered by Pliocene and Quaternary sedimentary deposits (Petit et al., 1990, Carcoana, 1990, Turta et al., 2007). A succession of clastic rocks characterize Pliocene deposits (Sarmatian and Pannonian age), while Quaternary formations are composed by alluvial sediments (sands and gravels).

Geological exploration made before 1960 has discovered an oil reservoir in the Pannonian formation. This sedimentary deposit formed by the moulding of the underlying metamorphic basement, represents an east-west oriented anticline upfold, the dips ranging between 4 and 8 degrees. The major Suplacu de Barcău fault has cut axially the tectonic structure, which limits the field to the south and east. The north and west borders of the field are represented by an aquifer (Petit et al., 1990, Carcoana, 1990, Turta et al., 2007, Ruiz et al., 2013).

The length of the oil bearing structure (western limb of the anticline) is approximately 15 km. Both depth and thickness of Pannonian formation increase from the east to west and the north to south. The depth is in the range of 35 m to 200 m and the net pay thickness varies between 4 m and 24 m. The reservoir rock is poorly sorted unconsolidated slightly marly sand with an average to coarse grain size (Petit et al., 1990, Carcoana, 1990, Panait-Patică et al., 2006, Ruiz et al., 2013). The total area of oilfield is 1700 ha (Panait-Patică et al., 2006).

Geological surveys have indicated the presence of asphalt-base-oil (Panait-Patică et al., 2006). Considering the features of this unconventional play (table 1), the Suplacu de Barcău structure can be classified as tar sand accumulation (Popescu and Anastasiu, 2017).

Table 1. *Main reservoir characteristics of Suplacu de Barcău structure (after Petit et al., 1990, Carcoana, 1990, Panait-Patică et al., 2006, Turta et al., 2007, Ruiz et al., 2013)*

| Parameter (measurement unit) | Values |
|------------------------------------|-----------|
| Initial reservoir pressure (bar) | 4-22 |
| Initial reservoir temperature (°C) | 18 |
| Average effective porosity (%) | 32 |
| Initial oil saturation (%) | 85 |
| Absolute permeability (mD) | 1700-2000 |
| Oil dynamic viscosity (mPa·s) | 2000 |
| Oil density (kg/m ³) | 960 |
| Connate water saturation (%) | 15 |

Carcoana (1990) have estimated the original volume of oil zone at 46.9×10^6 stock-tank m³. The oil production started in 1960, the dissolved gas expansion and pumping being the main mechanism. Based on initial oil rates of 2-5 m³/day/well, which

very rapidly decreased at 0.3-1 m³/day/well, the final oil recovery was estimated at 9% (Carcoana, 1990). In these circumstances, thermal methods were considered the only way to increase the oil recovery and production rate. These types of enhanced oil recovery (EOR) are appropriate to be applied to heavy oil reservoir with high oil viscosity such Suplacu de Barcău. In order to use the best technological and economical method, a steamdrive (SD) and in-situ combustion (ISC) field tests were conducted during 1963 to 1970. The initial pilot was an inverted 5-spot pattern of 0.5 ha located in the upper (southern) part of the structure, followed by a semi-commercial operation consisting of six adjacent patterns of 2 – 4 ha. Based on data collected during the progress of the operations, several conclusions has emerged (Panait-Patică et al., 2006, Turta et al, 2007):

- a cyclic steam stimulation (CSS) has to be used in order to prepare the production wells;
- for better results was necessary to convert the pattern exploitation to line drive exploitation (continuous combustion front);
- gradually sweeping the reservoir from the uppermost part to the lowest part of the structure was the adequate strategy for exploitation.

The ISC line drive exploitation started in 1979 moving progressively downstructure, parallel to isobaths (figure 1). The air injection well are located on the East-West line of more than 10 km, the distance between two adjacent wells within a row ranging between 50 – 10 m. Data regarding the oil wells production have been used to forecast an ultimate oil recovery of 55% and to estimate an ultimate oil recovery for the entire structure higher than 50% (Panait-Patică et al., 2006, Turta et al, 2007). By the beginning of 2010, more than 2700 wells were drilled in the field. The oil production at that time was 1200 m³/day from about 700 active wells, 80 wells were used for air injection and 20 to 24 wells per day were receiving CSS (Ruiz et al., 2013). Using monitoring data of the ISC combustion process, it can be predicted that the combustion front will cover the entire surface of the oil field in about 10 years and the commercial operation will last for more than 40 years (Turta et al., 2007).

