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SURFACE GEOCHEMICAL ANOMALIES IN THE VICINITY OF THE WAŃKOWA OIL FIELD (SE POLISH CARPATHIANS)

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Abstract: The oil accumulations discovered in the Skole Synclinorium (eastern part of Polish Outer Carpathians) are located in zones of pinch-out of the Kliva Sandstone. An example is the Wańkowa Oil Field, which contains the largest oil reserves in the region. As the seismic identification of this type of hydrocarbon trap is ambiguous, a surface geochemical survey was carried out in the vicinity of the Wańkowa Oil Field along an experimental line perpendicular to the fold axes. A traverse across the zones with anomalous seismic records indicated the presence of undiscovered lithological traps. During the surface geochemical survey, 94 samples of soil gas were collected from a depth of 1.2 m and then investigated chromatographically. The spacing of sampling sites was 100 m, which was reduced to 50 m in the Wańkowa Oil Field area. The maximum concentrations of CH_4 and total alkanes C_2-C_5 detected in samples were: 4250.0 ppm (0.425 vol. %) and 0.43 ppm, respectively. The first of these was detected at measurement point no. 86, located over the Wańkowa Field and the second at point no. 59, about 1,300 m south of the Wańkowa Field. The chemical analyses also detected maximum values of total alkenes C_2-C_4, H_2 and CO_2: 0.147 ppm, 0.042 vol. % and 4.4 vol. %, respectively. The results of the surface geochemical survey were integrated with observations on subsurface geological structures, which were interpreted on the basis of seismic data. This procedure permitted the documentation of anomalous concentrations of alkanes in the near-surface zone and contributed to an understanding of the tectonics of the hydrocarbon reservoirs in depth. The pattern of geochemical anomalies here is controlled by anticlines made up of Early Oligocene–Paleocene sediments and by overthrusts that displace these structures. The hydrocarbons migrated from condensate and/or oil accumulations located at various depths. The character of the anomalous zone discovered over the Wańkowa Oil Field is related to the effective sealing of hydrocarbon traps and/or the relatively low pressure caused by the production of oil for 130 years. However, this anomaly also may be the result of hydrocarbon migration from deeper, as yet undiscovered gas or gas-condensate accumulations, hosted in older reservoirs forming the hinge of the Ropienka-Łodyna Mine Anticline. The most pronounced anomalies were detected over the Wańkowa Village - Bandrów and Grabownica-Załuż anticlines. The active hydrocarbon dispersion in this zone may have resulted from the presence of overthrusts displacing the structures. Moreover, these anomalies may indicate the presence of shallow, maybe poorly sealed hydrocarbon accumulations.

Key words: Surface geochemical survey, soil gas, light hydrocarbons, oil traps, Skole Nappe, Outer Carpathians, Poland.

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INTRODUCTION

Most of the hydrocarbon deposits in the Polish Outer Carpathians were found in two areas: the central synclinorium of the Silesian Nappe and the inner synclinorium of the Skole Nappe (Kuśmierek, 2001).

The petroleum-prospective of the Skole Synclinorium has been studied for decades by geologists from the Polish Geological Institute (Szymakowska, 1960, 1961; Jasionowicz, 1961a, b; Żytko, 1961, 1969; Malata, 1994), the petroleum industry (numerous unpublished assessment reports, well-logs and lithostratigraphic columns), academic institutions (e.g., Leszczyński, 1987; Kotlarczyk and Leśniak, 1990; Köster *et al.*, 1998a, b; Kotarba *et al.*, 2007) and research projects (e.g., Kuśmierek *et al.*, 2013; Leszczyński *et al.*, 2013).

In the Skole Nappe, oil fields were discovered exclusively in its deepest part, described as the Skole Syclinorium and located between the San River valley and the state border. The largest oil field is Wańkowa (Fig. 1) with a total

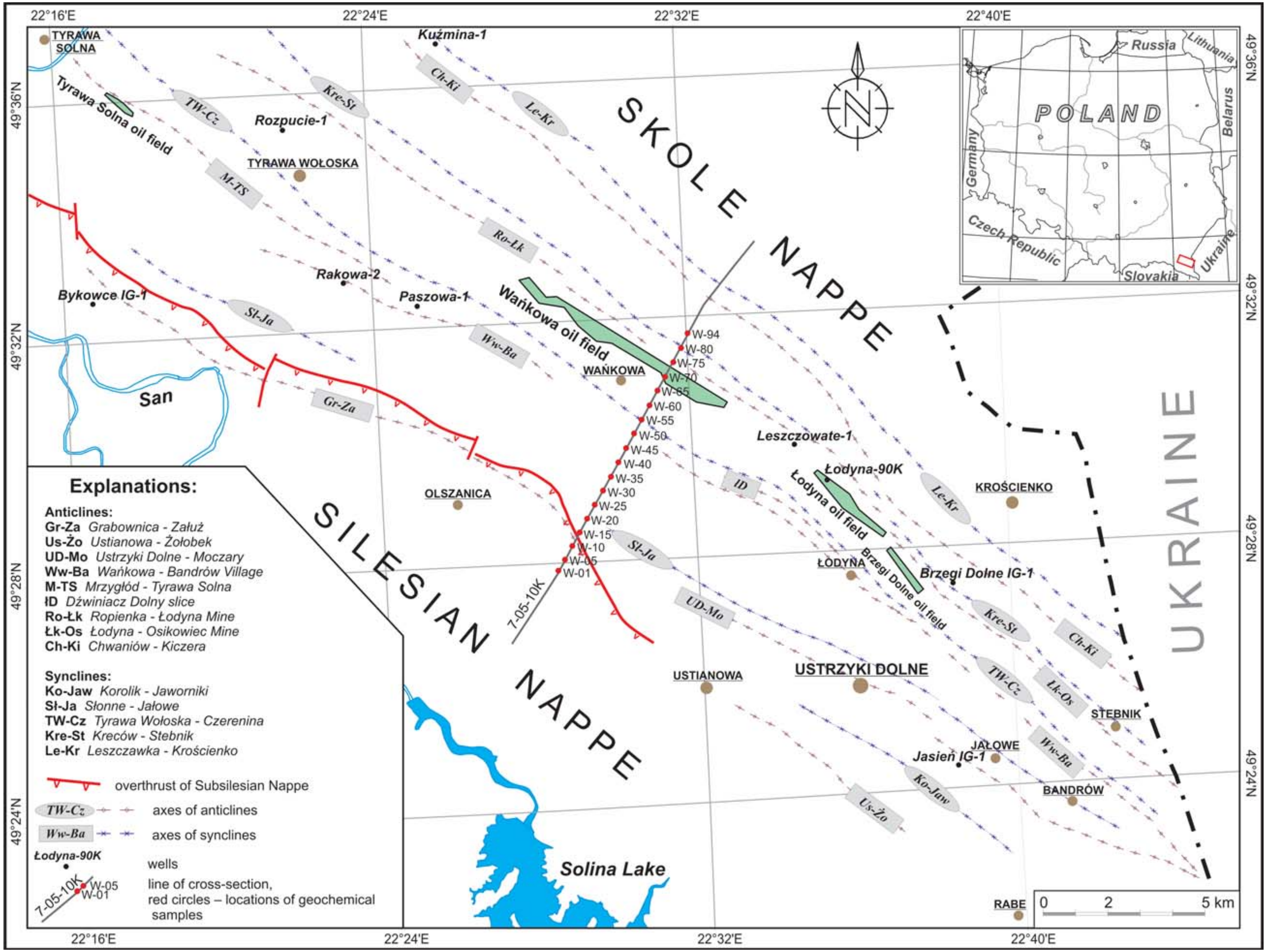


Fig. 1. Geological sketch map of study area with location of soil gas sampling sites (based on Kuśmierek *et al.*, 2013, modified).

oil production of 1.5 Mt. The Wańkowa oil accumulations are reservoired in pinch-outs of the Kliva Sandstone lenses, located at depths of 100 to 750 m (Marcinkowski and Szewczyk, 2008). The Kliva Sandstone is intercalated with the Menilite Shale (Lower Oligocene), which contain the greatest amounts of oil-prone type-II kerogen in the entire Carpathians (e.g., a median value of 10,6 wt. % TOC in the Wolica profile, Więcław *et al.*, 2008). Much lower amounts (0.09–4.12 wt. % TOC, Kosakowski *et al.*, 2009) of gas-prone type-III kerogen and sandstones with less favourable reservoir properties occur in the underlying, Eocene-Late Cretaceous sediments, in which small oil accumulations were discovered in the San River valley.

Geological interpretation of the new 2-D seismic survey "Paszowa-Brzegi Dolne" enabled specialists to recognize the tectonics of the petroleum reservoirs in the Skole Synclinorium. In particular, the potential structural traps were localized together with the oil generative kitchen in the Menilite Shales, the upper surface of which was determined from the modelling of their petroleum system (Maćkowski *et al.*, 2009).

