

MOLECULAR AND ISOTOPIC COMPOSITIONS OF GASES ADSORBED TO NEAR SURFACE SEDIMENTS AT STARUNIA PALAEOONTOLOGICAL SITE AND VICINITY (CARPATHIAN REGION, UKRAINE)

Marek DZIENIEWICZ, Henryk SECHMAN & Maciej J. KOTARBA

Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland, e-mail: dzieniew@agh.edu.pl

Dzieniewicz, M., Sechman, H. & Kotarba, M. J., 2009. Molecular and isotopic compositions of gases adsorbed to near surface sediments at Starunia palaeontological site and vicinity (Carpathian region, Ukraine). *Annales Societatis Geologorum Poloniae*, 79: 421–437.

Abstract: The near-surface geochemical survey of gases desorbed from sediment samples was carried out in the area of an abandoned ozokerite mine in Starunia, where remnants of mammoth and three woolly rhinoceroses and one almost completely preserved rhinoceros carcass were discovered in 1907 and 1929. Numerous hydrocarbon seeps (gas and oil “eyes”) occur on the surface of the study area. Analyses of molecular and stable carbon isotope compositions of adsorbed gases were carried out in two variants. The first included sampling of cuttings from 30 auger boreholes at depths of 4.8, 5.6 and 6.4 m. In total, 88 samples were collected. In the second variant core samples were collected from 17 selected boreholes. In total, 78 samples were taken from various depths to 12 m. The results of molecular composition analyses of desorbed gases indicated high saturation of near-surface sediments with the oil. The highest concentrations of alkanes were detected in Miocene strata. Hydrocarbon migration from deep accumulations to the surface was relatively fast and proceeded along the faults, fractures and cracks. In the near-surface zone hydrocarbons were subjected to oxidation and dehydrogenation, which resulted in generation of unsaturated hydrocarbons and hydrogen. These processes were most intensive in the Pleistocene sediments and in the mine dumps. Increased concentrations of hydrogen may also originate from water radiolysis in the presence of hydrocarbons. Concentrations of carbon dioxide in the adsorbed gases show the higher values in comparison with the analysed gaseous compounds. However, a slight increase in CO₂ concentration was detected in the mine dump, which may indicate conditions more favourable for hydrocarbon oxidation. Carbon dioxide from the analysed adsorbed gases is of thermogenic origin. Occasionally, insignificant influence of secondary hydrocarbon oxidation and/or Quaternary organic matter can be observed. Concentrations of alkanes, alkenes and carbon dioxide in the gas derived from desorption of rock samples are lower and the concentration of hydrogen is higher than those measured in free gases. This indicates that additional effects from recent (*e.g.* microbial) processes are absent.

Key words: near-surface geochemical survey, adsorbed gases, origin of gaseous hydrocarbons, origin of carbon dioxide, Quaternary sediments, Starunia palaeontological site, Carpathian region, Ukraine.

Manuscript received 6 May 2009, accepted 7 October 2009

INTRODUCTION

At the end of the 19th and in the first half of the 20th centuries ozokerite (earth wax) was mined in the Starunia area, about 130 kilometres southeast of Lviv, Ukraine (Fig. 1), from the Miocene Vorotyscha beds of the Boryslav-Pokuttya Unit of the Carpathian Foredeep (Alexandrowicz, 2004, 2005; Koltun *et al.*, 2005). In 1907, remnants of mammoth and woolly rhinoceros were found in No. 4 (“Mammoth”) shaft of the ozokerite mine at depths of 12.5 and 17.6 m, respectively. In 1929, in a special shaft sunk at the expense of the Polish Academy of Arts and Sciences, a unique, almost fully preserved woolly rhinoceros was found

at 12.5 m depth, within the Pleistocene sediments saturated with oil and brine (Kotarba, 2002; Alexandrowicz, 2004, 2005; Kubiak & Drygant, 2005).

Studies on variability of concentrations of gaseous *n*-alkanes, gaseous alkenes and carbon dioxide as well as stable carbon isotope composition of carbon dioxide from gases adsorbed in the near-surface zone were a part of an interdisciplinary research project carried out in the years 2006–2009 at the Starunia palaeontological site (Kotarba, 2009). General information covering the history of the area, the details of geology and the results of earlier research were re-

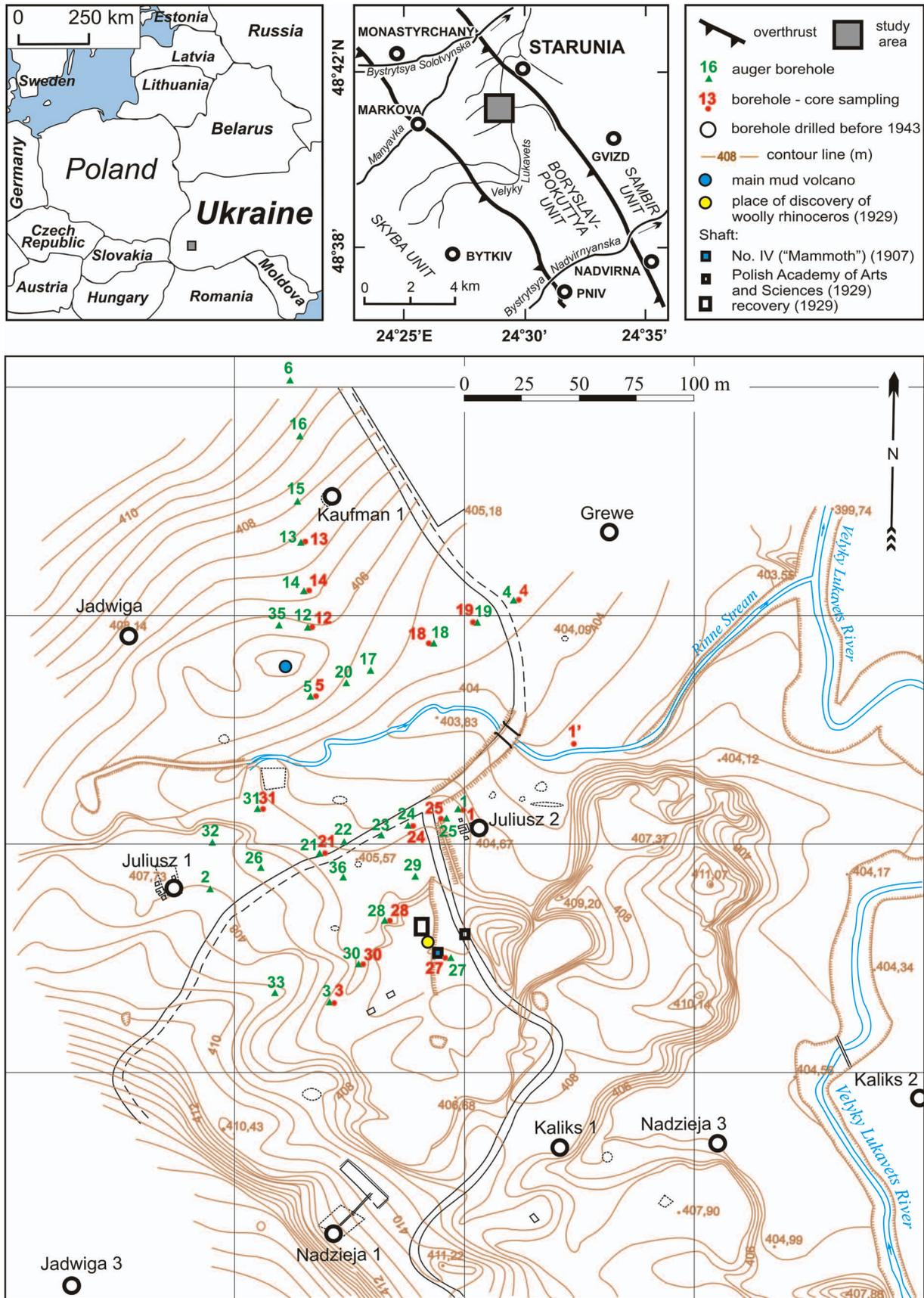


Fig. 1. Sketch map of the Starunia palaeontological site and surrounding area (Carpathian region, Ukraine) with the location of auger drillings and boreholes