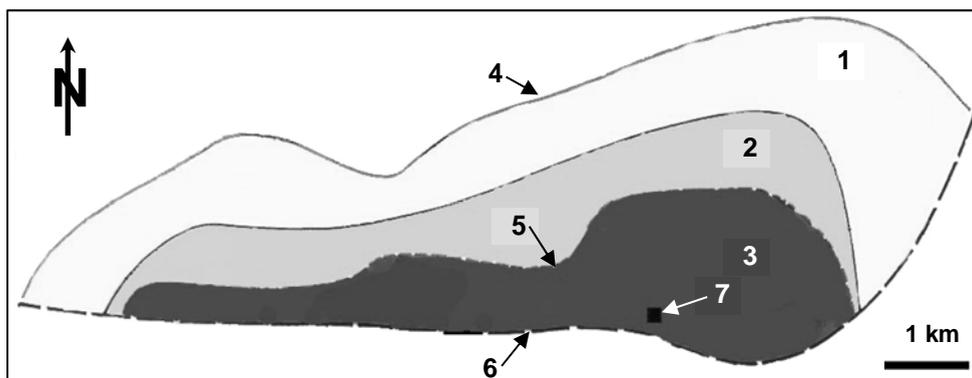


Fig. 1. Schematic map of Suplacu de Barcău ISC operation (after Păduraru and Pantazi, 2000). Legend: 1 – combustion unaffected area, 2 – combustion affected area, 3 – swept zone, 4 – water-oil contact, 5 – combustion front, 6 – Suplacu de Barcău fault, 7 – initial pilot ISC

During the exploitation process, some temperature measurements taken in the wells recorded maximum values of around 600°C. As a result of the combustion process, an increase of concentration in natural emulgators in the produced oil, such as asphaltene, resins, naphthenic acids and finely dispersed solid particles, have been observed (Turta et al., 2007). Carcoana (1990) noticed some peculiarities of the water extracted from the production wells: yellow color, decreased values of pH and salinity, increased values of sulfate and iron content. The produced gases from the same wells have 11-15% CO₂, nitrogen, traces of CO, possible unreacted O₂ and sometimes H₂S. Panait-Patică et al. (2006) presented additional data regarding the composition of produced gas: the presence of unsaturated hydrocarbon and up to 17 – 19%CO₂. Saturated and some unsaturated and aromatic hydrocarbon were found in the fluid processing.

Almost since the beginning of the application of the ISC technique, leakage to the surface of combustion gases was observed as mud and steam volcanos-like phenomenon which appeared high structurally through or between adjacent wells to air injectors. These events were still appearing even after the advancement of the combustion front down the structure. Moreover, hazardous gases were detected in the basement of some houses located above the combustion zone (Carcoana, 1990). The most likely cause of the escaping gas would be whether the very small depth of the reservoir or the improper sealing of some old production wells (Turta et al., 2007).

Despite the long history of oil production from Suplacu de Barcău structure (nearly 60 years), very few data are published about the environmental impact of exploitation operations. Pavelescu et al. (2008) analyzed ten surface soil samples for total petroleum hydrocarbons (TPH) using two analytical techniques: infrared and fluorescence spectroscopy. The aim of the study was a preliminary evaluation of soil pollution with petroleum products in order to establish the appropriate method for bioremediation. The TPH concentrations in soil samples varied between 3000 and 27000 mg/kg, high above the intervention level (2000 mg/kg) for industrial sites according to Romanian legislation (MAPPM Order no. 756/1997). Grec and Maior (2008) performed a more detailed study regarding the negative impact produced by the oil extraction on the air, soil and water quality in Suplacu de Barcău area. Soil samples were collected from 10 drillings at a depth of 0.2 m and 0.5 m and 6 groundwater samples were taken from wells used by population for drinking water. The values of TPH in soil samples ranged between 2074.10 mg/kg and 112154.90 mg/kg. The petroleum products concentrations in groundwater were very high, from 0.2 mg/L to 0.7 mg/L.

