Historical and geochemical outlines of the oil-gas seepage near Turzovka town; Flysch belt, NW Slovakia

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Abstract: Small oil deposits located in Korňa near the town of Turzovka in north-western Slovakia and other small deposits located in the Miková region of northern-eastern Slovakia were the first oil deposits discovered and exploited in these parts of the Western Carpathians. Small volumes of oil, natural gas and water rises to the surface on a northern slope in Korňa and several tenths of metres further on these descends into the soil cover and entered the local Kornianka creek. Korňa and its broader surrounds are geologically part of the Magura Nappe of the Carpathian Flysch Belt. The preliminary gas chromatography results indicate weakly biodegraded mature oil with a prevailing aliphatic hydrocarbon fraction. Weak biodegradation and continuous outflow over 100 years following its discovery in 1901 indicate its connection with a deeper oil reservoir. Although methane is the dominant component of this natural gas, the presence of higher gaseous hydrocarbons with the methane carbon isotopic composition indicates a methane gas associated with the main stage of oil generation.

Key words: Western oil/gas seepage, geochemical features, Flysch Belt, NW Slovakia

1.INTRODUCTION

Oil-gas seepage in Korňa village occurs in the protected natural area of Kysuce in the Turzovka town cadastre, about 20 km from the town of Čadca. Geologically, this is located in the broader area of Turzovka, composed of Flysch sequences of the Magura Nappe; to a lesser extent also the Silesian Nappe reaches into this broader area.

Discoveries of oil and gas seepages in this area, and also in Papradno, Čadca, and Svrčinovec, date to the end of 19^{th} century. The systematic oil prospecting based on surface hydrocarbon shows was undertaken here until 1932, and Korňa oil was produced until 1910. Oil-gas seepage and the potential hydrocarbon source-rocks were evaluated using the routine organic geochemical methods and gas chromatography. Seepage oil represents thermally mature light oil, which originated during the main phase of oil generation, accompanied by natural gas with a prevalence of methane.

Since 1973, this oil seepage has become a protected natural heritage in Slovakia, known as the "Korňa Oil Spring Natural Monument". Available written data concerning the historical well distribution sketch-maps, and the relationships of natural gas to oil depth and chemical composition, shows that this water-oil-gas outflow is most likely not of natural origin, but flows out from one of the original prospecting wells.

2.BRIEF HISTORICAL OVERVIEW OF EXPLORATION AND PRODUCTION

Exploratory activities in the Turzovka town vicinity began following oil seepage discovery in 1898, near the "Živčákovci" farmhouse southwest of Nižná Korňa, 4 km northwest of Turzovka (Fig. 1). In 1899, a local freeholder named L. Holczman dug pits to a depth of 5.8 and 10 m, each of which contained small amounts of oil. In the same year, he rented the "Gabi", "Hugo" and "Lipolt" state mine fields.

The "Ungarische Naphtaerzeugung Montangesellschaft" was founded at the start of the 1900's, and this company initiated the first deep borehole, T–I that reached a depth of 702.6 m. This penetrated an oil-bearing horizon at 98 to 100 m, and the whole drilling was accompanied by numerous oil appearances. The following T–II borehole in 1902 was about 57 meters southeast from the T–I borehole, and this reached a depth of 310 m and produced approximately 25 metric tons (t in further text) of oil. The final T–III borehole was made to a depth of 214.7 m by the "Holczman-Bondy" company in 1920, and this was located approximately 302 m east of the T–II boreholes. This produced about 505 t of oil before the drill site was burnt due to carelessness in May 1921. L. Holczman sold his mining holdings to the State after this incident, and the Czechoslovak State Mine company renewed exploration activities in 1926. A new Turzovka–1 borehole was drilled in 1927–1928 to a depth of 452.65 m in the vicinity of Predmier village, and this produced approximately 86 t of crude oil. The following Turzovka–2 borehole at a depth of 452.65 m was 100 m south of this and it produced about 65 t of crude oil. In the following years, the Czechoslovakian State