The integration of the geological interpretation of the seismic survey with sedimentological, thickness and palaeostructural analysis of the Menilite Beds revealed the potential for undiscovered lithological traps (i.e., stratigraphic traps) possibly existing in the limbs of the folds of the Skole Synclinorium (Leszczyński *et al.*, 2013).

In order to verify this hypothesis, multivariate analysis of the seismic record was carried out, which led to the localization of two zones, where such lithological traps might have existed. One such locality is the 7-05-10K seismic profile (Fig. 1), at right angles to the fold axes and cutting across the Wańkowa Oil Field (Stefaniuk *et al.*, 2013).

The location of a surface geochemical survey along the 7-05-10K seismic profile resulted from: (1) an experiment, which linked the survey results with a shallow oil accumulation in the Wańkowa Field, (2) the seismic interpretation of the deep tectonics of petroleum reservoirs in the Skole Synclinorium and (3) the inferred position of undiscovered lithological traps (Stefaniuk *et al.*, 2013).

In the survey, the authors applied the "free gas" method, based upon the detection and analysis of micro-concentrations of gaseous hydrocarbons in the near-surface zone, to which these compounds have migrated from petroleum accumulations (e.g., Sokolov and Grigoriev, 1962; Jones and Drozd, 1983; Horvitz, 1985; Rice, 1986; Klusman, 1993; Tedesco, 1995; Saunders *et al.*, 1999; Jones *et al.*, 2000; Schumacher, 2000; Herbert *et al.*, 2006; Sechman *et al.*, 2011). These results may provide complementary information, supporting petroleum exploration in a given area.

It must be emphasized that surface geochemical surveys of the Polish part of the Outer Carpathians were initiated long ago by the staff of the Department of Geoanalyses of the Petroleum Institute in Kraków, now the Oil and Gas Institute, Kraków (see e.g., Szura and Klewski, 1949; Strzetelski, 1955; Celary *et al.*, 1961, Karaskiewicz, 1961; Głogoczowski, 1963; Olewicz, 1965; Matyasik and Kupisz, 1996). In the years 1972–1985, the survey was continued and extended by a working group from the University of Mining and Metallurgy (AGH University of Science and Technology) in Kraków. This survey focused on both the central and eastern parts of the Outer Carpathians (see Dzieniewicz *et al.*, 1978, 1979a, b; Dzieniewicz and Rusta, 1979). In the years 2007–2008, preliminary geochemical studies were undertaken along the regional traverses across the Polish and the Ukrainian Carpathians (Dzieniewicz and Sechman, 2008; Sechman and Dzieniewicz, 2009). The results provided valuable data on manifestations of petroleum potential in particular tectonic units of the Carpathians. Unfortunately, at this time no comprehensive statistical analysis of measured hydrocarbon concentrations and geochemical indices has been carried out for integration with available interpretations of seismic data.

The studies by the authors were intended to reveal and analyse the character of surface gaseous anomalies existing over the Wańkowa Oil Field as well as over the outcrops and overthrusts of the oil-bearing strata in the Skole Synclinorium and in the marginal zone of the Silesian Nappe. According to seismic data (Stefaniuk *et al.*, 2013), and petroleum system modelling (Maćkowski *et al.*, 2009) in these zones, lithological traps and generative kitchens of liquid hydrocarbons may occur.

GEOLOGICAL SETTING AND PETROLEUM OCCURRENCES

Lithostratigraphy of the Skole Nappe

The basic information on lithofacies development of the Skole Nappe (Kotlarczyk, 1978; Kotlarczyk and Uchman, 2012) and the style of deep tectonics were provided by deep drilling completed in the years 1971–1988 (Żytko, 2004, 2006; Malata and Żytko, 2006). The detailed interpretation of the seismic 2-D profile "Paszowa-Brzegi Dolne" (Kuśmierek *et al.*, 2013) was particularly useful in providing geological-seismic cross-sections and structural maps of potential traps.

The oldest sediments of the Skole Nappe are known from the Kuźmina-1 well (Malata and Żytko, 2006) and include the Spas Shales Formation (Barremian–Cenomanian), dominated by thick-bedded sandstones (the so-called Kuźmina Sandstone), of thickness up to 200 m (Wagner, 2008). These are overlain by siliceous marls (Turonian–Coniacian), about 130 m thick, with mottled and spotted shales in the bottom part (Fig. 2).

The stratigraphic thickness of the overlying Senonian–Paleocene Inoceramian Beds (Ropianka Formation; Kotlarczyk, 1978) exceeds 1,200 m. This lithologically diversified succession includes several members (depositional cycles), comprising normal flysch (mostly calcareous) with thick packets of marls and shales intercalated with thick-bedded sandstones. The Inoceramian Beds (Ropianka Formation) are overlain by the Hieroglyphic Formation, which are fine-grained, siliceous sandstones and intercalated, green shales (Late Paleocene–Eocene) of stratigraphic thickness about 125 m.

The youngest sediments, known as the Menilite-Krosno Series (Jucha and Kotlarczyk, 1958), reveal diachronic lithofacies boundaries of its members in relation to the thin-bedded Jasło Limestone horizon. Moreover, the thicknesses

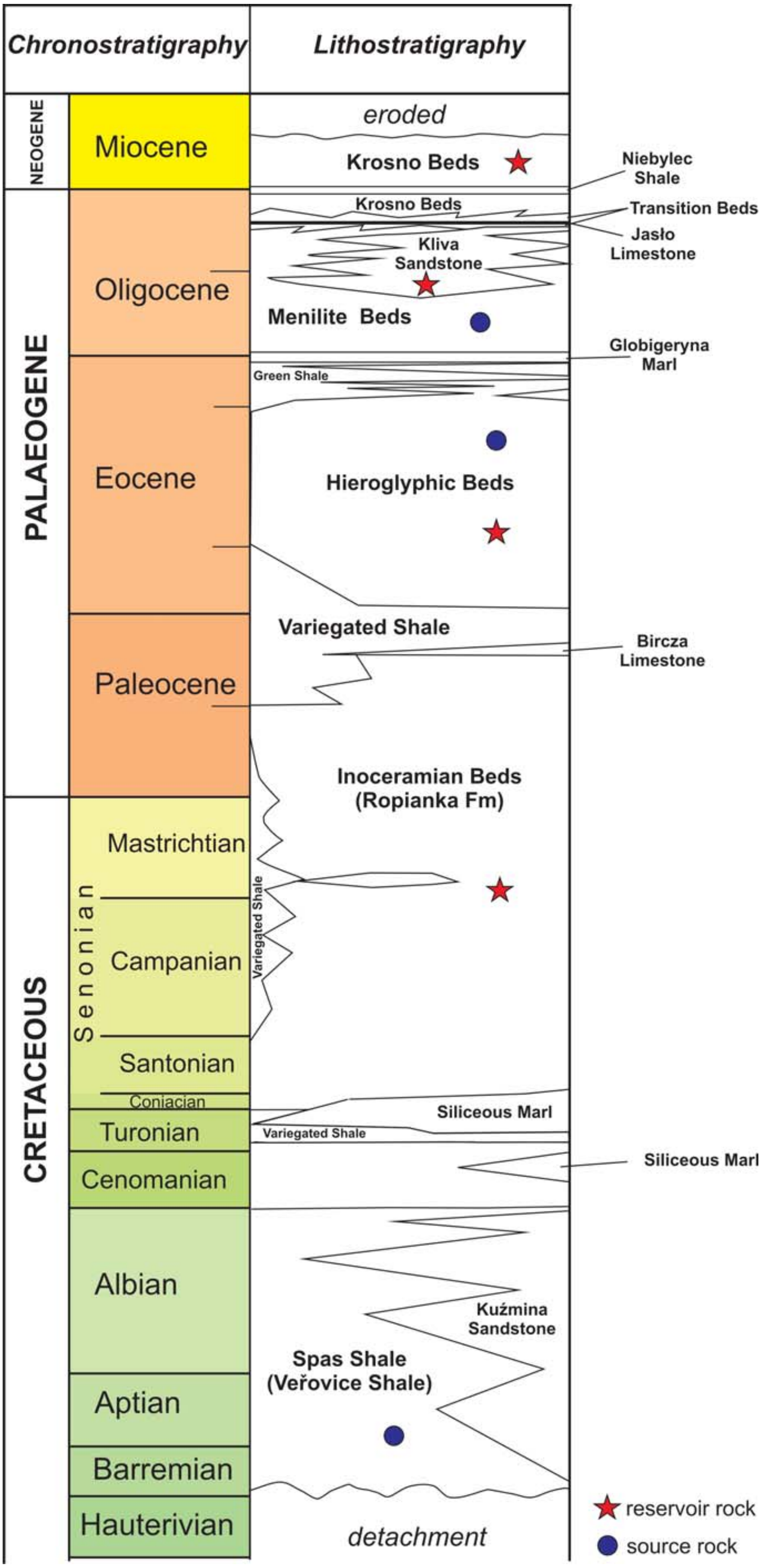


Fig. 2. Lithostratigraphic column of the Skole Nappe in the study area (after Kotlarczyk, 1978; Leszczyński *et al.*, 2013, modified).