MATERIALS AND METHODS

Sampling

In order to make an up to date assessment of the petroleum products concentration in Suplacu de Barcău area, surface water, groundwater and soil samples were collected during two field campaigns carried out in 4th November 2015 and 10th May 2016. Despite the preliminary nature of this assessment, the main objective in selecting sampling sites was the best possible coverage area of the oilfield. Surface water samples were collected from 2 points: a small creek (W1) at the roadside located in the northern

part of the Suplacu de Barcău area, close to air compression station and Borumlaca Valley (W2), a left tributary of Barcău River, which is crossing the village, being the main collector of the runoff water (figure 2). Groundwater samples were taken from 11 wells used by the population as drinking water, positioned on the whole surface of the Suplacu de Barcău rural area (figure 2). The samples from W3 to W13 were collected during the first campaign, while the samples W4.1, W5.1 and W6.1 were taken in the second. The waters were sampled in polyethylene containers of 500 ml.

Soil sampling was made in multiple sites (figure 3) of the oil field trying to characterize the impact of different type of oil well: productive, decommissioned and abandoned. The land use was also various, from farmland to land areas close to the active or abandoned well pad. In the first campaign, 4 soil samples (S1, S2, S3, S5) were taken, the other 6 samples (S1.1, S2.2, S2.3, S4, S6, S6.1) being collected in the second campaign. In the case of two sites, two samples were taken at different depths: S2.2 at 10 cm and S2.3 at 30 cm, respectively S6 at 10 cm and S6.1 at 30 cm. The other samples were collected from the depth of 10 cm. A blank sample located at about 1 km to the south of Suplacu de Barcău village, in an unaffected area of oil exploitation, was taken also from the depth of 10 cm. Soil samples (500 g) were collected with a stainless hand auger, after removing the vegetation and the sand/stones from the surface (Pinedo et al., 2014). The soil samples were stored in labeled polyethylene bags.

All the samples were transported to the laboratory in cold (4°C) and dark conditions.

The water pH, redox potential (ORP), electrical conductivity (EC), total dissolved solids (TDS), and salinity were measured in situ using a portable multiparameter (WTW multi350i, Germany).

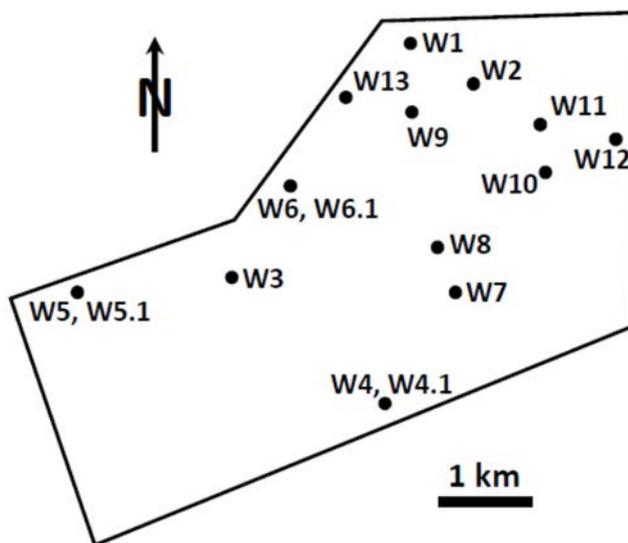


Fig. 2. Location of water samples in the Suplacu de Barcău oilfield

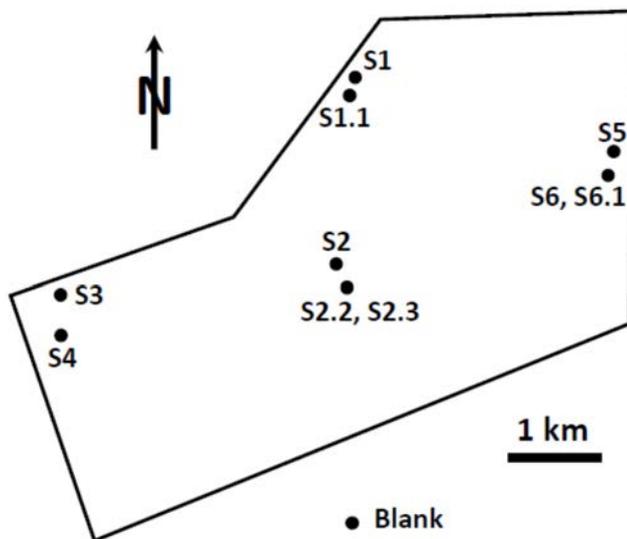


Fig. 3. Location of soil samples in the Suplacu de Barcău oilfield

Water samples processing

The water samples used for anions analysis were previously filtered through 0.20 μm pore syringe filters in order to remove the impurities.