ported on in a special monograph (Kotarba, *ed.*, 2005) and in recent publications (Kotarba *et al.*, 2008a; Kotarba & Stachowicz-Rybka, 2008; Sokołowski *et al.*, 2009; Sokołowski & Stachowicz-Rybka, 2009; Stachowicz-Rybka *et al.*, 2009) and in references therein.

In 2004, a preliminary soil gas geochemical survey was carried out in the area of the abandoned ozokerite mine at Starunia (Kotarba *et al.*, 2005, 2008b), and in 2007 a detailed soil gas geochemical survey was completed (Sechman *et al.*, 2009). The results of geochemical research together with combined geoelectric (Mościcki, 2009) and microgravity surveys (Porzucek & Madej, 2009a, b) enabled the authors to select the zones suitable for a detailed, deeper geochemical survey. In total, 30 measurement sites were selected for the near-surface geochemical survey down to 4 m depth (Kotarba *et al.*, 2009). At the same sites geochemical research was undertaken at selected depths of 4.8, 5.6 and 6.4 m. Analysed were gases adsorbed in rocks from the near-surface zone. Samples were taken from cuttings derived from auger drillings. Moreover, core samples for adsorbed gases analyses were collected from 17 selected boreholes down to 12 m depth.

The main objective of this study was to determine the composition and concentration of gaseous *n*-alkanes, alkenes, carbon dioxide and hydrogen in gas samples desorbed from sediment collected from depths down to 12 m. Moreover, these samples were analysed also for stable carbon isotope composition of carbon dioxide. The results enabled the authors to evaluate the spatial distribution of concentrations of analysed gases. These results supplement the geochemical analyses performed with free gas method (Sechman *et al.*, 2009; Kotarba *et al.*, 2009). The comparison of both variants enables for a more detailed geochemical characteristic of near-surface zone and the processes occurring there. This should enable one to define the environment in which the Pleistocene vertebrates died and were preserved.

METHODS

Field work and sampling procedure

Field geochemical studies of adsorbed gases were carried out in June and October, 2007, and included sampling of cuttings and drill cores. Under the notion of “adsorbed gases” we should understand a gas bounded with adsorption forces, in the form of an inclusion and also accumulations in inter-grain macro- and mezzo-pores.

Cuttings were sampled in 30 selected 70 mm diameter auger boreholes. Samples (100 g each) were taken from depths of 4.8, 5.6 and 6.4 m. In total, 88 samples were collected.

Drill cores were sampled in 17 selected boreholes (Nos 1, 1', 3, 4, 5, 12, 13, 14, 18, 19, 21, 24, 25, 27, 28, 30 and 31) drilled with the UGB-50 vibratory probe (diameter 12 cm). Planned sampling depths: 0, 2, 4, 6, 8, 9, 10, 11 and 12 m sometimes were modified due to lithology of penetrated rocks and drill-core recovery. In total, 78 such samples were taken.

Generally, the sampled cuttings and cores represented: Quaternary clayey muds and coarse clastic rocks saturated with bitumen, mine dump (waste), and Miocene rocks in the form of clayey muds, sandstone-claystone breccia with halite, potassium-salt, gypsum and calcite layers, and veins of ozokerite.

The collected samples were transported to the AGH University of Science and Technology in Kraków, Poland, for degassing and laboratory analyses.

Laboratory procedure

Both the cuttings and the drill core samples were subjected to thermal-vacuum degassing combined with mechanical granular disintegration.

For degassing 30 g of rock, the sample was placed in a glass box and saturated NaCl solution was added. The box was then tightly closed with a rubber plug and connected to a special vacuum pump which produced -0.7 MPa underpressure. Simultaneously, the box was heated to hard red radiation. During degassing which lasted 15 minutes the sample was continuously disintegrated with the magnetic agitator. The released gas filled the chamber of the pump and a proper amount was collected for chromatographic analysis.

Analytical methods

Gas samples were analysed chromatographically for concentrations of alkanes (methane, ethane, propane, *i*-butane, *n*-butane, *neo*-pentane, *i*-pentanes and *n*-pentane), alkenes (ethylene, propylene, and 1-butene), hydrogen and carbon dioxide. A total of 166 gas samples were studied, which gave 2,158 single chromatographic analyses.

Analyses were carried on using the FISSONS Instruments GC 8160 and the Carlo Erba Instruments GC 6300 devices. The analytical procedure was consistent with that published by *e.g.* Sechman and Dzieniewicz (2007) and Sechman *et al.* (2009).

For stable carbon isotope analyses carbon dioxide was isolated chromatographically and then transmitted to a Finnigan Delta Plus mass spectrometer. Results were presented in δ -notation relative to the PDB standard. Analytical precision is estimated to be ± 0.2 ‰.

Statistical procedure

The measured concentrations of gaseous hydrocarbons, hydrogen and carbon dioxide together with isotopic composition data $\delta^{13}\text{C}(\text{CO}_2)$ (only for cutting samples) were characterized by means of principal statistical parameters (minimum and maximum values, medians, arithmetic means, number of samples over detection limits, standard deviations and percentages of samples in selected concentration classes). These parameters were determined and calculated separately for each analysed component and, additionally, for total concentrations of gaseous hydrocarbons heavier than methane (total $\text{C}_2\text{-C}_5$ alkanes), for total concentrations of gaseous alkenes $\text{C}_2\text{-C}_4$ as well as for the carbon dioxide/methane index $\{\text{CDMI} = [\text{CO}_2/(\text{CO}_2 + \text{CH}_4)] 100 (\%) \}$

and the hydrocarbon index [$C_{HC} = CH_4/(C_2H_6 + C_3H_8)$] ratios. Moreover, statistical parameters were determined separately for concentrations of compounds in gases desorbed from cuttings and from drill cores.

Populations of methane, total C₂-C₅ alkanes, total C₂-C₄ alkenes, carbon dioxide and hydrogen concentrations measured in gases desorbed from cuttings and drill cores were processed and maximum values, arithmetic means and medians were calculated. Additionally, for samples from cuttings, statistical parameters were calculated separately for each sampling depth: 4.8, 5.6 and 6.4 m. For core samples statistical parameters were calculated for each identified lithostratigraphic horizon.

Qualitative evaluation of all measured methane, total C₂-C₅ alkanes, total alkenes C₂-C₄, carbon dioxide and hydrogen concentrations was based upon probability plots drawn separately for gases derived from cuttings and from core samples. In each plot boundaries between distinctive subsets were marked for each studied set of concentrations. Boundary values were determined graphically from the visible slope changes of particular curves. The boundary values of subsets were then applied as values of contour lines in distribution maps of methane, total C₂-C₅ alkanes, total alkenes C₂-C₄, carbon dioxide and hydrogen concentrations. Such maps were constructed for each sampling depth (4.8, 5.6 and 6.4 m) and for the distinguished lithostratigraphic horizons. For the latter, averaged values were calculated for a given horizon in a particular well. For gases derived from cuttings the surface distribution of $\delta^{13}C(CO_2)$ was drawn, as well.