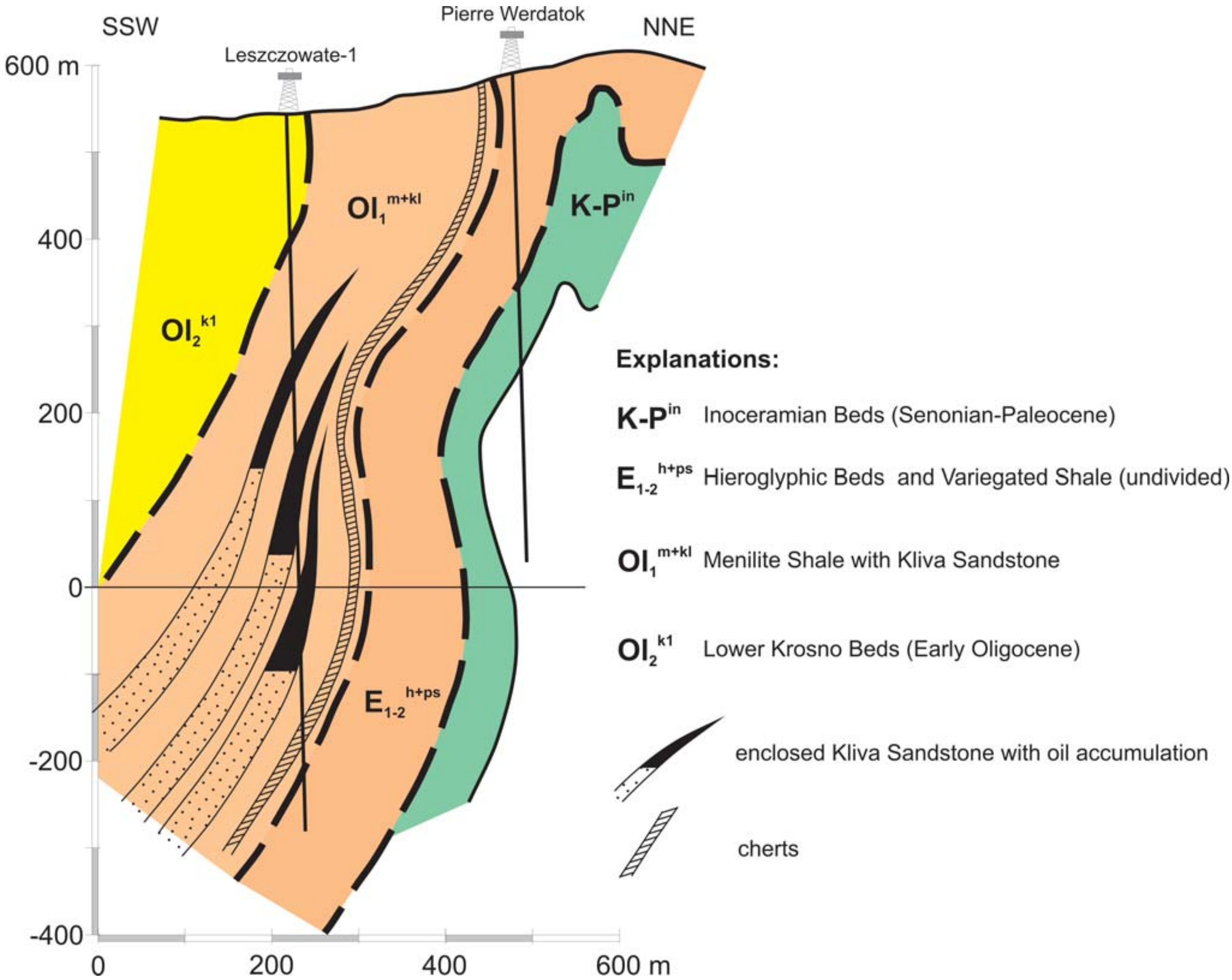


Fig. 3. Schematic geological cross-section through the eastern part of the Wańkowa Oil Field (after Szewczyk and Szeremeta, 2010, modified).

of these members change markedly in the limbs of the folds (Jucha, 1969).

The stratigraphy of the sub-Jasło Limestone succession (Jucha, 1969) includes the older member, the so-called Menilite Beds with the Globigerina Marl in the bottom part and in the area southwest of the Wańkowa-Bandrów Anticline, the so-called Transitional Beds (transitional to the Krosno Beds lithofacies) with the Jasło Limestones.

The characteristic feature of the Menilite Beds is the presence of black and brownish shales, hornstones, hard marls and pelitic platy limestones, quartz arenites with abundant glauconite (Kliva type), all forming thin to thick beds and lenses (several centimetres thick) or isolated laminae in wacke sandstones. The hornstones, most common in the bottom part of the succession, are used for distinguishing the Subchert Beds.

In the supra-Jasło Limestone succession, Malata and Rączkowski (1996) distinguished:

– the top part of the Menilite Beds, known from the northeastern part of the study area; the full succession of the Transitional Beds or its upper part, known from the area southwest of the Wańkowa Village-Łodyna Anticline and the Lower Krosno Beds (younger Oligocene), is developed as thick-bedded (up to 3 m) sandstones;

– the Upper Krosno Beds with a layer of Niebylec Shale in the bottom part, of thickness from 20 to 80 m (Early Miocene), grading up the sequence to a shale complex, up to 250 m thick (Malata, 1994).

Tectonic style of folds and overthrusts

The changes in thickness and lithology of the Menilite-Krosno Beds in the limbs of anticlines, when observed in their outcrops (see e.g., Szymakowska, 1961; Jasionowicz, 1961b; Żytko, 1973), indicate that already in the Early Oligocene the uplifts and depressions were formed at the bottom of the sedimentary basin and then were transformed into synsedimentary folds of variable amplitude.

The most remarkable changes of thickness occur in the Menilite Beds in the southwestern limb of the steeply dipping (locally overturned) Ropienka-Łodyna Mine Anticline. Data from numerous boreholes revealed that the oil-bearing layers of the Kliva Sandstone pinch out towards the hinge of the anticline (Fig. 3).

The results of structural interpretation of the 2-D seismic survey "Paszowa-Brzegi Dolne" (Kuśmierek *et al.*, 2013) demonstrated that the tectonic arrangement of the deep-seated structures is dominated by monovergent, imbricated overthrusts, dipping to the southwest, which frame from the northeast the culmination of the Chwaniów-Kiczera and Wańkowa Village-Bandrów anticlines. The overthrusts are accompanied by only locally developed slice folds and flat-arcuate detachments, formed usually within buried structural depressions.

The main overthrusts (of an out-of-sequence type) interpreted in seismic profiles can be divided between two belts (Kuśmierek *et al.*, 2013):

– a southern belt, along which the Wańkowa Village-Bandrów Anticline and the Dźwiniacz Dolny slice fold were thrusted onto the Tyrawa Wołoska-Czerenina Syncline;

– a northern belt defined as an overthrust or a system of thrusts of the Ropienka-Łodyna Mine and the Chwaniów-Kiczera anticlines over the Leszczawka-Krościenko Syncline.

Oil and gas potential and the petroleum system of the Skole Synclinorium

In the synclinal zone of the Skole Nappe (named the Skole Synclinorium), between the San River valley and the state border (i.e., in the Stebnik-Bandrów area, Fig. 1), oil fields were discovered only in the Menilite Beds (Early Oligocene). The reservoir rocks are the Kliva Sandstone, which are interbedded with the Menilite Shale. The shales are the hydrocarbon source rocks, famous for its content of oil-prone type-II and mixed II/III kerogen, which is the highest in the entire Outer Carpathians (Więcław *et al.*, 2008; Kosakowski *et al.*, 2009).

It is important to note that all the oil fields discovered in this area occur in the limbs of the Tyrawa Wołoska-Czerenina Syncline, although the Kliva Sandstone of favourable reservoir properties and the Menilite Shale of high source-rock potential are known from numerous outcrops and wells (e.g., Matyasik, 1994, 2011).

The intensive folding and slicing of the Skole Synclinorium between the villages of Brzegi Dolne and Bandrów facilitated the migration of hydrocarbons, as documented by numerous oil seeps clustered over the culminations of folds, overthrusts and faults, and fractured clayey-sandy series as well as in the outcrops of the Kliva Sandstone and, rarely, the upper member of the Inoceramian Beds (Kuśmierek *et al.*, 2013). However, in the zones where the Kliva Sandstones pinch-outs were effectively sealed, the largest oil fields, Wańkowa and Łodyna, accumulated (Marcinkowski and Szewczyk, 2008). Modelling of the petroleum system demonstrated that the Menilite Shale might have attained the thermal maturity suitable for generation of liquid hydrocarbons only in the eastern part of the Skole Synclinorium (Maćkowski *et al.*, 2009; Kosakowski, 2013). The top surface of the oil window for type-II/-III kerogen prior to inversion of the tectogen was determined from the modelling of thermal transformations of organic matter at a depth of below 2,700 m in the Tyrawa Wołoska-Czerenina Syncline and even much deeper in the Leszczawka-Krościenko limb, as observed e.g., in the Kuźmina-1 well (Kuśmierek, 1995; Maćkowski *et al.*, 2009). In contrast, this surface was found in the Słonne-Jałowe Syncline at a depth of 3,000– 3,500 m, owing to the shallower position of the structural depression under the cover of older strata of the overthrusted Subsilesian Nappe.