For petroleum hydrocarbons analysis, a sample volume of 100 ml was transferred into pre cleaned glass containers, the sample was acidified to $\text{pH} < 2$, by adding HCl 37%. Then the extraction solvent (n-hexane) was added and the bottles were vigorously stirred for 5 min. The solvent was allowed to separate for 5 minutes and the bottles were allowed to depressurize. The organic suspension was collected separately and filtered through 0.20 μm pore syringe filters in order to remove the impurities (Brost et al., 2011), (www.oilinwatermonitors.com). The extraction method, known as *fastHEX* is adapted to US EPA Method 1664 (1996) used for the extraction of petroleum hydrocarbons from aqueous matrix impurities (Brost et al., 2011), (www.oilinwatermonitors.com). Hexane is an organic solvent with a density lower than water, non-fluorescent, which extract all types of crude oil with high efficiency.

Soil samples processing

The soil pH, electrical conductivity (EC) and salinity were measured in a aqueous suspension 1:5 (v:v) using a portable multiparameter (WTW multi 350i, Germany) (SR ISO 10390:1999).

For petroleum hydrocarbons analysis, the soil samples were air dried, homogenized, grounded and sieved ($< 2 \text{ mm}$). An amount of 10 g soil sample was transferred to a glass container, mixed with the extraction solvent (n-hexane), and

vigorously stirred for 5 min. The solvent was allowed to separate for 5 minutes and the bottles were allowed to depressurize. The organic suspension was collected separately and filtered through 0.20 μm pore syringe filters in order to remove the impurities (Brost et al., 2011), (www.oilinwatermonitors.com).

Ion chromatographic analysis

The analyzed anions included F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} . These parameters were analyzed by ion chromatography using an IC 1500 Dionex system (SUA).

Fluorometric analysis

The processed samples were analyzed by fluorescence spectrometry using a Turner TD-500 fluorometer, designed to analyze the content of oil, condensate gas and refined hydrocarbons in water and soil samples. The fluorometer has two analysis channels operating at different wavelengths: (1) with fluorescence excitation in the UV spectrum and (2) with fluorescence excitation in the VIS range (typically used for high concentrations, over 100 ppm and up to 10000 ppm) (Belore et al., 2009, Brost et al., 2011), (www.oilinwatermonitors.com).

Before analysis, the fluorometer was calibrated using a blank (n-hexane) and a set of standard solutions. Calibration once performed will be stored in the device memory. According to information provided by the supplier, the linear domain is between 0 and 100 ppm (www.oilinwatermonitors.com).

RESULTS AND DISCUSSION

Water samples

The analyzed water samples were generally neutral having the pH within the national limits for surface (6.5 – 8.5) and drinking water (6.5 – 9.5). Three underground samples (W3, W4, W4.1) proved to be more acidic than the national limits. Both surface and underground water had relatively low levels of electrical conductivity (624-663 $\mu\text{S}/\text{cm}$, respectively 672-1970 $\mu\text{S}/\text{cm}$). All the underground waters had the EC within national standards (2500 $\mu\text{S}/\text{cm}$) for drinking water (Law 458 from 8th July 2002) (table 2 and 3).

The F^- , Br^- and PO_4^{3-} were not detected in the analysed waters, while NO_2^- was detected only in sample W11 (0.2 mg/l), within the national limit (0.5 mg/l) for drinking water (Law 458 from 8th July 2002). Based on Cl^- , NO_3^- , and SO_4^{2-} content, the surface waters belong to 3rd quality class, exception for W1 sample which can be classified as 2nd quality class, considering the NO_3^- content (table 2).

The concentrations for petroleum hydrocarbon (PH) in surface water samples are presented in table 2. These values have been compared with acceptable limit from national legislation regarding the surface water quality (MO 1146/2002).