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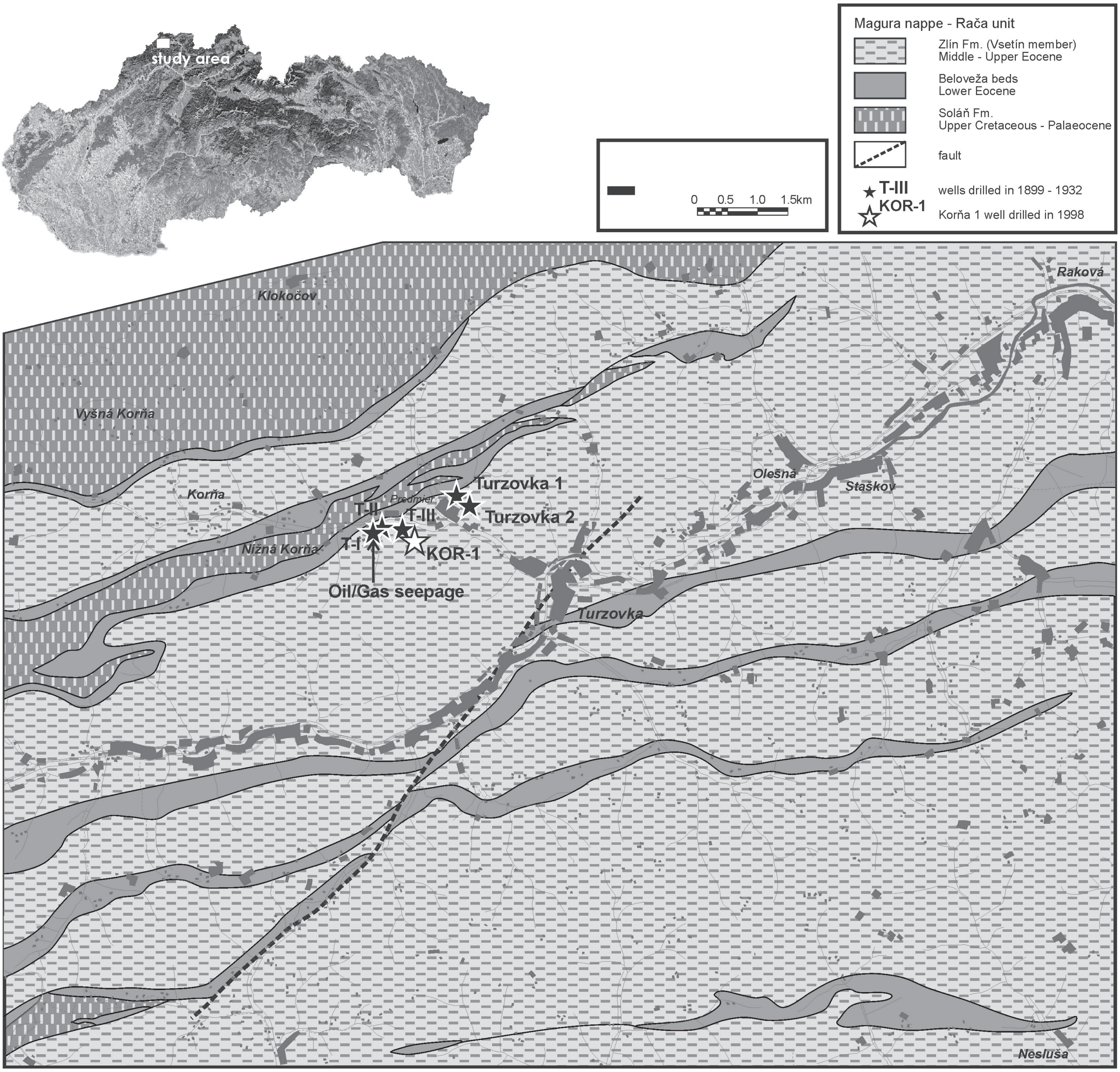

Fig. 1. **Simplified geological map of Turzovka surroundings with historical and new exploration objects and the position of the oil/gas seepage (modified after Pereszlényi et al., 1999).**

Mining company drilled only two unsuccessful boreholes at the nearby village of Staškov, and therefore drilling activities ceased in this region. The latest references to insignificant productions were noted in the World War II period. According to various sources, a total of 200 t of crude oil was produced in this region. The structure of the oil-geological relationships in the Turzovka region were mainly described by Zuber (1899), Posewitz (1907), Böck (1909), Jahn (1917, 1919), Kettner (1921), Kodym (1922), Jahn & Schnabel (1922), Kodym & Hynie (1926), Kodym et al. (1930), Sommermaier (1939), Matějka (1953), and Plička & Liškutinová (1958), plus many other authors. Based on the information of these authors also the historical aspects of oil production in Turzovka vicinity is compiled. The most recent Korna–1 well was drilled by SPP š.p. Branch VVNP Oil Co. Bratislava in 1998 about 500 m east of the above described oil seepage. More details were published by Vitáloš (2004). These historical and most recent boreholes are shown in a section of the geological map of the Turzovka village surrounds in Fig. 1.