Selected examples of changes in concentrations of hydrocarbons, carbon dioxide and hydrogen with the depth were plotted against the lithological columns.

RESULTS AND DISCUSSION

Analyses of gas samples desorbed from cuttings

The analysed gases obtained from 4.8, 5.6 and 6.4 m sampling depths vary in their molecular compositions and gas indices within the following ranges (Tables 1, 2): CH₄ from 1.99 to 346 ppm (mean 10.1 ppm), total C₂-C₅ alkanes from 0.29 to 6,550 ppm (mean 279 ppm), of which C₂H₆ from 0 to 1,340 ppm (mean 18.9 ppm), C₃H₈ from 0.015 to 1,510 ppm (mean 40.3 ppm), *i*-C₄H₁₀ from 0 to 582.3 ppm (mean 24.1 ppm), *n*-C₄H₁₀ from 0.029 to 1,340 ppm (mean 74.2 ppm), *neo*-C₅H₁₂ from 0 to 7.3 ppm (mean 0.43 ppm), *i*-C₅H₁₂ from 0.15 to 1,070 ppm (mean 77 ppm) and *n*-C₅H₁₂ from 0 to 700 ppm (mean 43.9 ppm), total C₂-C₄ alkenes from 0 to 2.48 ppm (average 0.128 ppm), CO₂ from 0.175 to 0.523 vol% (mean 0.302 vol%), H₂ from 0 to 0.726 vol% (mean 0.023 vol%), C_{HC} from 0.07 to 196.5 (mean 13.1), CDMI from 88.1 to 99.9 (mean 99.7), and $\delta^{13}C(CO_2)$ from -14.8 to -8.8‰.

Among analysed concentrations and indices attention should be paid to relatively high variability of total C₂-C₅ alkanes concentrations compared to those of methane. Also characteristic is the increase of mean concentrations of homologues with the increasing number of carbon atoms in the molecule (Table 1). This may indicate pollution of rocks with oil and a higher adsorption potential of the environment for larger hydrocarbon molecules (Karcev *et al.*, 1954; Starobiniec, 1986). Small amount of alkenes in relation to alkanes points to relatively high migration rate of hydrocarbons towards the surface (Saunders *et al.*, 1999). Limited range of carbon dioxide concentrations together with almost identical values of median and arithmetic mean indicate that in this population anomalous values are rare, contrary to the concentrations of hydrogen (Table 2). Anomalous concen-

Table 1

Principal statistical parameters of alkanes concentrations and hydrocarbon index for adsorbed gas of cuttings sampled at depths of 4.8, 5.6 and 6.4 m

Statistical parameters	Unit	CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>neo</i> -C ₅ H ₁₂	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂	Total C ₂ -C ₅ alkanes	C _{HC} **
Minimum	(ppm)	1.99	0.0	0.015	0.0	0.029	0.0	0.15	0.0	0.29	0.07
Maximum	(ppm)	346.0	1340.0	1510.0	582.3	1340.0	7.3	1070.0	700.0	6550.0	196.5
Median	(ppm)	3.26	0.08	2.38	6.08	10.36	0.04	18.3	9.36	53.47	1.48
Mean	(ppm)	10.1	18.9	40.3	24.1	74.2	0.43	77.0	43.9	279.0	13.1
Standard deviation	(ppm)	37.0	143.0	168.0	68.4	190.0	1.1	170.0	107.0	790.0	28.8
Number of samples*		88	68	88	85	88	48	88	86	88	88
Percentage of samples	(%)	100.0	77.3	100.0	96.6	100.0	54.5	100.0	97.7	100.0	100.0

* – number of samples with concentration of component over detection limit

$$** - C_{HC} = \frac{CH_4}{C_2H_6 + C_3H_8}$$

Table 2

Principal statistical parameters of alkenes, carbon dioxide and hydrogen concentrations, carbon dioxide – methane index and stable carbon isotope composition of carbon dioxide for adsorbed gas of cuttings sampled at depths of 4.8, 5.6 and 6.4 m

Statistical parameters	Unit	C ₂ H ₄	C ₃ H ₆	1-C ₄ H ₈	Total C ₂ -C ₄ alkenes	CO ₂ **	H ₂ **	CDMI***	δ ¹³ C (CO ₂) [#]
Minimum	(ppm)	0.0	0.0	0.0	0.0	0.175	0.0	88.10	-14.8
Maximum	(ppm)	1.19	0.78	1.70	2.48	0.523	0.726	99.93	-8.8
Median	(ppm)	0.0	0.0	0.0	0.034	0.296	0.011	99.88	-11.3
Mean	(ppm)	0.032	0.030	0.066	0.128	0.302	0.023	99.66	-11.2
Standard deviation	(ppm)	0.132	0.093	0.230	0.348	0.064	0.077	1.27	1.4
Number of samples*		41	40	26	68	88	67	88	53
Percentage of samples	(%)	46.6	45.5	29.5	77.3	100	76.1	100	60.2

* – number of samples with concentration of component over detection limit; ** – minimum, maximum, median, mean and standard deviation values in vol%

*** – $CDMI = \frac{CO_2}{CO_2 + CH_4} \times 100\%$; # – minimum, maximum, median, mean and standard deviation values in %

trations of hydrogen result also from radiolysis of water at the presence of hydrocarbons (Hawkes, 1972; Starobiniec, 1986).

Methane concentrations can be divided into four sub-sets, in which values over 8 ppm can be regarded as anomalous (Fig. 2A). For total alkanes C₂-C₅ six such sub-sets were distinguished and 20 ppm concentration was taken as threshold value for anomalies (Fig. 2B). Cumulative curve for total alkenes C₂-C₄ concentrations revealed 0.2 ppm as threshold of anomalous values (Fig. 2C). Finally, for hydrogen the anomalous threshold concentration was 0.017 vol% (Fig. 2D) and for carbon dioxide it was 0.37 vol% (Fig. 2E).

Generally, concentrations of both methane and total alkanes C₂-C₅ show increasing trends with depth, whereas the alkenes and hydrogen concentrations trend to decrease. Carbon dioxide concentrations show only minor changes with depth; maximum values oscillate around 0.5 vol%, whereas means and medians are about 0.3 vol% each (Table 3). Such relationships indicate that hydrocarbons ascending from the depth towards the surface are subjected to oxidation and dehydrogenation (Morrison & Boyd, 1983).