Based on petroleum hydrocarbons content, the surface waters can be classified as 1st quality class (SW2) and 2nd quality class (SW1).

Table 2. *The quality parameters for the analyzed surface water samples*

| | pH | ORP (mV) | EC (µS/cm) | salinity (‰) | Cl ⁻ (mg/l) | NO ₃ ⁻ (mg/l) | SO ₄ ²⁻ (mg/l) | PH (µg/l) |
|-------------------------------|---------|----------|------------|--------------|------------------------|-------------------------------------|--------------------------------------|-----------|
| W1 | 7.2 | -36.8 | 624 | 0 | 87.1 | 4.64 | 121.9 | 170 |
| W2 | 6.7 | -21.1 | 663 | 0 | 101.18 | 19.4 | 134.6 | 35 |
| 1 st quality class | 6.5-8.5 | - | - | - | 25 | 4.4 | 60 | -* |
| 2 nd quality class | | - | - | - | 50 | 13.3 | 120 | 100* |
| 3 rd quality class | | - | - | - | 250 | 24.8 | 250 | 200* |
| 4 th quality class | | - | - | - | 300 | 49.6 | 300 | 500* |
| 5 th quality class | | - | - | - | >300 | >49.6 | >300 | >500* |

* Order no. 161 / 16th February 2006 for the approval of the Normative on classification of surface water quality for establishment of water bodies ecological status; ** Order no. 1146/2002 for the approval of the Normative regarding the reference objectives for the classification of surface water quality

The underground waters have higher levels of dissolved ions (table 3), ranging between 46.1 and 348.5 mg/l for Cl⁻, between 7.6 and 156.1 mg/l for NO₃⁻ and between 81.2 and 385.3 mg/l for SO₄²⁻. Some of the analyzed samples exceeded the limits regulated by national legislation for NO₃⁻ (50 mg/l), Cl⁻ (mg/l) and SO₄²⁻ (mg/l) content in drinking water (Law no. 458 of 8 July 2002).

The PH contents of groundwater samples are displayed in table 3. Highest concentrations have been recorded for the samples taken in the central part of the oilfield (W9, W11, W12, W13). This samples are located in a narrow elongated area, oriented approximately from west to east, the samples at the western (W13) and eastern (W12) ends of the alignment, having higher concentrations than the two central samples (W9, W11).

Table 3. *The quality parameters for the analyzed groundwater water samples*

| | pH | ORP (mV) | EC (µS/cm) | salinity (‰) | Cl ⁻ (mg/l) | NO ₃ ⁻ (mg/l) | SO ₄ ²⁻ (mg/l) | PH (µg/l) |
|------|-----|----------|------------|--------------|------------------------|-------------------------------------|--------------------------------------|-----------|
| W3 | 6.4 | 2.6 | 678 | 0.1 | 89.9 | 20.9 | 140.5 | 184 |
| W4 | 5.9 | 34.2 | 720 | 0.1 | 214.3 | 76.5 | 148.1 | 15 |
| W4.1 | 6.1 | 18.5 | 1156 | 0.5 | 170.2 | 23.3 | 124.1 | 17 |
| W5 | 6.9 | -32.5 | 672 | 0.1 | 62.8 | 79.4 | 125.1 | 16 |
| W5.1 | 7.2 | -43.0 | 1005 | 0.4 | 74.4 | 58.8 | 100.7 | 17 |
| W6 | 6.6 | -6.4 | 1234 | 0.6 | 125.4 | 23.7 | 121.1 | 11 |
| W6.1 | 7.0 | -20.0 | 1452 | 0.5 | 238.7 | 20.1 | 119.8 | 33 |