The oil expelled from the Menilite Shale was undoubtedly reservoired in the Kliva Sandstone interbeds. The intensity of the intra-reservoir migration of oil was controlled by both the reservoir properties of the Kliva Sandstone and the structural height of potential generative kitchens, which induced the pressure gradients.

Both the geochemical and petrophysical characteristics of the oil-bearing lithofacies of the Skole Nappe, together with the results of petroleum exploration, justify the separate categorization of the hydrocarbon potential of the Cretaceous–Paleocene and Eocene–Oligocene exploration targets. Geochemical studies revealed significant differences in TOC contents and the type of kerogen and the degree of its transformation into liquid and gaseous hydrocarbons (Kosakowski *et al.*, 2009).

The Cretaceous–Paleocene sediments contain almost exclusively the gas-prone type III kerogen. In the study area, gases originating from the Oligocene strata are similar in molecular composition, except for gas from the Brelików-110 well (Br-110), which shows much lower concentrations of methane and its homologues by comparison with the gases from other wells (Table 1). The dominant gas is methane (from 24.5 to 79.0 vol. %). Among alkanes the most abundant is ethane (1.1 to 8.9 vol. %). The values of C_1/C_2 and $C_1/(C_2 + C_3)$ ratios (Table 1) indicate thermogenic origin of all analyzed gases. The values of C_2/C_3 ratio vary from 0.2 to 1.1 (Table 1), which is typical of gases accompanying oils. Concentrations of nitrogen in Oligocene strata change from about 2 vol. % (e.g., in the Łodyna-10 well) to over 50 vol. % in the Br-110 well.

METHODOLOGY

Field sampling of soil gases and analytical procedure

The field work included geochemical sampling at 94 sites spaced 100 m apart along the line of the 7-05-10K seismic profile, extending between Olszanica Dolna and Ropienka Górna villages. The sampling sites were positioned on a 1:25,000-scale topographic map sheet by measuring the azimuths and distances. Additionally, each site was GPS-positioned with the Garmin Oregon 650t device. Sampling was carried out between September 25 and 27, 2013, under stable atmospheric conditions and at an air temperature about +14 °C. Samples of soil gases were collected with a special geochemical probe and a gas-tight syringe and vessel (Dzieniewicz and Sechman, 2001, 2002). The probe was hammered down to a depth of 1.2 m and the gas was recovered with the gas-tight syringe into the vessel. Details of the sampling procedure were presented in previous publications (see e.g., Dzieniewicz and Sechman, 2008; Sechman and Dzieniewicz, 2009; Sechman *et al.*, 2011, 2012; Sechman, 2012).

Table 1

Molecular composition of natural gases from boreholes and oil fields
(after unpublished data of the Polish Oil & Gas Co. and Karnkowski, 1999)

Well/ field	Molecular composition (vol. %)							Hydrocarbon ratios			
	CH_4	C_2H_6	C_3H_8	C_4H_{10}+	N_2	O_2	CO_2	C_1/C_2	$C_1/(C_2+C_3)$	C_2/C_3	$C_2/(C_3+C_4)$
Br-64[1)]	57.1	6.1	5.8	~6.0	13.4	1.2	10.1	9.4	4.8	1.1	7.1
Br-110[1)]	24.5	3.0	3.1	~10.0	50.6	7.8	7.0	8.2	4.0	1.0	11.0
Br-157[1)]	70.7	6.7	8.2	~4.0	0.4	0	3.6	10.6	4.7	0.8	4.8
Ki-18[1)]	74.5	6.6	6.2	~6.0	0.2	0	5.9	11.3	5.8	1.1	7.1
Ł-65[2)]	69.7	8.9	8.6	4.9	2.7	n.a.	0.3	7.8	4.0	1.0	5.9
Ł-107[2)]	67.3	8.4	8.4	6.4	2.2	n.a.	2.6	8.0	4.0	1.0	7.4

C_1/C_2 (methane/ethane); C_2/C_3 (ethane/propane); $C_1/(C_2+C_3)$ (methane/ethane+propane); $C_2/(C_3+C_4)$ (ethane/propane+butanes); 1) – natural gas accompanying oil of Wańkowa Oil Field, after unpublished data of the Polish Oil & Gas Co.; 2) – natural gas accompanying oil in Łodyna Oil Field, after Karnkowski (1999)

The molecular composition of the soil gases was analyzed at the Laboratory of Gas Chromatography of the Department of Fossil Fuels. The authors used FISSONS Instruments GC 8160 and CARLO ERBA Instruments GC 6300 gas chromatographs, equipped with FID and TCD detectors. In each sample, methane, ethane, propane, *i*-butane, *n*-butane, *neo*-pentane, *i*-pentane, *n*-pentane, ethylene, propylene, *1*-butene, hydrogen and carbon dioxide were determined. The detection limit for FID is 0.01 ppm for hydrocarbons. The analytical precision is 2% of the measured value and 10% at the detection limit. The FISSONS instrument with FID detector uses a metal column filled with activated alumina (mesh 100/120). The flow rate of the carrier gas (helium) was 60 ml/min. The programmed column temperatures were: 80 °C for 3 min, 80–200 °C increment at a rate of 30 °C/min and 200 °C for 3 min. The FID working temperature was 270 °C, the injection chamber temperature was 120 °C, and the volume of each injected sample was 2 ml.

The TCD detection limits for carbon dioxide and hydrogen are 100 ppm and 10 ppm, respectively, at an estimated precision of 2% of the measured value and 10% at the detection limit. The CARLO ERBA Instrument GC 6300 gas chromatograph was equipped with a thermal-conductivity detector (TCD) and a dual column system. The following analytical conditions were applied: metal columns filled with the Molecular Sieve 5A (for the analysis of hydrogen) and HaySep (for the analysis of carbon dioxide); flow rate of carrier gas (argon) 30 ml/min; a constant column temperature of 65 °C, the volume of sample was 2 ml, injected with an automatic valve. More details of the methodology of the chromatographic analyses were presented in several earlier publications (see Dzieniewicz and Sechman, 2008; Sechman and Dzieniewicz, 2009; Sechman *et al.*, 2011, 2012, 2013; Sechman, 2012).

Statistical procedure

The statistical processing of the measured concentrations of alkanes (methane, ethane, propane, *i*-butane, *n*-butane, *neo*-pentane, *i*-pentane, *n*-pentane), alkenes (ethylene, propylene, *1*-butene), hydrogen and carbon dioxide consisted of the determination of maximum and minimum values, arithmetic means, standard deviations, medians, skewness and percentages of values above the detection limits, related to the overall population of samples collected. Moreover, statistical parameters were calculated also for total alkanes C_2-C_5 and total alkenes C_2-C_4 (Tables 2 and 3) as well as for geochemical ratios $C_1/\Sigma(C_2$-$C_5)$, C_2H_6/C_3H_8 (below marked as C_2/C_3) and C_2H_6/C_2H_4, below marked as $C_2/C_{2=}$ (Table 4). These ratios enabled the preliminary genetic evaluation of gas sources, their character and the intensity of microbial processes operating in the near-surface zone, controlled by the relative intensity of hydrocarbon microseepage from deep accumulations to the surface.

For populations of the geochemical ratios $C_1/\Sigma(C_2$-$C_5)$ (Fig. 4A, B), $C_2/C_{2=}$ (Fig. 4C, D) and C_2/C_3 (Fig. 4E, F), histograms and probability plots were constructed. The numbers of intervals in the histograms were determined as rounded values of the square roots of data numbers (Krysicki *et al.*, 1994). The first and last intervals remained open. Both the histograms and probability plots then were used for the evaluation of the distribution patterns of sets of concentrations and calculated coefficients and for the identification of outstanding sub-sets. Relationships were analyzed between concentrations of ethane and propane, using directional correlations and correlation plots in the Cartesian coordination system (Fig. 5) in order to obtain information on the character of deep-seated accumulations (Jones and Drozd, 1983).

In order to determine objectively the anomalies, the iteration method was applied for determination of background values (Dzieniewicz and Sechman, 2001; Sechman and Dzieniewicz, 2011), then the threshold values of anomalies were calculated and the geochemical anomalies were identified. Background values were determined for the sets of methane, total alkanes C_2-C_5 and total alkenes C_2-C_4 concentrations. Then, the background values were applied to the normalization of concentrations within the sets.