The lateral distribution of concentration of analysed gases at depths of 4.8, 5.6 and 6.4 m is presented in Figures 3 to 8. The ranges are chosen according to subsets marked in Fig. 2. The number of sites with anomalous methane concentration (over 8 ppm) increases with depth (Fig. 3A, B, C). The highest number of sites with anomalous concentration of total C₂-C₅ alkanes (over 20 ppm) occurs at a depth of 5.6 m (Fig. 4B), while concentration of total C₂-C₄ alkenes over 0.2 ppm occurs most commonly at a depth of 4.8 m (Fig. 5A). The highest number of sites with anomalous concentration of hydrogen (over 0.017 vol%) occurs at a depth of 4.8 m (11 sampling sites) whereas the lowest – at a depth of 6.4 m (9 sampling sites) (Fig. 6A, C). The anoma-

Table 3

Principal statistical parameters of alkanes, alkenes, hydrogen and carbon dioxide concentrations and stable carbon isotope composition of carbon dioxide for adsorbed gas of cuttings sampled at depths of 4.8, 5.6 and 6.4 m

Component	Depth (m)	No. of samples	Maximum (ppm)	Mean (ppm)	Median (ppm)
Methane	4.8	30	33.9	5.5	3.4
	5.6	30	41.2	7.9	3.2
	6.4	28	346.0	17.3	3.2
Total C ₂ -C ₅ alkanes	4.8	30	2410.0	247.0	47.1
	5.6	30	1920.0	220.7	47.9
	6.4	28	6550.0	375.2	58.1
Total C ₂ -C ₄ alkenes	4.8	30	2.5	0.237	0.050
	5.6	30	0.37	0.050	0.027
	6.4	28	1.7	0.111	0.035
			(vol%)	(vol%)	(vol%)
Hydrogen	4.8	30	0.73	0.039	0.011
	5.6	30	0.051	0.015	0.011
	6.4	28	0.072	0.015	0.009
Carbon dioxide	4.8	30	0.456	0.302	0.299
	5.6	30	0.523	0.305	0.298
	6.4	28	0.494	0.298	0.294
			(‰)	(‰)	(‰)
δ ¹³ C (CO ₂)	4.8	12	-8.8	-10.7	-10.5
	5.6	13	-9.1	-11.6	-11.8
	6.4	28	-8.9	-11.2	-11.3

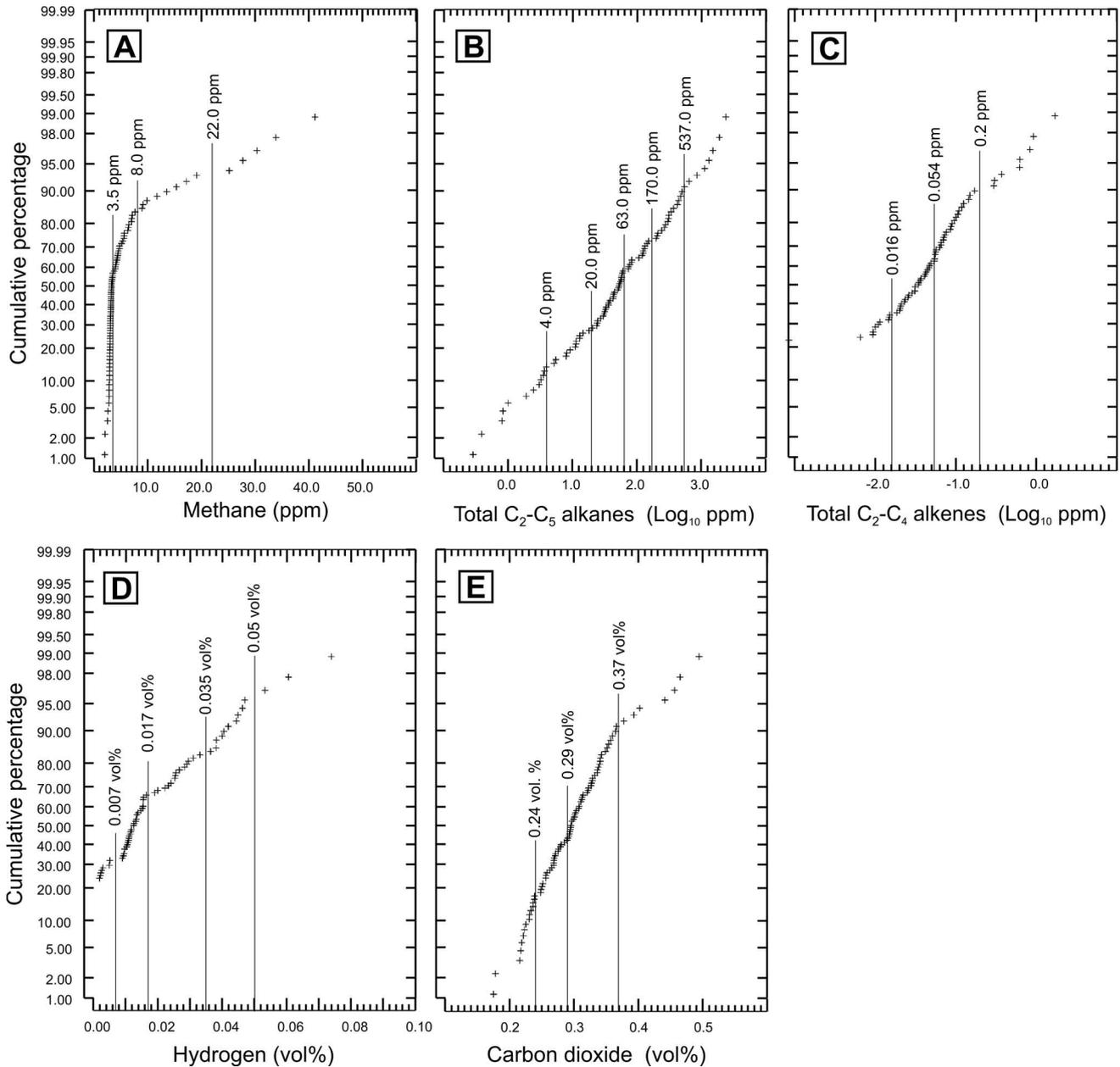


Fig. 2. Cumulative frequency diagrams of (A) methane, (B) total C₂-C₅ alkanes, (C) total C₂-C₄ alkenes, (D) hydrogen and (E) carbon dioxide concentrations measured in adsorbed gas of cuttings sampled at depths of 4.8, 5.6 and 6.4 m

lous concentration of CO₂ (over 0.37 vol%) at a depth of 4.8 m was found at 4 sampling sites, while at the depths of 5.6 m and 6.4 m the anomalies were observed at 3 sampling sites (Fig. 7A, B, C).

The lateral distributions presented above generally support the earlier observations, according to which concentration of methane and total alkanes C₂-C₅ reveals increasing trends with the depth, concentration of alkenes and hydrogen demonstrates decreasing trends, whereas concentration of carbon dioxide remains relatively stable.