3. OIL-GAS SEEPAGE DESCRIPTION

The seepage-site is located between Predmier and Nižná Korňa villages in a grassy field slope above the state road, approximately 65 m from the nearest farmhouse (Fig. 1). A small terrain depression about 1.5 meters in diameter occurs here, as shown in the photography (Fig. 2). Water flows from this depression at approximately 0.1–0.2 $l \cdot s^{-1}$, and an oil film of rusty-red to dark

Fig. 2. General view to the oil/gas seepage and its drainage trench (photo: first author, July 2010).

brown colour is visible on the water surface. Bubbles of natural gas rise to this water surface in irregular intervals, and the water and oil drain to a narrow trench slope before disappearing underground approximately 50–60 metres further along. The soil in the seepage surrounds, and also along the drainage trench, is strong infiltrated by crude oil, and local residents report that this water-oil outflow occasionally reached the nearby Kornianka creek, which flows about 110 meters below and parallel to the state road.

According to the study of ancient maps published by several authors, referred to in the previous paragraph and to the natural gas presence and its chemical composition, the seepage location most likely corresponds to the drilling point of the historical T–1 well, as indicated also in Fig. 1. The T–1 well penetrated the Zlín Formation, Beloveža Beds, and the Soláň Formation.

4. PETROLEUM-GEOLOGICAL OUTLINE OF THE TURZOVKA SURROUNDS

The Western Carpathian portion of the Flysh Belt is at the junction of the Western European Platform of the Bohemian Massif slopes and the Western Carpathians. This position results in a complicated geological structure with a large accumulation of Flysh sediments. The Flysh units are mostly composed of Cretaceous to Oligocene pelitic formations with sandy deposits, and the Flysh as a whole, is thrusted over the crystalline basement of the Bohemian Massif platform and its Palaezoic to Mesozoic-Cenozoic sedimentary cover. The western fronts of these Flysch nappes are situated in the Czech Republic, and they are thrusted through the Neogene sediments of the Carpathian foredeep.

Pelitic Flysh formations generally contain a fair amount of organic matter which occurs in various thermal maturity stages depending on their geological history, and also on their actual position. Active generating source rocks can occur to a depth of 8 km, and the organic matter in the sediments of this platform on Slovak territory is prevailingly in the passive or relict generation stage. Although Palaeozoic and Mesozoic-Cenozoic source rocks in the active generation stage are recognized only in Czech territory, active generating source rocks may also occur in the broader area of Turzovka. While this area comprises Flysh sequences of the Magura Nappe and the Rača Unit, as depicted in Fig. 1; to a lesser extent the Godula sequence of the Silezian Nappe also extends into this area.

With regard to further oil-geological research, three potential prospective depth zones can be distinguished in the western part of the Slovak Flysch Belt (Pereszlényi et al., 1997).

The first etage is represented by platform sediments deeply buried beneath the Flysch nappes. In the Klokočov surrounding area, these sediments can be expected at an approximate depth of 2500–3500 m. From economical and oil-geological points of view, this is almost the only place in Slovakia where the platform can be reached by boreholes at an acceptable depth.

The second etage contains the lower part of Flysh sequences characterized by less complicated geological structure, and by the presence of reservoir rocks. This is the Obidowa-Slopnice Unit, which was penetrated by the Oravská Polhora–1 borehole to a depth of 2200 meters in the western part of the Flysch Belt. Oil brines were obtained from this regionally extended unit.

Finally, the third etage is composed of shallow Flysh sequences close to the front of the Magura thrust which were strongly tectonically disturbed. Since oil generating source rocks occur at a relatively shallow depth, this has resulted in numerous surface oil appearances. Consequently, oil deposits were discovered at depths of 100 to 500 m at the beginning of the 20th century, due to the oil traces apparent on the surface.