The location patterns of sampling sites used in the surface geochemical survey correspond to the aims of the studies. A wide range of spacings – from several to several hundreds of metres – is recommended in the literature (see Sokolov and Grigoriev, 1962; Philp, 1987; Tedesco, 1995;

Table 2

Principal statistical parameters of alkanes concentrations in 94 soil-gas samples

Statistical parameters		Alkanes								Total C_2-C_5 alkanes
		CH_4	C_2H_6	C_3H_8	*i*-C_4H_{10}	*n*-C_4H_{10}	*neo*-C_5H_{12}	*i*-C_5H_{12}	*n*-C_5H_{12}	
Minimum	(ppm)	0.8	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	n.d.	b.d.l.	b.d.l.
Maximum	(ppm)	4250	0.24	0.12	0.04	0.05	0.01	n.d.	0.03	0.43
Mean	(ppm)	58.0	0.028	0.007	0.001	0.003	0.000	-	0.001	0.04
Median	(ppm)	1.8	0.013	0.000	0.000	0.000	0.000	-	0.000	0.02
Standard dev.	(ppm)	448.5	0.045	0.018	0.004	0.009	0.001	-	0.005	0.07
Skewness	(ppm)	9.2	3.1	4.7	6.3	4.0	5.9	-	4.5	3.7
Percentage of samples*	(%)	100.0	67.7	31.2	11.8	23.7	4.3	0.0	5.4	76.3

* – percentage of samples with concentration of given component over detection limit; b.d.l. – below detection limit; n.d. – not detected

Matthews, 1996; Sechman *et al.*, 2011). The selected sampling pattern must provide random data. The differences between values obtained from adjacent sites may be extreme, as they reflect more or less natural processes. In order to reduce measured values to their natural distributions, the normalized values of analyzed geochemical indices were filtrated. Although this procedure partly distorts the patterns obtained, it facilitates their interpretation. The values of analyzed geochemical indices were filtrated with a three-point filter (Sechman and Dzieniewicz, 2007, 2011).

Changes of normalized and filtrated values of concentrations were presented as plots superimposed onto the geological-seismic cross-section.

RESULTS AND DISCUSSION

Statistical analysis of hydrocarbons concentrations measured in soil-gas samples

The statistical parameters presented in Table 2 demonstrate low concentrations of methane in most of the analyzed samples (median – 1.8 ppm). Methane was detected in all samples, in amounts ranging from 0.8 to 4250.0 ppm. Only in the sample taken at measurement point no. 86, located over the Wańkowa Oil Field, a very high methane concentration was revealed. This particular concentration of methane is interpreted as the result of a recent generative process (e.g., Davis and Squires, 1954; Gole and Butt, 1985; Starobinetz, 1986; Whiticar *et al.*, 1986; Klusman, 1993; Whiticar, 1999; Jones *et al.*, 2000; Kotelnikova, 2002; Sechman *et al.*, 2012). Such an interpretation is indicated by the absence or very low concentrations of heavier homologues and by very high values of the $C_1/\Sigma(C_2$-$C_5)$ ratio (Table 3). The percentages of samples, in which alkanes were recorded, decrease with an increasing number of atoms in the molecules. Such relationships prove that hydrocarbons detected in the near-surface zone originated from deep sources (Sokołov and Grigoriev, 1962; Jones and Drozd, 1983; Harbert *et al.*, 2006). A simple method without expensive isotopic analysis, which enabled the authors to distinguish methane migrated out of deep sources from that generated recently in the soil is the calculation of the $C_1/\Sigma(C_2$-$C_5)$ ratio from concentrations detected in each sample of soil gas (e.g., Davis and Squires, 1954; Gole and Butt, 1985; Starobinetz, 1986; Whiticar *et al.*, 1986; Klusman, 1993; Jones *et al.*, 2000; Sechman *et al.*, 2012).

Ethane was found in 67.7% of the analyzed samples with concentration of up to 0.24 ppm. Its mean concentration is 2 times higher than the median value. This indicates anomalous values in this data set. The next homologues – propane, *i*-butane and *n*-butane – occur in about 31%, almost 12% and 23.7% of the analyzed samples, respectively. Their maximum and mean concentrations decreased stepwise. Only traces of *neo*-pentane and *n*-pentane were detected and the concentration of *i*-pentane was lower than the detection limit of the FID detector. Concentrations of total alkanes C_2-C_5 above the detection limit were encountered in about 76% of the analyzed samples and their maximum concentration is 0.43 ppm (Table 2). When compared to methane, this sample population is characterized by a slightly lower difference between the mean and median values and by a lower standard deviation and skewness. It should be noted that the concentrations of higher alkanes measured in the soil-gas samples of the area studied were relatively lower than in the other areas of the Polish Outer Carpathians (Dzieniewicz *et al.*, 1978, 1979a, b; Sechman and Dzieniewicz, 2009). However, the statistical parameters of total alkanes C_2-C_5 data set indicate several anomalous values, measured in soil-gas samples along the profile in the area studied.

Among unsaturated hydrocarbons, the most common is ethylene, which was detected in over 50% of the samples analysed. Its maximum concentration was 0.122 ppm and the mean value was 0.008 ppm. The higher alkenes occur in trace amounts. Propylene was found in 35% of samples, its maximum concentration was 0.023 ppm. 1-Butene was detected in about 40% of samples and its maximum concentration was 0.049 ppm (Table 2). The maximum concentration of total alkenes C_2-C_4 was 0.147 ppm and the mean value was 0.018 ppm. As in the case of total alkanes C_2-C_5, the total alkenes were detected in about 76% of analysed samples. The presence of alkenes in the near-surface zone still remains a matter for discussion. According to some authors, small amounts of alkenes can be generated elsewhere in soil

Table 3

Principal statistical parameters of alkenes, hydrogen and carbon dioxide concentrations in 94 soil-gas samples

Statistical parameters		Alkenes			Total C_2-C_4 alkenes	H_2**	CO_2**
		C_2H_4	C_3H_6	1-C_4H_8			
Minimum	(ppm)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02
Maximum	(ppm)	0.122	0.023	0.049	0.147	0.042	4.40
Mean	(ppm)	0.008	0.004	0.006	0.018	0.004	0.84
Median	(ppm)	0.005	0.000	0.000	0.013	0.000	0.69
Standard dev.	(ppm)	0.015	0.006	0.009	0.021	0.008	0.66
Skewness	(ppm)	4.9	1.5	2.3	3.1	2.4	2.3
Percentage of samples *	(%)	51.6	35.5	39.8	75.3	25.5	100.0

* – percentage of samples with concentration of given component over detection limit; ** – minimum, maximum, mean, median, standard deviation and skewness in vol.%, b.d.l. – below detection limit

gas at shallow depths during biochemical reactions (Smith and Ellis, 1963; Gole and Butt, 1985; Ullom, 1988; Klusman, 1993). Other authors suggest that relatively high amounts of ethylene and propylene may result from both the biotic and abiotic oxidation of some part of the ethane and propane, which migrated from deep-seated hydrocarbon accumulations (Saunders *et al.*, 1999; Jones *et al.*, 2000; Harbert *et al.*, 2006; Klusman, 2006, 2009, 2011). New results (Klusman, 2009, 2011) revealed that the stepwise oxidation of an alkane by bacterial processes is occurring in the order: alkane $\rightarrow$ alkene $\rightarrow$ alcohol $\rightarrow$ aldehyde $\rightarrow$ carboxylic acid $\rightarrow$ acetate $\rightarrow$ carbon dioxide. Moreover, the author claims that these bacterial processes are occurring in a limited supply of oxygen and depend on season, temperature of the soil and humidity (Klusman, 2006). Following Saunders *et al*. (1999), Jones *et al*. (2000) and Harbert *et al*. (2006), the present authors assume that time is an important parameter which controls the intensity of biochemical reactions. The longer the alkanes remain under the influence of particular, stable conditions, the greater their bacterial destruction. Thus, the active (relatively fast) migration of alkane molecules along fractures and faults does not leave sufficient time for their stepwise oxidation even to alkenes. Hence, the high ratio of saturated to unsaturated hydrocarbons may evidence relatively active migration of alkanes from deep accumulations towards the surface (Saunders *et al.*, 1999; Jones *et al.*, 2000; Harbert *et al.*, 2006). The surface geochemical survey carried out along the line crossing the Wańkowa Oil Field showed a dominance of alkanes over alkenes, as demonstrated by absolute concentrations of the analyzed alkanes and alkenes (Tabs 2, 3), and by relatively high values of $C_2/C_{2=}$ ratio (Tab. 4). Considering that soil-gas samples were collected under stable atmospheric conditions and analyzed in a short time span, and taking into account the theory developed by Saunders (1999), the authors conclude that in the study area the dominating process was the active microseepage of alkanes from generative kitchens or deep accumulations towards the surface.