As mentioned above, values of the hydrocarbon (C_{HC}) index, carbon dioxide/methane (CDMI) index and $\delta^{13}\text{C}(\text{CO}_2)$ of adsorbed gas of cuttings collected from 4.8, 5.6 and 6.4 m sampling depths vary in narrow ranges (Tables 1, 2). For comparison, values of hydrocarbon index,

carbon dioxide/methane index and $\delta^{13}\text{C}(\text{CO}_2)$ of “free” gases collected from 0.8, 1.6, 2.4, 3.2 and 4.0 m sampling depths (Kotarba *et al.*, 2009) vary within the following ranges: C_{HC} from 2.6 to 94,252 (mean 1,168, difference 94,247, 150 samples), CDMI from 1.8 to 99.8 (mean 63.8, difference 98.0, 150 samples), and $\delta^{13}\text{C}(\text{CO}_2)$ from -20.1 to 24.3‰ (mean -8.0‰, difference 44.4‰, 63 samples). These results demonstrate that values of the two gas indices and the stable carbon isotope ratio are always considerably higher for free gases than for adsorbed gases. Small changes of $\delta^{13}\text{C}(\text{CO}_2)$ values of adsorbed gases with the sampling depth from 4.8 through 5.6 to 6.4 m (Table 2, Fig. 8A, B, C) indicate that carbon dioxide is of thermogenic origin and only occasionally insignificant influence of secondary oxidation of hydrocarbons and/or Quaternary organic matter

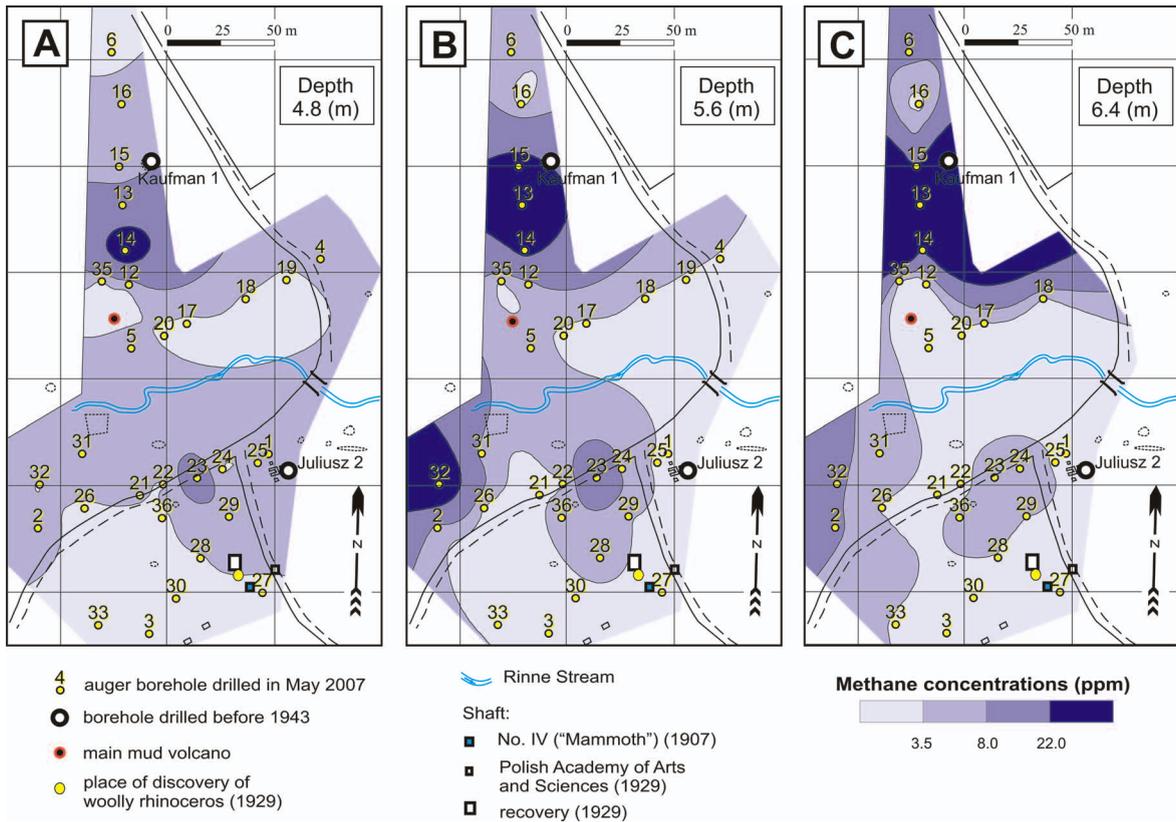


Fig. 3. Contour maps of methane concentrations in adsorbed gas of cuttings sampled at depths of (A) 4.8 m, (B) 5.6 m, and (C) 6.4 m

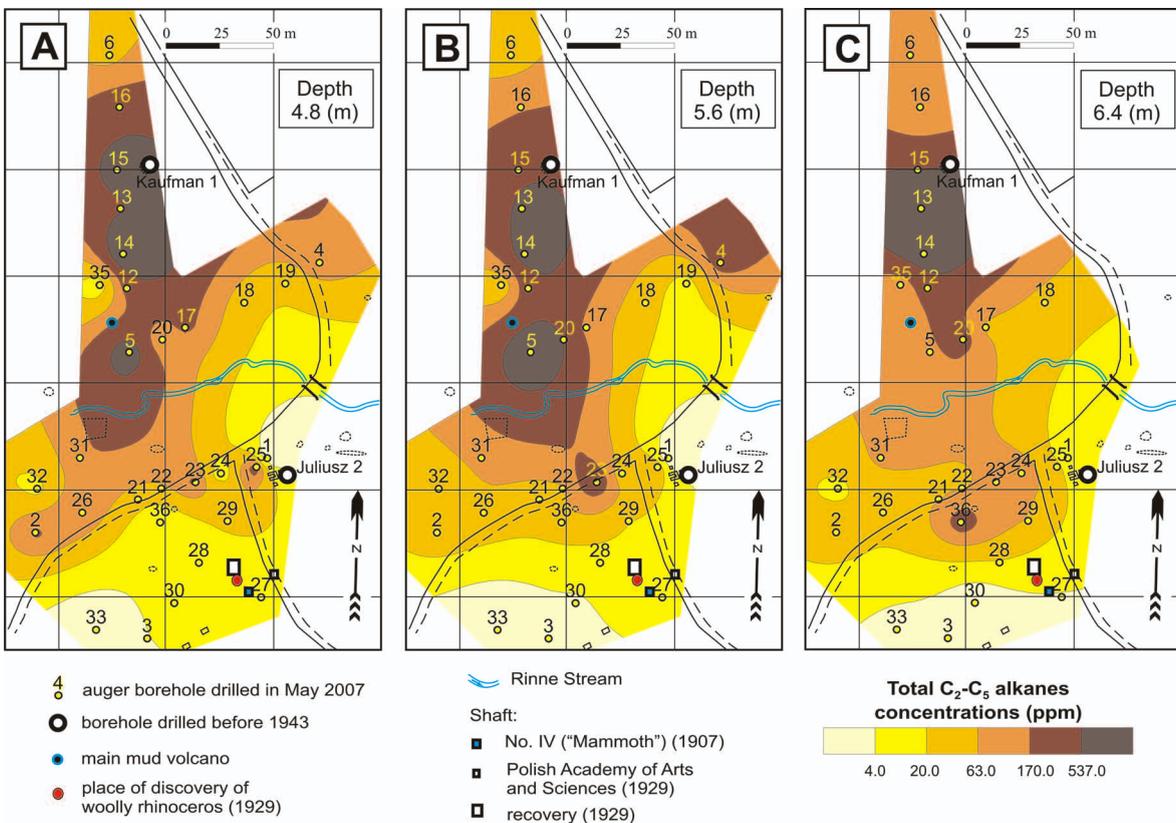


Fig. 4. Contour maps of total C₂-C₅ alkanes concentrations in adsorbed gas of cuttings sampled at depths of (A) 4.8 m, (B) 5.6 m, and (C) 6.4 m