Comprehensive geological information concerning the broad area of this described seepage was recently published by Potfaj et al. (2003).

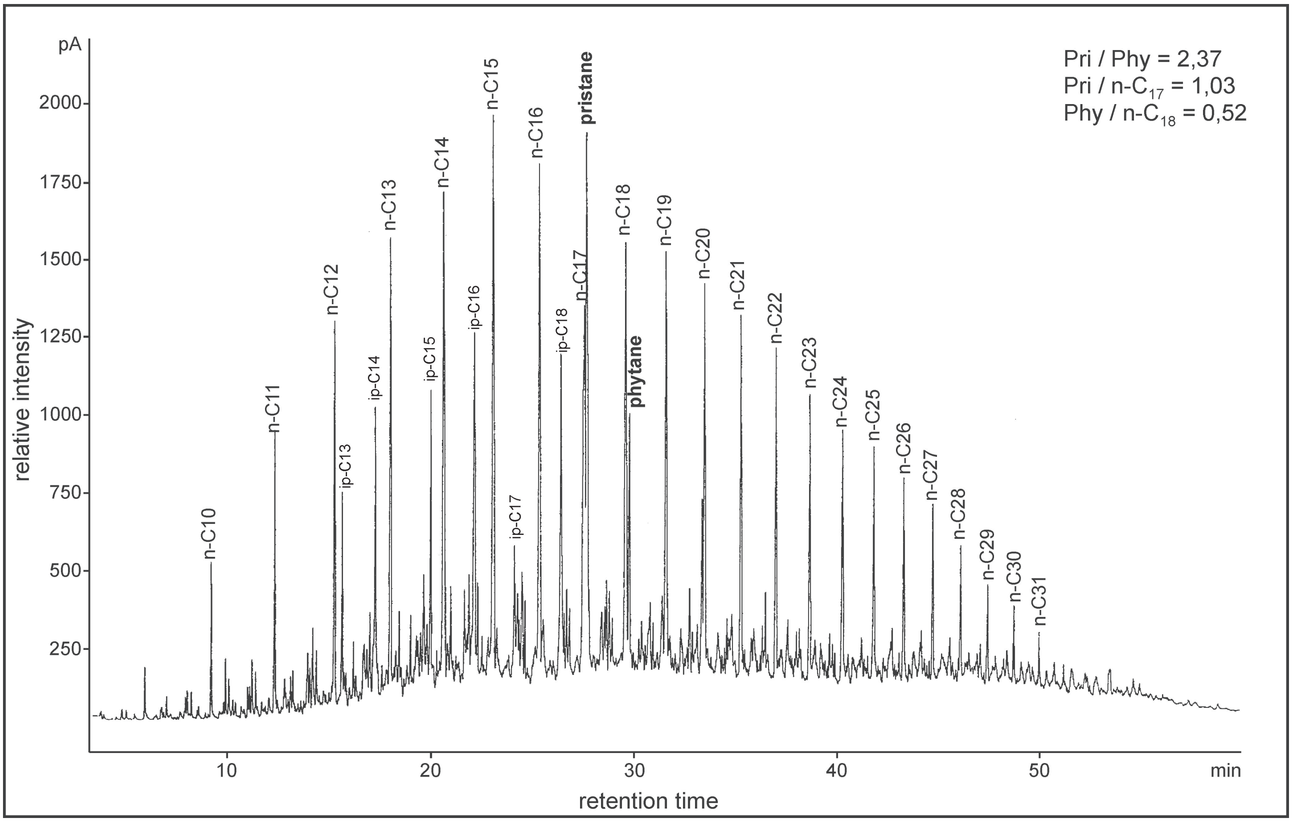

Fig. 3. Aliphatic fraction of crude oil isolated from water (Korňa oil seepage).