The hydrogen concentrations in the samples analyzed varied from 0 to 0.042 vol. %. Hydrogen was detected in about 26% of all analyzed samples and its mean value was 0.004 vol. % (Tab. 3). Relatively low concentration of hydrogen and lack of correlation with higher alkanes indicate

Table 4

Principal statistical parameters of hydrocarbon ratios

Statistical parameters	Hydrocarbon ratio		
	C_2/C_3	$C_2/C_{2=}$	$C_1/\Sigma C_2$-C_5
Minimum	0.73	0.33	17.2
Maximum	12.83	28.13	212740.0
Mean	3.36	4.12	3595.6
Median	2.37	2.90	76.5
Standard deviation	2.72	5.66	25520.0
Skewness	3.8	1.9	8.1

C_2/C_3 (ethane/propane), $C_2/C_{2=}$ (ethane/ethylene); C_1/SC_2-C_4 (methane/total C_2-C_4 alkanes)

its microbial origin (Pallasser, 2000; Head *et al.*, 2003; Dolfing *et al.*, 2008).

Concentrations of carbon dioxide were found in all of the samples analyzed. Maximum concentration reached 4.4 vol. %. The mean and median values are relatively low when compared with the results of other studies (e. g., Sechman *et al.*, 2012). The small difference between the mean and median values and the low skewness (Tab. 3) indicate a small number of anomalous values in the data set. This is why the measured concentration of carbon dioxide is not significant for interpretation. The polygenetic character of carbon dioxide (Savary and Pagel, 1997; Pallasser, 2000; Head *et al.*, 2003; Dolfing *et al.*, 2008) and its small number of anomalous values indicate low activity of microbial processes in the near-surface zone and/or low activity in terms of the migration of carbon dioxide from the deep subsurface.

Statistical analysis of hydrocarbon ratios

The values of $C_1/\Sigma(C_2$-$C_5)$ ratio vary within 6 orders of magnitude. The set shows a notable difference of mean and median values as well as a very high standard deviation (Table 4), which exceeded 1000 in one sample indicating the presence of recently generated microbial methane. The histogram of $C_1/\Sigma(C_2$-$C_5)$ values has an asymmetric pattern and a high frequency of the last, open interval (Fig. 4A).

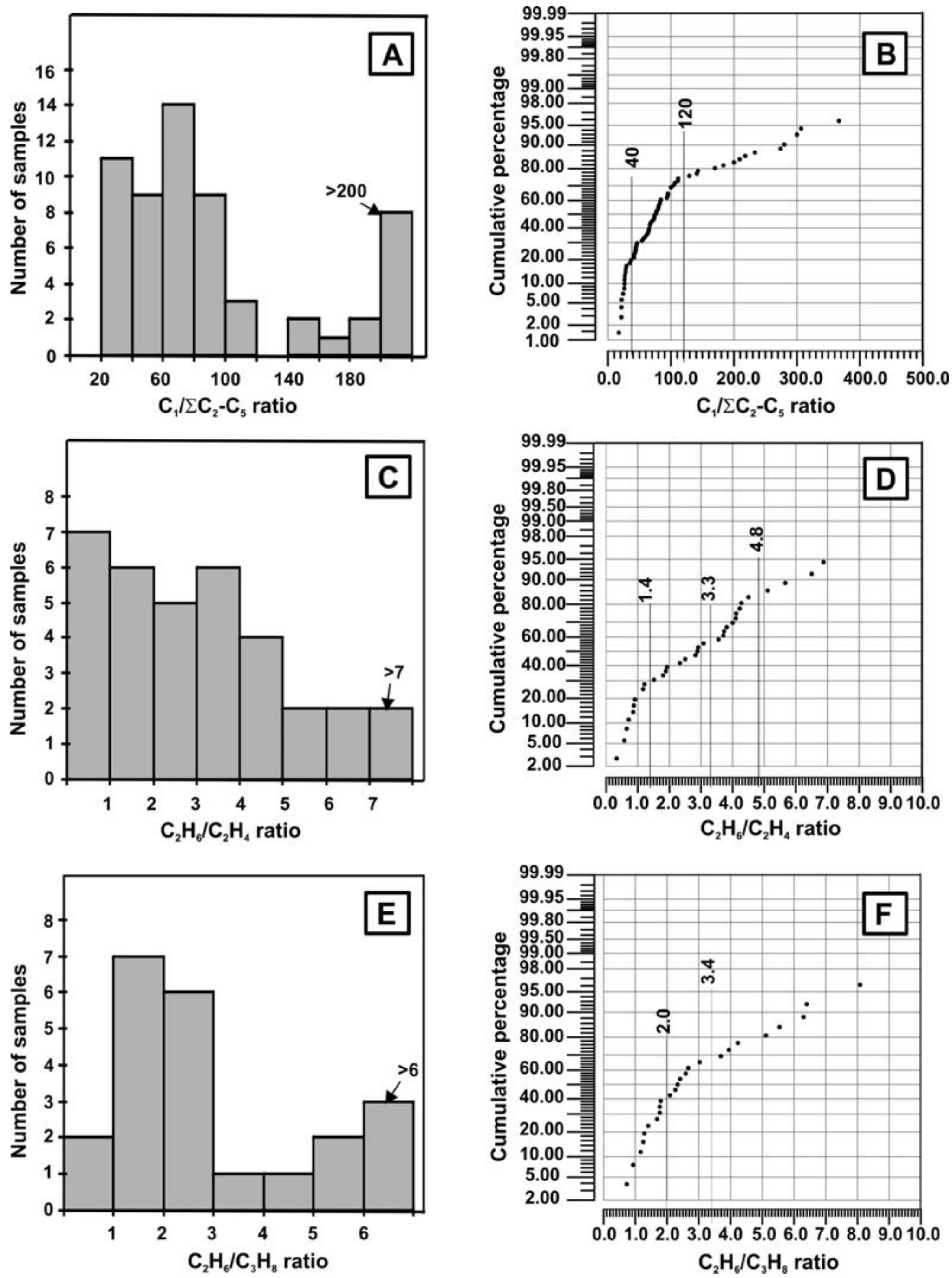


Fig. 4, Histograms and cumulative frequency diagrams of $C_1/\Sigma(C_2$-$C_5)$ (A, B), $C_2/C_{2=}$ (C, D) and C_2/C_3 (E, F) ratios calculated for soil-gas data.

The set of $C_1/\Sigma(C_2$-$C_5)$ values contains characteristic sub-sets: <40, 40–120 and >120 (Fig. 4B). Considering the modal interval, which is 60–80 (Fig. 4A), the authors deduced the dominance of gas-condensate character of deep hydrocarbon dispersion sources (Jones and Drozd, 1983).

The statistical distribution of the C_2/C_3 ratio shows a unimodal, right-skewed pattern (Fig. 4E) with 2–3 intervals dominating. The relatively narrow range of C_2/C_3 values, the low median and the small difference between median and mean values (Tab. 4) indicate the presence of oil-condensate accumulations in the study area. Moreover, the somewhat wider range of $C_2/C_{2=}$ values (Fig. 4C) supports the opinion of the authors about the diversified and active seepage of hydrocarbons towards the surface.

The histogram of $C_2/C_{2=}$ values is close to logarithmic and, right-skewed (Fig. 4C). The following sub-sets were distinguished: <1.4, 1.4–3.3, 3.3–4.8 and >4.8 (Fig. 4D). The statistical distributions attest to the variable character of hydrocarbon seepage, whereas the low concentrations of alkanes and the high mean value of $C_2/C_{2=}$ ratio evidence an active microseepage of alkanes from deep accumulations (Saunders *et al.*, 1999).

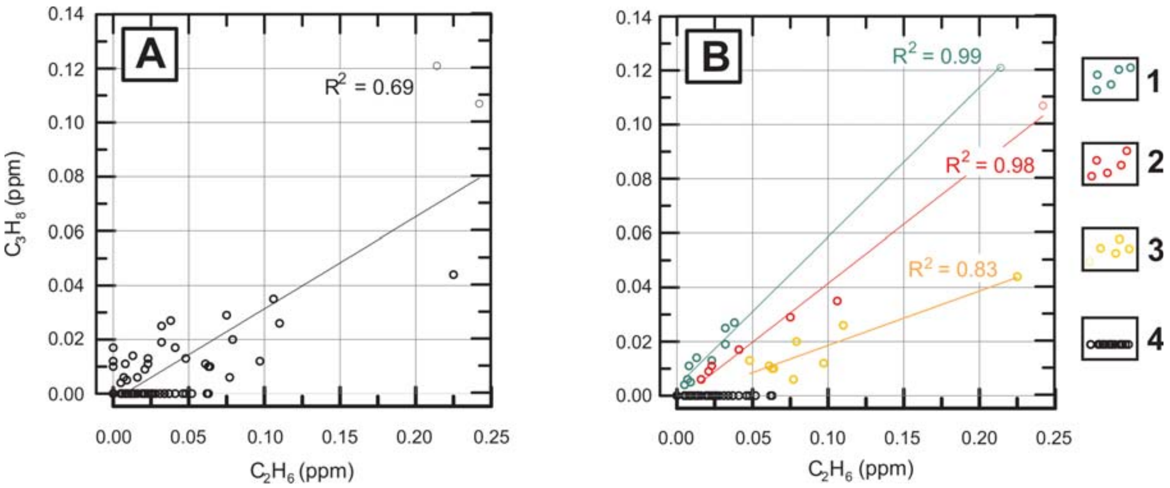


Fig. 5. Scatter-plots of ethane versus propane concentrations for whole dataset (**A**) and for sub-sets (**B**): *1* – C_2/C_3 <2.0; *2* – C_2/C_3 from 2.0 to 3.4; *3* – C_2/C_3 over 3.4; *4* – propane concentrations below detection limit of FID detector.