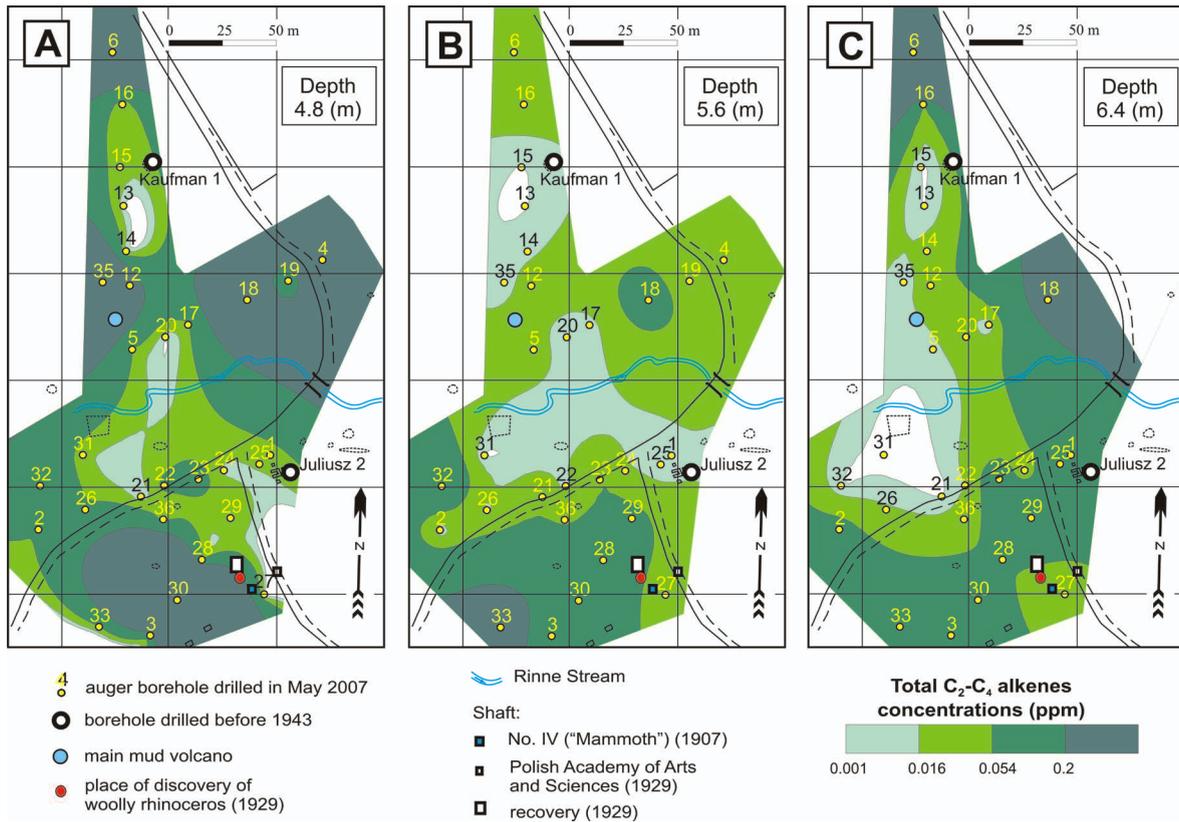


Fig. 5. Contour maps of total C₂-C₄ alkenes concentrations in adsorbed gas of cuttings sampled at depths of (A) 4.8 m, (B) 5.6 m, and (C) 6.4 m

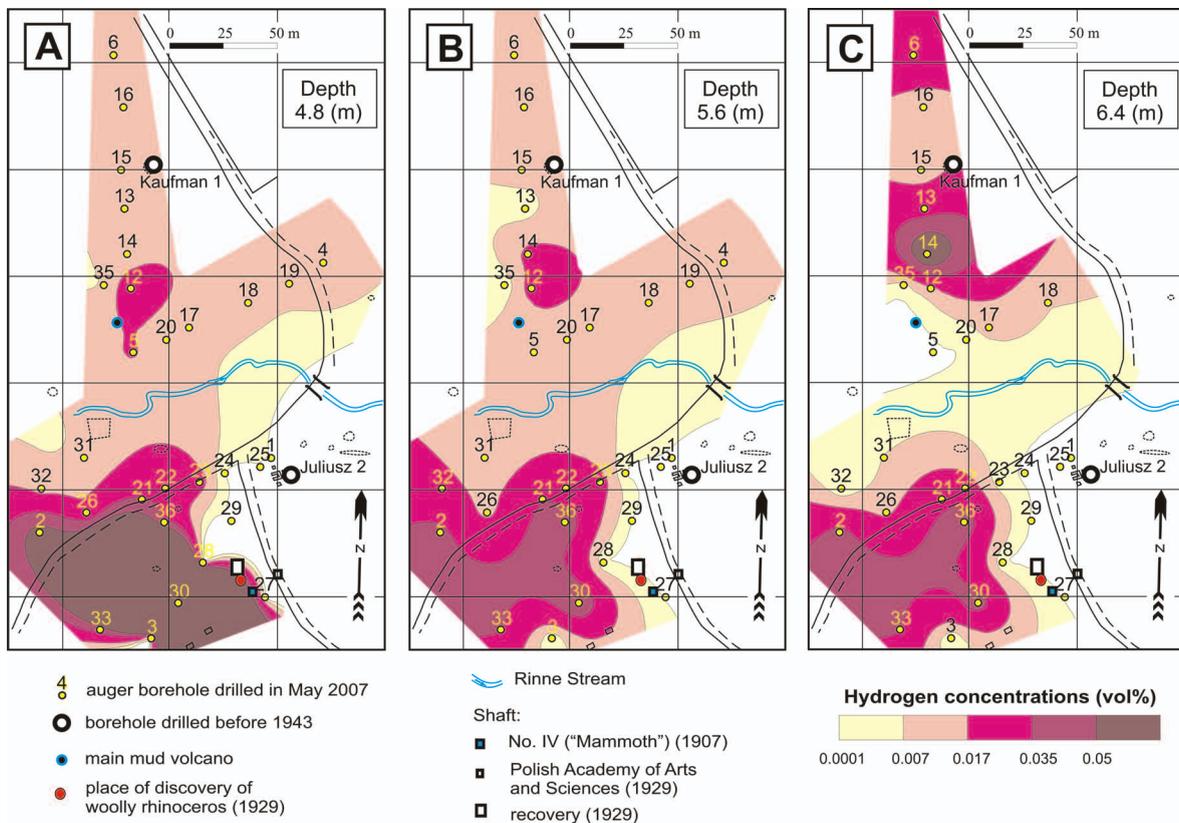


Fig. 6. Contour maps of hydrogen concentrations in adsorbed gas of cuttings sampled at depths of (A) 4.8 m, (B) 5.6 m, and (C) 6.4 m