| | pH | ORP (mV) | EC ($\mu\text{S/cm}$) | salinity (‰) | Cl ⁻ (mg/l) | NO ₃ ⁻ (mg/l) | SO ₄ ²⁻ (mg/l) | PH ($\mu\text{g/l}$) |
|---------------------------------------|---------|----------|-------------------------|--------------|------------------------|-------------------------------------|--------------------------------------|------------------------|
| W7 | 6.7 | -18.5 | 1178 | 0.5 | 124.5 | 49.8 | 243.5 | ND |
| W8 | 7.1 | -29.0 | 1095 | 0.5 | 46.1 | 8.1 | 87.9 | ND |
| W9 | 7.0 | -26.2 | 996 | 0.4 | 113.2 | 7.6 | 125.1 | 2399 |
| W10 | 7.1 | -28.1 | 1970 | 1.0 | 348.5 | 106.3 | 153.2 | 5 |
| W11 | 7.1 | -28.0 | 1755 | 0.9 | 101.5 | 156.1 | 385.3 | 3463 |
| W12 | 7.1 | -26.3 | 1218 | 0.6 | 122.8 | 24.8 | 115.8 | 1878 |
| W13 | 7.0 | -15.7 | 1048 | 0.5 | 144.7 | 28.3 | 81.2 | 1107 |
| underground water_alert level* | | | | | | | | 100 |
| underground water_intervention level* | | | | | | | | 600 |
| drinking water ** | 6.5-9.5 | | 2500 | | 250 | 50 | 250 | |

*Decision no. 449/2013 regarding the amendment and completion of the annex to the Government Decision no. 53/2009 approving the National Plan for the protection of groundwater against pollution and deterioration; **Law no. 458 of 8 July 2002 on the quality of drinking water

Nine of the analyzed underground water (64%), had a low level of petroleum hydrocarbons (5 – 35 $\mu\text{g/l}$), below the alert level (100 $\mu\text{g/l}$) for underground water (HG 449/2013). Considerably higher concentrations were detected in samples W9 (2399 $\mu\text{g/l}$) and W11 (3463 $\mu\text{g/l}$), where the petroleum hydrocarbons content exceeded the intervention level for underground water regulated by national legislation (600 $\mu\text{g/l}$) (HG 449/2013).

Soil samples

The analyzed soil samples proved to be neutral to slightly basic, having the pH between 7.7 and 8.0, with relatively low levels of electrical conductivity (28.8 – 163.7 $\mu\text{S/cm}$) and salinity (0‰), reflecting the low content of dissolved salts.

The values of TPH concentrations in soil are very variable due to the specific nature of sampling sites (table 4).

Table 4. The quality parameters for the analyzed soil samples

| Soil samples | | Depth (m) | pH | EC ($\mu\text{S/cm}$) | PH(mg/kg) |
|--------------|----------------------------------|-----------|-----|-------------------------|-----------|
| S1 | close to air compression station | 0.10 | 7.7 | 124.0 | 12460 |
| S1.1 | | 0.10 | 7.9 | 163.7 | 5135 |
| S2 | agricultural | 0.10 | 7.8 | 100.5 | 2460 |
| S2.2 | | 0.10 | 7.7 | 121.1 | 282 |
| S2.3 | | 0.30 | 7.6 | 114.2 | 225 |

PRELIMINARY DATA REGARDING THE CONTENT OF PETROLEUM PRODUCTS IN WATER ...

| | | | | | |
|--|---------------------------------|------|-----|-------|--------|
| S3 | vicinity of abandoned oil wells | 0.10 | 7.7 | 39.0 | 24105 |
| S4 | | 0.10 | 7.9 | 77.4 | 610801 |
| S5 | vicinity of active oil wells | 0.10 | 7.8 | 107.0 | 5092 |
| S6 | | 0.10 | 8.0 | 83.6 | 347 |
| S6.1 | | 0.30 | 8.0 | 80.6 | 277 |
| Blank | background | 0.10 | 7.6 | 28.8 | ND* |
| Normal concentration (mg/kg)** | | | | | 100 |
| Alert level - soil for sensitive use (mg/kg)** | | | | | 200 |
| Alert level - soil for less sensitive use (mg/kg)** | | | | | 1000 |
| Intervention level - soil for sensitive use (mg/kg)** | | | | | 500 |
| Intervention level - soil for less sensitive use (mg/kg)** | | | | | 2000 |

*ND-Not Detected; **Order no. 756 of 3 November 1997 for the approval of the regulation on environmental pollution assessment