Within the set of C_2/C_3 ratio values, the subsets <2, 2–3.4 and >3.4 were distinguished (Fig. 4F). The highest frequency of the 1-2 modal interval, together with the distribution of ratio values 0–3.4 close to normal, confirms the dominance of the oil-condensate character of the deep hydrocarbon accumulations (Nikonov, 1971).

A correlation between C_2H_6 and C_3H_8 concentrations was presented as a plot drawn in the Cartesian coordinates system (Fig. 5A). The coefficient of determination is R^2 = 0.69, which indicates a rather moderate correlation and suggests that alkanes detected in the near-surface zone have migrated from several sources that were diverse in composition. However, the coefficients of determination for C_2H_6 and C_3H_8 calculated for the subsets of C_2/C_3 values distinguished are much higher: 0.99 and 0.98 for <2.0 and 2.0–3.4 sub-sets, respectively (Fig. 5B). This is yet another argument supporting the dominance of gas-condensate deep sources (Jones and Drozd, 1983; Sechman and Dzieniewicz, 2009; Sechman *et al.*, 2011). Similar conclusions can be drawn when the relations between log ($C_2/C_3 + C_4$) and log ($C_1/C_2 + C_3$) coefficients are analyzed (Fig. 6). In this diagram, the authors marked points representing soil-gas samples of anomalous (above the background) total alkane C_2-C_4 concentrations. Additionally, this diagram was supplemented with points representing the composition of gaseous hydrocarbons from the Wańkowa and Łodyna deposits (Tab. 1). The positions of points representing gases from both the Łodyna and Wańkowa deposits confirm their common genesis. Moreover, their molecular compositions are very similar and their positions in the diagram related to points representing the compositions of soil gases enabled the authors to conclude that hydrocarbons detected in the near-surface zone have migrated from deep-seated accumulations. During the microseepage from depths, hydrocarbons are subjected to (among other phenomena) natural chromatography (Sokolov and Grigoriev, 1962; Starobinetz, 1986; Jones *et al.*, 2000). As a result, the flux of hydrocarbons towards the near-surface zone becomes depleted of larger (heavier) molecules. The effects of such a process are seen in Fig. 6 as a "shift" of points representing soil

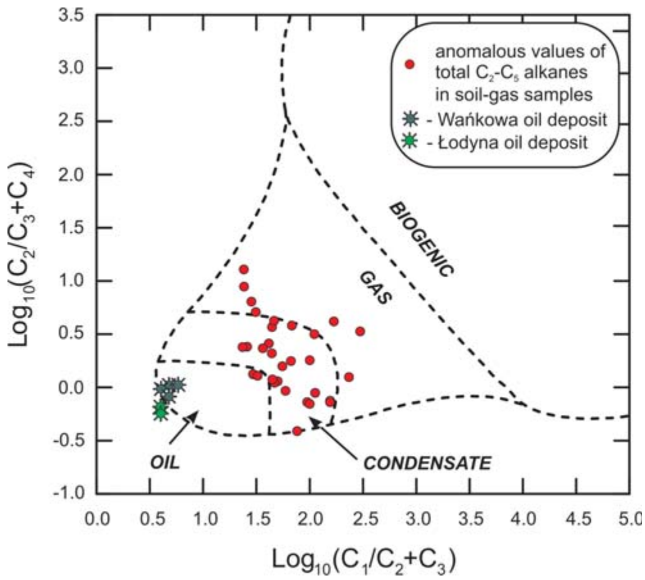
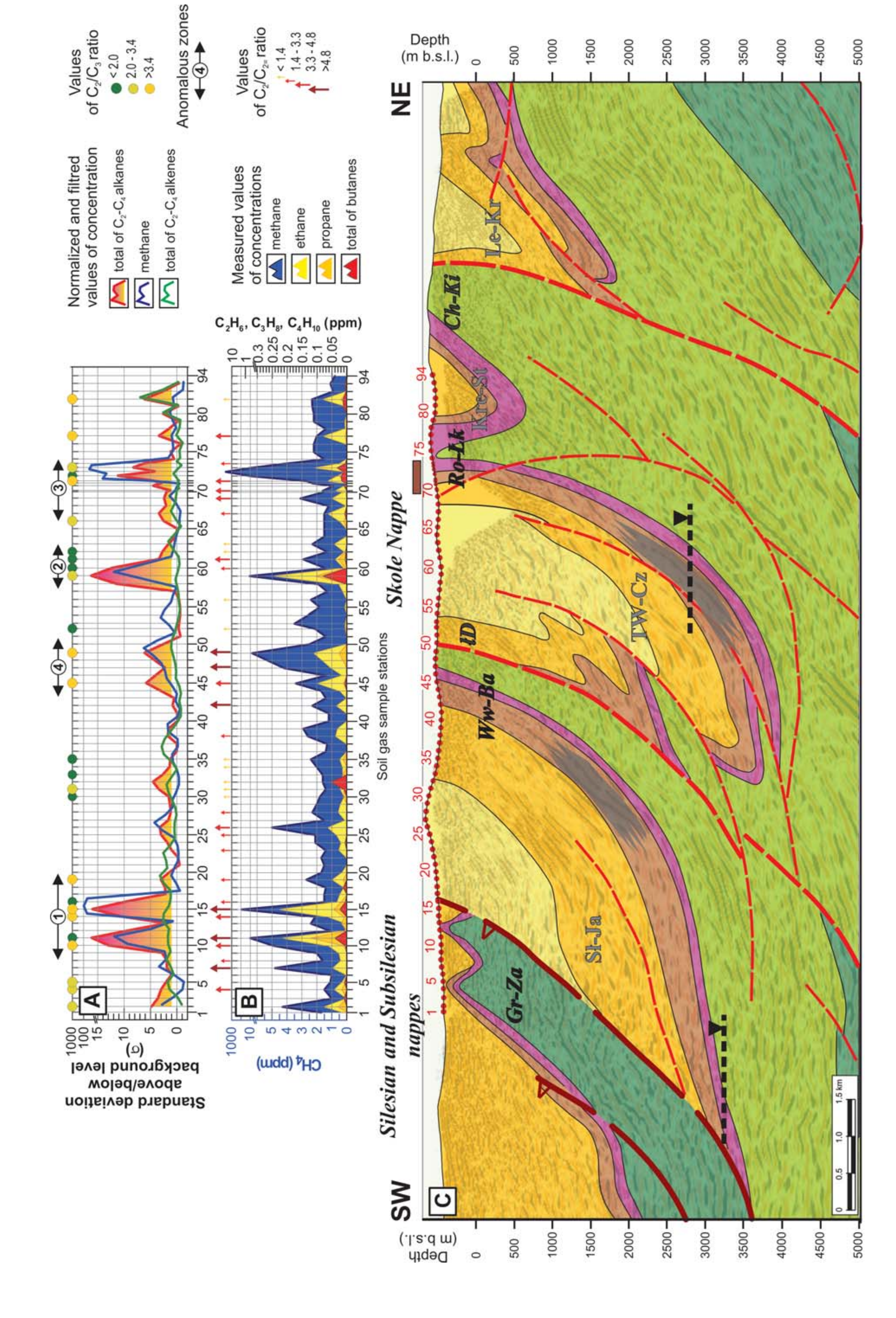


Fig. 6. Composition cross-plot of soil gas samples (fields boundaries after Jones *et al.,* 2000).

gases towards the higher values of coefficients. The positions of the soil-gas points support again the opinion of the authors on the condensate character of deep hydrocarbon accumulations (Fig. 6).