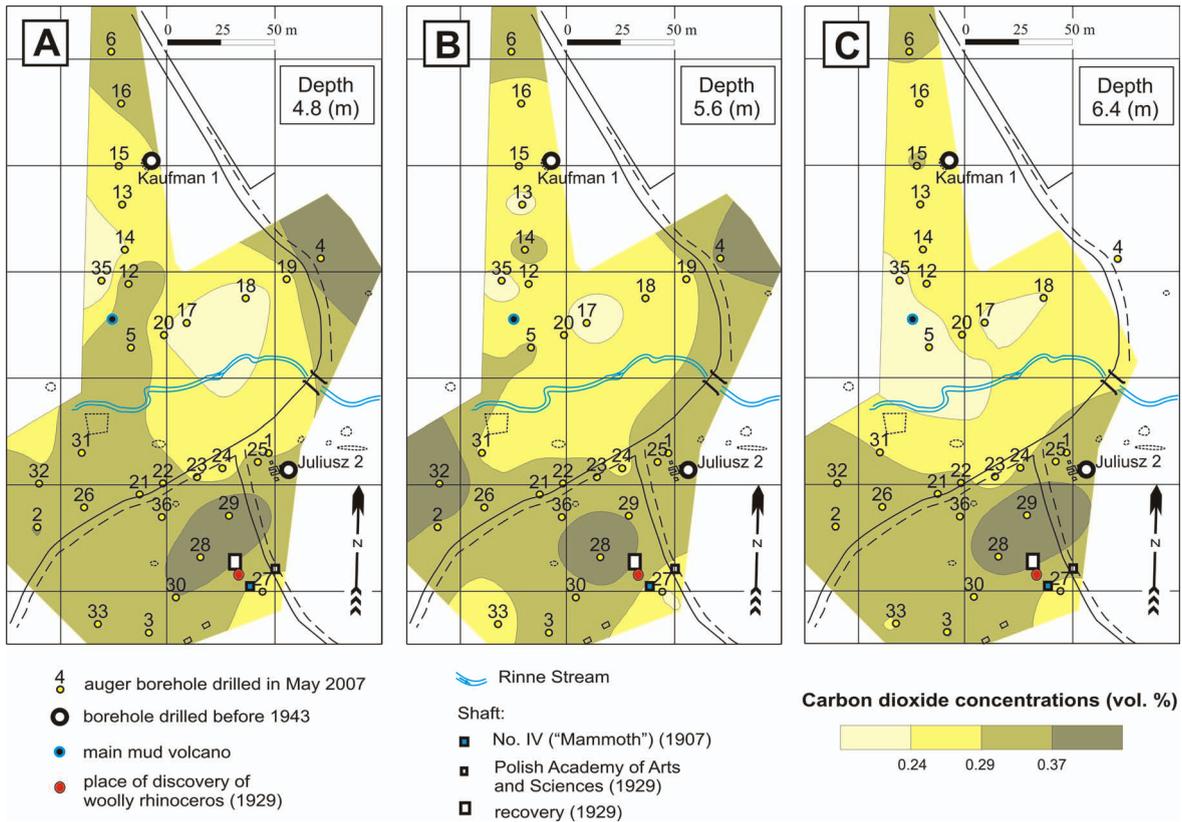


Fig. 7. Contour maps of carbon dioxide concentrations in adsorbed gas of cuttings sampled at depths of (A) 4.8 m, (B) 5.6 m, and (C) 6.4 m

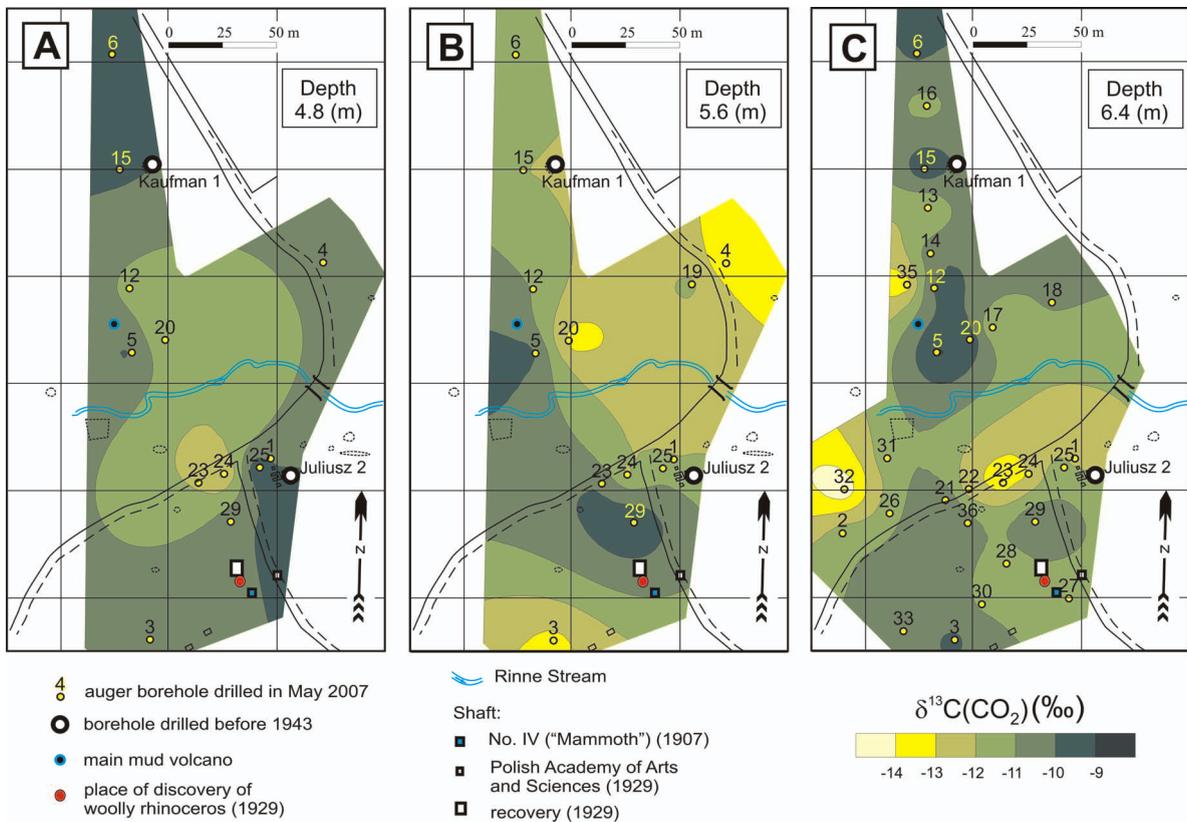


Fig. 8. Contour maps of $\delta^{13}\text{C}(\text{CO}_2)$ values in adsorbed gas of cuttings sampled at depths of (A) 4.8 m, (B) 5.6 m, and (C) 6.4 m

Table 4

Principal statistical parameters of alkanes concentrations for adsorbed gas of core samples collected down to 12 m depth

Statistical parameters	Unit	CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>neo</i> -C ₅ H ₁₂	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂	Total C ₂ -C ₅ alkanes	C _{HC} **
Minimum	(ppm)	0.27	0.0	0.0	0.012	0.0	0.0	0.103	0.009	0.239	0.3
Maximum	(ppm)	9.91	0.358	12.3	23.7	85.2	0.497	230.0	162.0	505.0	433.0
Median	(ppm)	4.78	0.030	0.106	0.347	0.947	0.0	3.55	1.83	7.0	34.7
Mean	(ppm)	5.19	0.046	0.77	2.06	5.28	0.032	11.6	6.48	26.3	50.6
Standard deviation	(ppm)	1.59	0.059	2.03	4.33	12.7	0.082	28.3	19.3	63.4	65.8
Number of samples *		78	68	75	78	77	29	78	78	78	78
Percentage of samples	(%)	100	87.2	96.2	100.0	98.7	37.2	100.0	100.0	100.0	100.0

* – number of samples with concentration of component over detection limit

$$** - C_{HC} = \frac{CH_4}{C_2H_6 + C_3H_8}$$

Table 5

Principal statistical parameters of alkenes, carbon dioxide and hydrogen concentrations and carbon dioxide – methane index for adsorbed gas of core samples collected to 12 m depth