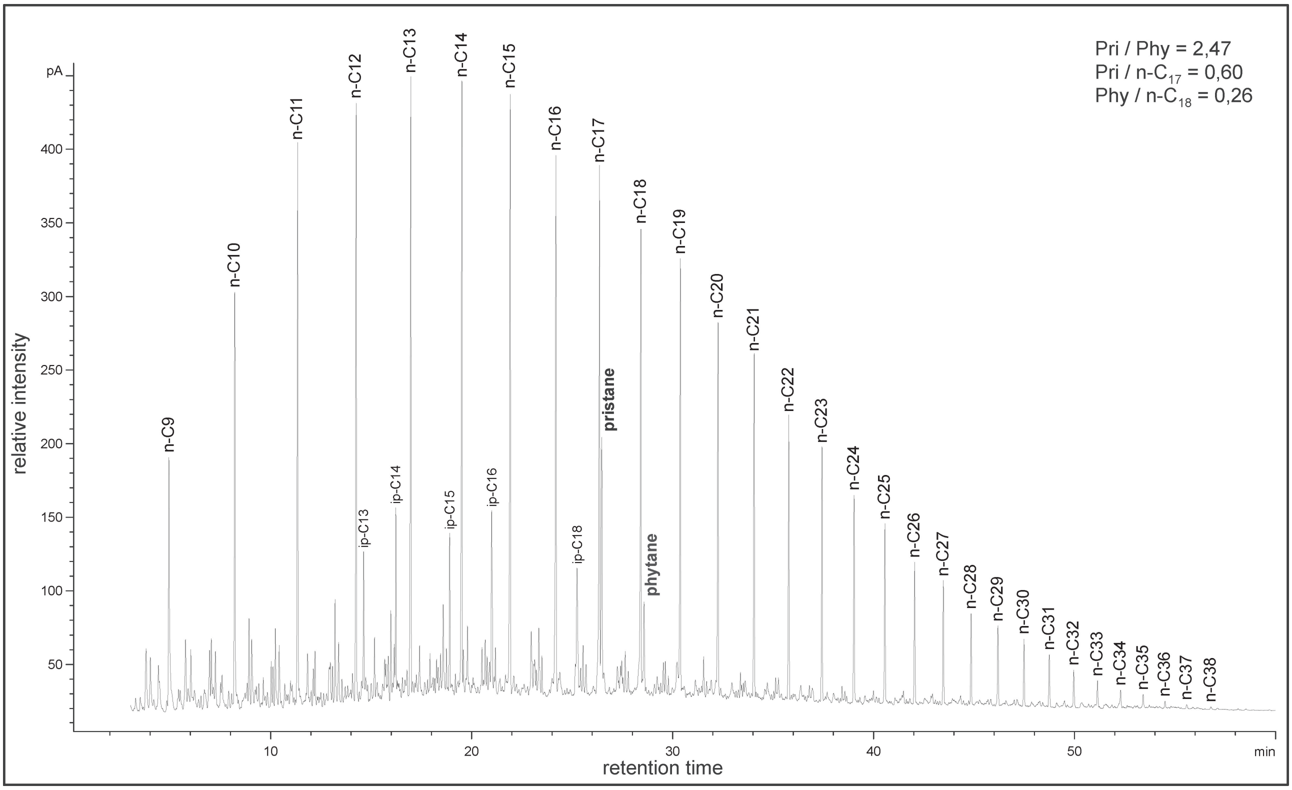

Fig. 4. Aliphatic fraction of crude oil Korňa-1/190 m borehole.

5. METHODS AND RESULTS

Oil samples were taken from the previously described oil-gas seepage at the water surface level, and additional oil samples were taken directly from the Korňa–1 borehole at a depth of 190 m. The crude oil, plus the seepage oil separated from water in the laboratory, were fractionated to aliphatic and aromatic fractions and to NSO compounds. The aliphatic fraction was analyzed at the Czech Geological Survey (CGS) Prague Brno branch, using Varian 3500 Gas Chromatography with the following equipment: capillary column of 30 m coated by 0.1 mm thick DB–1 fill with an inner diameter of 0.32 mm, with helium carrier gas and a FID detector. The temperature regime used was heating from 50 to 100°C by 10°C·min^{-1}, and then to 300°C by 3°C·min^{-1}. The resultant gas chromatograms are presented in Figs. 3 and 4.

Natural gas from 190 m and 560 m in the Korňa–1 well was transferred from drill-tubing into a vacuum sample-tube, while the natural gas from oil-gas seepage by underwater gas bubbles transfering into a sample tube previously washed in the original seepage medium. Because the natural gas was removed from water by carbon dioxide, this component (CO_2) was not considered in interpretation of the results. While helium, argon, oxygen, nitrogen, carbon dioxide, and the hydrocarbon gases methane to pentane (C_1 to C_5) were analyzed using GC-TCD, FID gas chromatography, the individual hydrocarbons in the propane to heptane groups (C_1 to C_7) were analyzed using capillary gas chromatography. Chemical composition of the natural gas was analyzed in the CGS Prague, Brno branch, and the isotopic composition was analyzed in CGS Prague laboratories by the method of Buzek & Michalíček (1989). These analytical results of both chemical and isotopic composition are presented in Tab. 1.