The highest values of petroleum hydrocarbons are recorded for the samples taken close to the abandoned wells (S3, S4) from the western part of the oilfield. Technical accidents or uncontrolled extraction operation on the well pad can be the cause of oil spilling affecting surrounding area. No rehabilitation actions have been noticed in this area. High values of PH in uncultivated soil samples (S1, S1.1) have been found in the northern part of the oilfield, close to the air compressed station and other industrial facilities. Soil samples (S5, S6, S6.1) taken from the eastern zone of active oil wells are showing high to moderate values, caused by the extraction operations. On vertical profile, a slight decreasing trend has been noticed comparing the concentration of S6 and S6.1 samples. Moderate and high PH concentrations have been identified on soil samples (S2, S2.2, S2.3) collected from the people farmland located on the west-central part of the village. On this site, the downward decreasing trend of recorded values on surface versus deep sample (S2.2 vs. S2.3) has been also observed. This contamination probably is due to the adjacent location of some oil wells to tested farmland. The blank sample contains virtually no petroleum products.

Two PH values recorded for farmland samples (S2.2, S2.3) are above alert level, and one value (S2) is exceeding by more than four times the intervention level, indicating a seriously contaminated soil. Two samples (S6, S6.1) collected from an area close to a new active well are below alert level for industrial areas, indicating a good management of oil extraction. The other soil samples have PH concentrations high above intervention level for industrial sites, the contamination source being either the uncontrolled historic production activities specific to the abandoned wells (S3, S4), either the poor management of active wells (S5) or other industrial facilities (S1, S1.1).

CONCLUSIONS

For some of the investigated sampling points, the obtained results reflect the impact of the anthropic activities carried out in Suplacu de Barcău area. Based on petroleum hydrocarbons content, the surface waters can be classified as 1st and 2nd quality class. The content of petroleum hydrocarbons for some of the analyzed groundwater's was higher than the intervention level, regulated by national legislation. High levels of petroleum hydrocarbons were detected in some soil samples, especially for those taken close to the abandoned wells, which could be correlated with possible oil spilling caused by technical accidents or uncontrolled extraction operation on the well pad.

For some ground waters, the level of NO_3^- , Cl^- and SO_4^{2-} exceeded the limits mentioned by national legislation.

In some of the analyzed soil samples, collected from an area close to a new active well, the petroleum hydrocarbons content was below the alert level for industrial areas, indicating a good management of oil extraction.

Acknowledgments

This work was supported by the PN II – Parteneriate grant (PCCA-2013) „Innovative technology for ex-situ bioremediation of soils polluted with hydrocarbons (BIORESOL)”, contract no. 91/2014.

REFERENCES

- Belore R.C., Trudel K., Mullin J.V., Guarino A., 2009, Large-scale cold water dispersant effectiveness experiments with Alaskan crude oils and Corexit 9500 and 9527 dispersants, *Marine Pollution Bulletin*, **58**, pp. 118–128.
- Brost D.F., Foster E., Holmes M, 2011, No-Solvent Oil-in-Water Analysis – A Robust Alternative to Conventional Solvent Extraction Methods, Turner Designs Hydrocarbon Instruments, Inc. <https://www.researchgate.net/publication/254520556>
- Butler R.M., 1991, *Thermal recovery of oil and bitumen*, Prentice Hall, Englewood Cliffs, New Jersey, 551 p.
- Carcoana A., 1990, Results and difficulties of the world's largest in-situ Combustion process: Suplacu de Barcau field, Romania. *SPE/DOE Seventh Symposium on Enhanced Oil Recovery*, **SPE/DOE 20248**, Tulsa, Oklahoma, USA, April 22-25, pp. 729-736.
- Decision no. 449/2013 regarding the amendment and completion of the annex to the Government Decision no. 53/2009 approving the National Plan for the protection of groundwater against pollution and deterioration.
- Fazecaș G., Moisa G., Marta D., Tivadar N., 2011, *Istoria comunei Suplacu de Barcău*, Editura Universității din Oradea, 216 p.