Distribution of surface geochemical anomalies in relation to geological structure and seismic anomalies

In the geological-seismic cross-section (Fig. 7), the authors distinguished 4 anomalous zones, arranged in a hierarchy corresponding to their importance for petroleum exploration (numbers 1–4). All of the anomalies distinguished reveal anomalous concentrations of methane and higher homologues, including butane. However, within particular anomalies the proportions of methane homologues and their relations to unsaturated hydrocarbons are varied. This, in


A
B
C
Standard deviation above/below background level (σ)
CH_4 (ppm)
C_2H_6, C_3H_8, C_4H_{10} (ppm)
Soil gas sample stations
Normalized and filtred values of concentration
total of C_2-C_4 alkanes
methane
total of C_2-C_4 alkenes
Measured values of concentrations
methane
ethane
propane
total of butanes
Values of C_2/C_3 ratio
< 2.0
2.0 - 3.4
>3.4
Anomalous zones
Values of $C_2/C_{2=}$ ratio
< 1.4
1.4 - 3.3
3.3 - 4.8
>4.8
Depth (m b.s.l.)
SW
NE
Silesian and Subsilesian nappes
Skole Nappe
Gr-Za
Sł-Ja
Ww-Ba
tD
TW-Cz
Ro-Lk
Kre-St
Ch-Ki
Le-Kr
1.5 km

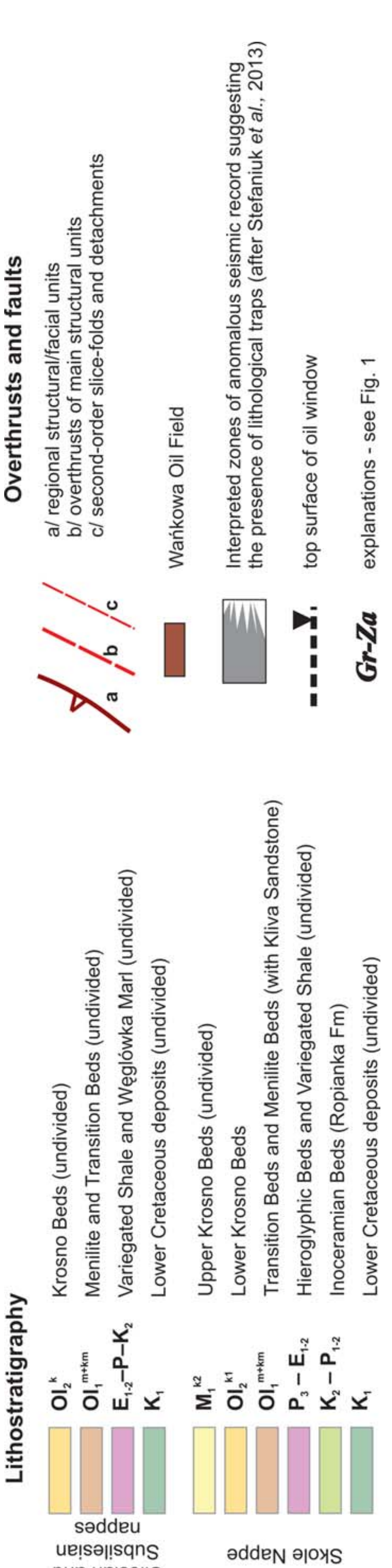


Fig. 7. Changes of normalized (**A**) and measured (**B**) concentrations of hydrocarbons detected in soil-gas samples collected along the geological-seismic cross-section (**C**). Geological interpretation after Kuśmierek *et al.* (2013).

turn, indicates differences in characters and depths of parent hydrocarbon accumulations.

Anomalous Zone No. 1 is located in the southwestern part of the cross-section, between sampling sites nos. 9 and 19 (length: 900 m). Methane concentrations exceed 80 ppm (Sampling Site no. 15) and alkanes C_2-C_5 concentrations reach 0.4 ppm (Fig. 7). Values of C_2/C_3 ratio indicate hydrocarbon migration from gas-condensate accumulations. In this zone, active microseepage of hydrocarbons prevails, as documented by the relatively high values of $C_2/C_{2=}$ ratio (Fig. 7). The wide range and contrasting character of this zone may indicate the presence of a relatively shallow hydrocarbon accumulation, presumably poorly sealed, owing to the advanced erosion of the Grabownica-Załuż Anticline.

Anomalous Zone No. 2 is located between sampling sites nos. 58 and 63 (length: 400 m). Here, maximum concentrations of methane and total alkanes C_2-C_5 (sampling site no. 59) are: 11.3 and 0.43 ppm, respectively (Fig. 7). Relationships between ethane and propane reflected in the C_2/C_3 ratio indicate hydrocarbon dispersion from oil-condensate accumulations, whereas the variability of $C_2/C_{2=}$ values implies the variable character of hydrocarbon seepage. The extremely high concentration of alkanes detected at sampling site no. 59 together with high amounts of propane and butane may indicate very active migration of alkanes along the overthrust of the Dźwiniacz Dolny slice fold, which displaces the top surface of oil generation window (Fig. 7).

Anomalous Zone No. 3 was found over the Wańkowa Oil Field. Relatively low anomalous concentrations of alkanes C_2-C_5 over the oil reservoirs located at depths of 100 to 750 m result from intensive and long-lasting (over 130 years) exploitation of this deposit and, probably, also from the effective sealing of oil traps in pinch-out zones of the Kliva Sandstone (Fig. 3). Such a concept is confirmed by the amount of oil production and the lack of oil seepages in this zone, so common in the outcrops of the Kliva Sandstone located close to the state border.

In Anomalous Zone No. 3, a very high, single concentration of methane was found (4,250 ppm). The relationships between methane and its higher homologues illustrated by an $C_1/\Sigma(C_2$-$C_5)$ ratio over 1,000 points to the diverse character of deep-seated hydrocarbon accumulations. The authors suggest that the surface geochemical signature may result from hydrocarbon dispersion from both the known oil deposit and from an undiscovered, gas or gas-condensate accumulation located deeper, in older reservoirs forming the hinge of the Ropienka-Łodyna Mine Anticline. An example might be the Łodyna Oil Field in which production comes also from gas-saturated Eocene sandstones.

Anomalous Zone No. 4 is located in the central part of the cross-section, between the sampling sites nos. 44 and 50. Maximum concentrations of methane and total alkanes C_2-C_5 (6.3 and 0.136 ppm, respectively) were detected at sampling site no. 49. These values are distinctly lower than those in the remaining anomalous zones described earlier. The changes of raw concentrations of methane and its higher homologues seen in distribution plots are left-skewed. Such a pattern may result from the impact of an inclined fault or overthrust surface on the direction of hydrocarbon migration. The distinct dominance of ethane over ethylene indicates an active microseepage of alkanes from source accumulations located at greater depths. During a seepage of this kind, alkanes are much strongly affected by selective differentiation and, thus, in the near-surface zone there are anomalies depleted in the heavier homologues. In this anomalous zone, butanes are practically absent and the remaining alkanes are depleted in relation to methane. It must be emphasized that the Anomalous Zone No. 4 is connected with the oil-generative kitchen located in the hinge of the Słonne-Jałowe Syncline through the outcrops of Early Palaeogene sediments that are referable to the Wańkowa Village-Bandrów Anticline. This kitchen is proposed as the source of the migrating hydrocarbons.

CONCLUSIONS

The results of a surface geochemical survey completed along the experimental 7-05-10K seismic profile, integrated with the results of seismic-based interpretation of deep tectonics of petroleum horizons, enabled the authors to conclude that:

1. The microconcentrations of hydrocarbons detected in 94 soil-gas samples collected along the geochemical line of sampling are highly variable. The greatest differences were found in methane concentrations: from 0.8 to 4250.0 ppm. Extreme methane concentrations detected in one sample result from recent biochemical processes operating in the soil.

2. The statistical analysis of geochemical indices indicates the dominance of active hydrocarbon dispersion from condensate and/or parent accumulations of oil located at various depths.

3. The distribution of the geochemical anomalies generally was controlled by anticlinal uplifts of Early Palaeogene (Early Paleocene–Oligocene) sediments and by overthrusts displacing these strata. In the buried hinge of the Tyrawa Wołoska-Czerenina Syncline, these sediments have entered an advanced stage of oil generation. The oil generated was then reservoired, among others, in traps of the Wańkowa Oil Field. In the Słonne-Jałowe Syncline, the sedimentary strata probably have attained only an initial generative stage and in the Kreców-Stebnik Syncline a generative stage has not been accomplished owing to the insufficient burial depth of the source rocks.

4. The relatively low, anomalous concentrations of alkanes C_2-C_5 over the oil horizons of the Wańkowa deposit located at depths from 100 to 750 m are related to the effective sealing of hydrocarbon traps and/or the relatively low pressure caused by the production of oil over a period of 130 years. However, the surface geochemical signature in this area also may have originated from the migration of hydrocarbons from yet undiscovered, deeper-seated gas or gas-condensate accumulation. The authors suggest that such accumulations may occur in older reservoirs, located in the hinge of the Ropienka-Łodyna Mine Anticline.

5. The active dispersion of hydrocarbons over the Wańkowa Village-Bandrów and Grabownica-Załuż anticlines can be explained by their tectonic disturbances, including the known overthrusts displacing both structures and also by still operating hydrocarbon generation and migration processes observed in many wells. Another possibility is the occurrence of shallow hydrocarbon accumulations.

Summing up, the authors recommend further, supplementary geochemical studies in the Wańkowa area. Such a survey might be run along the two parallel lines adjacent to the 7-05-10K seismic profile and along perpendicular lines crossing the anomalous zones.

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