6. OIL GEOCHEMISTRY

The distribution of n-alkanes in the aliphatic fraction of Korňa seepage oil shown in Fig. 3 indicates light oil (condensate) affected by weak biodegradation. Partial biodegradation is also evident from the predominance of pristane over n-C_{17} alkane, where pristane/n-C_{17} = 1.03 and phytane/n-C_{18} = 0.52. Because this oil and water mixture seeped onto the surface, it is difficult to assess whether biodegradation affected only the surface oil or also the deeper oil accumulation.

The n-alkane distribution of the aliphatic fraction (Fig. 4) of the Korňa–1 borehole taken with a bottom-hole sampler at the depth of 190 m indicates a non-biodegraded (pristane/n-C_{17} = 0.60; phytane/n-C_{18} = 0.26) mature light oil with density of 0,822 g.cm^{-3}. The clear predominance of pristane over phytane (Pri/Phy = 2.37 and 2.47 respectively), and the unimodal distribution with maximum n-alkanes in the C10-11 to C19-21 range in both oils indicate a terrestrial origin of organic matter deposited in rather oxidizing conditions.

7. GAS GEOCHEMISTRY

Natural seepage gas is due to sampling technology lightly "polluted" by atmospheric air as indicated by increased values of the atmospheric gases – oxygen, argon and nitrogen in Tab. 1. This gas exhibits an interesting hydrocarbon gas composition of methane (CH_4 = 63.8 vol. %; Tab. 1) together with a relatively high amount of higher gaseous hydrocarbons. The clear predominance of propane at 1.69 vol. % over ethane with 0.53 vol. % (Tab. 1) is not typical in natural conditions. Kofanov (1959) published a geochemical classification for natural gases and for gases associated with oil generation. He suggested some regularity in ethane-propane content and he allocated the hydrocarbon gases to three groups according to their affiliation with gas-condensate, pure gas, and gas-oil deposit types, as follows:

- the ethane-propane group (where ethane prevails over propane);
- the propane-ethane group (where propane prevails over ethane);
- the mixed group (where the ethane and propane contents are comparable).

This classification was considered for gas deposits in the Krasnodar area of Russia. When this was compared with other gas deposits in the former Soviet Union, it was clear that the ethane-propane group is the most frequent in natural conditions, and it occurs in all above mentioned types of gas deposit. The propane-ethane group is bound only to gas-oil deposits. The reason for this distribution is most likely due to the different solubility of hydrocarbon (HC) gases in water and in oil. Ethane is more soluble in water than the other HC gases, including methane. The solubility of hydrocarbons in oil increases with increasing molecular mass, and the gases associated with oil deposits belong to the ethane-propane group. Kofanov, (1959), proved in laboratory experiments that it is possible to obtain propane-ethane group gases with prevailing propane by repeatedly washing a mixture of ethane-propane gases, which are prevailingly ethane. The quantitative predominance of propane over ethane depends directly on intensity and time of the water-gas contact, and since the Korňa seepage represents a mixture of water, oil, and gas, it offers convenient conditions for such distribution of HC gases.

Natural gas from Korňa–1 borehole was taken from depths of 190 m and 560 m in 2001 and 2002 (Tab. 1). The isotopic composition of methane carbon ($\delta^{13}C$ = -35,9 ‰ to -37,0 ‰ PDB) provides evidence of thermogenic methane, and presence of higher hydrocarbon gases shows methane associated with oil generation at both depths. Small amounts of atmospheric gases, which were clearly smaller for seepage gas, indicate weak air pollution. Part of the oxygen was most likely used in organic compound formation and iron oxidation.