- Grec A. and Maior C., 2008, Earth oil extraction – major environmental pollution source. *Environmental Engineering and Management Journal*, **7** (6), pp. 763-768.
- Haynes R.J., Boggs T.A., Millemann R.A., Floran R.J., Hildebrand S.G., 1979, *Enhanced oil recovery: environmental issues and state regulatory programs*, ORNL/TM-6943, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA. 54 p.
- ISO 16703, 2004, *International standard: Soil quality – Determination of content of hydrocarbon in the range C10 to C40 by gas chromatography*.
- Law no. 458 of 8 July 2002 on the quality of drinking water.
- Manrique E., Thomas C., Ravikiran R., Izadi M., Lantz M., Romero J., Alvarado V., 2010, *EOR: current status and opportunities. SPE Improved Oil Recovery Symposium, SPE 130113*, Tulsa, Oklahoma, USA, April 24-28, pp. 1-21.
- Ministerial Order **756/1997**, for approval of *Regulations regarding environmental pollution assessment*.
- Ministerial Order **161/2006** for the approval of the *Normative on classification of surface water quality for establishment of water bodies ecological status*.
- Ministerial Order **1146/2002** for the approval of the *Normative regarding the reference objectives for the classification of surface water quality*.
- Okparanma R.N., Mouazen A.M., 2013, Determination of Total Petroleum Hydrocarbon (TPH) and Polycyclic Aromatic Hydrocarbon (PAH) in soils: A Review of Spectroscopic and Nonspectroscopic Techniques. *Applied Spectroscopy Reviews*, **48**, pp. 458–486.
- Panait-Patică A., Șerban D., Ilie N., 2006, Suplacu de Barcău field – a case history of a successful in-situ combustion exploitation. *SPE Europec/EAGE Annual Conference and Exhibition, SPE 100346*, Viena, Austria, June 12-15, pp. 1-10.
- Pavelescu G., Roman C., Pfeiffer E., Levei E.A., Miclean M., Savastru D., Cordos E., 2008, Evaluation of petroleum contaminants in soils in Suplacu de Barcau Area, Romania. *Proc. 4th European Bioremediation Conference, ID 084*, Crete, Greece, September 3-6, pp. 1-4.
- Păduraru R. and Pantazi I., 2000, IOR/EOR – Over six decades of Romanian experience. *SPE European Petroleum Conference, SPE 65169*, Paris, France, October 24-25, pp. 1-9.
- Petit H. J-M., Le Thiez P., Lemonnier P., 1990, History matching of a heavy-oil combustion pilot in Romania. *SPE/DOE Seventh Symposium on Enhanced Oil Recovery, SPE/DOE 20249*, Tulsa, Oklahoma, USA, April 22-25, pp. 737-749.
- Pinedo J., Ibanez R., Irabien A., 2014, A comparison of models for assessing human risks of petroleum hydrocarbons in polluted soils. *Environmental Modelling & Software*, **55**, pp. 61-69.
- Popescu B.M. and Anastasiu N., 2017, An overview of unconventional resources of Romania. Pending challenges. *The Handbook of Environmental Chemistry* (S.S. Zhitsov (ed.), *Shale Gas: Ecology, Politics, Economy*), **52**, pp. 97-139.
- Ruiz J., Naccache P., Priestley A., Glatz G., Crecana V., 2013, Modeling in-situ combustion in a heavy oil field in Romania. *SPE Heavy Oil Conference, SPE 165490*, Calgary, Alberta, Canada, June 11-13, pp. 1-9.
- Santos R.G., Loh W., Bannwart A.C., Trevisan O.V., 2014, An overview of heavy oil properties and its recovery and transportation methods. *Brazilian Journal of Chemical Engineering*, **31** (03), pp. 571-590.
- Sarathi P., 1999, *In-Situ Combustion Handbook – Principles and Practices*, National Petroleum Technology Office, U. S. Department of Energy, Tulsa, Oklahoma, Report DOE/PC/91008-0374, OSTI ID 3174, 423 p.

SR ISO 10390:1999 Soil quality. Determination of pH.

Turta A.T., Chattopadhyay S.K., Bhattacharya R.N., Condrachi A., Hanson W., 2007, Current status of commercial in situ combustion projects worldwide. *Journal of Canadian Petroleum Technology*, **46** (11), pp. 8-14.

Zoveidavianpoor M. and Jalilavi M., 2014, Qualitative analysis of enhanced oil recovery: impacts on air, surface water and groundwater. *International Conference on Chemical, Environment & Biological Sciences (CEBS-2014)* Sept. 17-18, 2014 Kuala Lumpur, Malaysia, pp. 11-15.

*** www.oilinwatermonitors.com, Accessed on 1st November 2016.