The most evident difference between the seepage- and borehole gases is mainly in the volumes of methane and higher hydrocarbons. As discussed above, the surface seepage gas represents an open system where the chemical composition is influenced by atmospheric air pollution and by increased bacterial activity. Furthermore, the presence of natural gas in the

Tab. 1. **Chemical and isotopic composition of natural gas from Korňa oil-gas seepage and Korňa-1 borehole. Explanations: d.l. = detection limit; n.a. = non analyzed; PDB = Pee Dee Belemnite; C_1 = methane; C_{2+} = higher hydrocarbon gaseous homologues.**

gas component	d.l.	Seepage surface (1994)	Korňa-1 borehole 190 m (2001)	Korňa-1 borehole 560 m (2001)	Korňa-1 borehole 190 m (2002)	Korňa-1 borehole 560 m (2002)
		% V/V	% V/V	% V/V	% V/V	% V/V
hydrogen	0.002	<0.05	0.040	0.00	0.010	0.078
helium	0.002	<0.001	0.011	0.01	0.016	0.009
argon	0.005	0.457	0.380	0.015	0.029	0.000
oxygen	0.002	0.000	0.151	0.216	0.391	0.332
nitrogen	0.002	12.000	2.250	1.130	1.620	1.745
carbon dioxide	0.005	n.a.	0.020	<0.004	0.009	0.240
methane	0.002	63.800	92.700	96.278	93.800	94.700
ethane	0.002	0.533	2.760	1.740	2.820	2.160
propane	0.002	1.690	1.090	0.226	0.815	0.427
2-methylpropane	0.002	1.870	0.372	0.059	0.219	0.112
n-butane	0.002	2.810	0.313	0.072	0.161	0.083
2.2-dimetylpro-pane	0.002	0.151	0.009	0.002	0.005	0.003
cyklopentane	0.002	0.302	0.004	0.001	0.001	0.001
2-methylbutane	0.002	5.370	0.137	0.040	0.056	0.041
n-pentane	0.002	3.230	0.071	0.211	0.026	0.023
hexanes	0.002	7.840	0.075	0.024	0.022	0.034
heptanes	0.002	23.80	0.021	0.01	0.003	0.013
Total	-	100	100	100	100	100
		C1/C2+ = 2.68	**C1/C2+ = 19.10**	**C1/C2+ = 22.73**	**C1/C2+ = 43.98**	**C1/C2+ = 32.7**
		C2+ = 23.79	**C2+ = 4.85**	**C2+ = 4.13**	**C2+ = 2.19**	**C2+ = 2.89**
Izotopic analysis		**$\delta^{13}C$**		**$\delta^{13}C$**		**$\delta^{13}C$**
		‰ PDB		**‰ PDB**		**‰ PDB**
methane		-35.40		-35.98		-37.0
ethane		-26.13		-25.56		-27.8

seepage indicates that the shallow oil accumulation and deeper gas sources represents an man-made penetration, i.e. the former historical T–1 borehole. Evidence for this is contained in the last paragraph of "Petroleum-geological outline" above, and also in historical production data results. Natural gas deposits most likely represent the main migration agent of this seepage over the last hundred years.

The second less pronounced difference is the higher C2+ hydrocarbons volumes at the 190 m depth compared to 560 m depth in the Korňa–1 well. This is also expressed by the relationship of methane to higher hydrocarbons (C1/C2+ in Tab. 1). Possible contact between natural gas and crude oil at the 190 m depth most likely explains the increased C2+ values.

8. CONCLUSIONS

The natural gases and crude oils from open seepage and closed borehole systems, in one of the earliest oil production regions in European history, were evaluated using organic-geochemical methods.

The seepage oil is a light condensate type affected by weak biodegradation. A small amount of this oil plus water seeped to the surface, carried by a natural gas lift. This occurred over a hundred years at the location of a former historical borehole. The oil from the shallow 190 m depth in this Korňa–1 borehole is mature, light, non biodegraded oil.

Due to its permanent contact with water, the hydrocarbon gas composition of the seepage natural gas was most likely modified to a hydrocarbon gas mixture with propane prevailing over ethane. The original "drier" gas composition is enriched with higher C2+ hydrocarbons due to the contact with this oil accumulation. The natural gas from both depths in the Korňa–1 well is a thermogenic gas associated with oil generation; the higher 190 m position is slightly enriched in higher hydrocarbons compared to the deeper 560 m position, probably due to the contact with oil.

The higher hydrocarbon amount in the seepage (C2+ = 23,79 vol. %) is much more pronounced if compared with the increased value in Korňa–1 well (C2+ = 4,85 and 4,13 vol. %).

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