Statistical parameters	Unit	C ₂ H ₄	C ₃ H ₆	1-C ₄ H ₈	Total C ₂ -C ₄ alkenes	CO ₂ **	H ₂ **	CDMI***
Minimum	(ppm)	0.0	0.0	0.0	0.016	0.14	0.0	99.5
Maximum	(ppm)	1.21	1.28	0.952	3.44	1.05	3.0	100.0
Median	(ppm)	0.060	0.032	0.034	0.136	0.26	0.076	99.8
Mean	(ppm)	0.087	0.058	0.071	0.216	0.28	0.109	99.8
Standard deviation	(ppm)	0.152	0.155	0.125	0.415	0.12	0.338	0.1
Number of samples*		77	57	58	78	78	61	78
Percentage of samples	(%)	98.7	73.1	74.4	100.0	100.0	78.2	100.0

* – number of samples with concentration of component over detection limit; ** – minimum, maximum, median, mean and standard deviation values in vol%

$$*** - CDMI = \frac{CO_2}{CO_2 + CH_4} \cdot 100\%$$

can be observed. On the contrary, isotopic composition of free gases reveals that this gas component is polygenetic: thermogenic, microbial and generated during oxidation of hydrocarbons, and recent, residual organic matter (Kotarba *et al.*, 2009). This effect of isotopic fractionation can be caused by two reasons: (1) increasing content of thermogenic gases at depth, and (2) higher content of microbial and oxidized forms of carbon dioxide in free gases, and their escape to the atmosphere during degassing of rock samples. The higher values of hydrocarbon C_{HC} and carbon dioxide methane CDMI indices in adsorbed gases than in free gases can be caused by the same reasons.

Analyses of gas samples desorbed from drill cores

The analysed gases obtained from depths 0–12 m are variable in their molecular composition. Molecular composition and gas indices of analysed gases vary within the following ranges (Tables 4, 5): CH₄ from 0.27 to 9.91 ppm (mean 5.19 ppm), total C₂-C₅ alkanes from 0.24 to 505 ppm (mean 26.3 ppm), of which C₂H₆ from 0 to 0.36 ppm (mean 0.046 ppm), C₃H₈ from 0 to 12.3 ppm (mean 0.77 ppm), *i*-C₄H₁₀ from 0.012 to 23.7 ppm (mean 2.06 ppm), *n*-C₄H₁₀ from 0 to 85.2 ppm (mean 5.28 ppm), *neo*-C₅H₁₂ from 0 to 0.5 ppm (mean 0.032 ppm), *i*-C₅H₁₂ from 0.103 to 230 ppm

Table 6

Principal statistical parameters of methane, total C₂-C₅ alkanes and total C₂-C₄ alkenes concentrations for adsorbed gas of core samples from near-surface geological strata

Geological strata	No. of samples	Methane (ppm)			Total C ₂ -C ₅ alkanes (ppm)			Total C ₂ -C ₄ alkenes (ppm)		
		Maximum	Mean	Median	Maximum	Mean	Median	Maximum	Mean	Median
Pleistocene	19	6.82	4.93	4.73	113.6	26.5	11.8	0.307	0.202	0.210
Holocene	16	5.86	4.67	4.72	73.21	10.7	1.6	0.49	0.142	0.112
Mine dump	12	6.77	4.99	4.99	10.28	4.66	4.6	3.44	0.576	0.201
Miocene	30	9.91	5.65	4.99	504.7	43.7	12.4	0.283	0.125	0.114

Table 7

Principal statistical parameters of carbon dioxide and hydrogen concentrations for adsorbed gas of core samples from near-surface geological strata

Geological strata	No. of samples	Carbon dioxide (vol%)			Hydrogen (vol%)		
		Maximum	Mean	Media	Maximum	Mean	Media
Pleistocene	19	0.51	0.31	0.28	3.004	0.232	0.077
Holocene	16	0.35	0.27	0.26	0.121	0.062	0.078
Mine dump	12	1.05	0.34	0.26	0.341	0.136	0.106
Miocene	30	0.43	0.25	0.24	0.142	0.045	0.036

(mean 11.6 ppm) and *n*-C₅H₁₂ from 0.009 to 162 ppm (mean 6.48 ppm), total C₂-C₄ alkenes from 0.016 to 3.44 ppm (average 0.22 ppm), CO₂ from 0.14 to 1.05 vol% (mean 0.28 vol%), H₂ from 0 to 3.0 vol% (mean 0.11 vol%), hydrocarbon (C_{HC}) index from 0.3 to 433 (mean 50.6), and carbon dioxide/methane (CDMI) index from 99.5 to 100.0 (mean 99.8).

Generally, the concentrations of methane and total C₂-C₅ alkanes are lower in samples taken from drill cores than in those derived from cuttings, except for alkenes and hydrogen which are somewhat higher in the drill-core samples. Concentrations of carbon dioxide are lower than in samples from cuttings.

Statistical parameters calculated for lithostratigraphic horizons demonstrated that the highest concentrations of methane and total alkanes C₂-C₅ occurred in Miocene strata and the lowest ones were found in Holocene sediments and in mine wastes (Table 6). The highest concentrations of alkenes and carbon dioxide were observed in wastes from mine dump and the lowest ones were indicated in Miocene rocks (Tables 6, 7). Although the numbers of analysed samples are poorly representative from statistical point of view, the regularities disclosed are well-reasoned and demonstrate that migration rates through the Miocene strata were higher than those through Pleistocene and Holocene deposits. Decreasing migration rate facilitates dehydrogenation of gases, which may lead to formation of alkenes (Saunders *et al.*, 1999). Increasing concentrations of carbon dioxide in mine wastes with simultaneous decrease of higher alkanes is interpreted as an effect of bacterial oxidation of the latter compounds (Lundegard *et al.*, 2000; Whiticar *et al.*, 1986). It is supported also by higher concentrations of methane in mine wastes, compared to Holocene sediments (Table 6).

Cumulative plots of concentrations of methane, total alkanes C₂-C₅, total alkenes C₂-C₄, hydrogen and carbon dioxide in samples from drill cores were divided into several subsets (Fig. 9), which gave rise to selection of threshold values for anomalies: for methane – 5 ppm (Fig. 9A), for total alkanes C₂-C₅ – 17 ppm (Fig. 9B), for total alkenes C₂-C₄ – 0.12 ppm (Fig. 9C), for hydrogen – 0.085 vol% (Fig. 9D), and for carbon dioxide – 0.33 vol% (Fig. 9E).

The highest number of sampling sites with anomalous concentrations of alkanes (5 ppm for methane, 177 ppm for total alkanes C₂-C₅) was found in Miocene strata whereas the lowest ones were encountered in Holocene deposits (Figs 10, 11). However, in Miocene sediments the lowest number of anomalous concentrations of total alkenes C₂-C₄, hydrogen and carbon dioxide were noticed (Figs 12, 13, 14). The highest number of anomalous concentrations of total alkenes C₂-C₄ and hydrogen were observed in Pleistocene sediments (Figs 12B, 13B). These data indicate that favourable conditions for oxidation and dehydrogenation of ascending alkanes exist in younger sediments (Saunders *et al.*, 1999; Whiticar & Faber, 1986). In the study area, generation of alkenes and hydrogen was most intensive in the Pleistocene.

$\delta^{13}\text{C}(\text{CO}_2)$ values of gases desorbed from drill cores at the sampling depths from 2.0 to 8.0 m vary in a very narrow range, from –13.5 to –10.3‰ (Table 8). Similarly as gas from samples desorbed from cuttings, carbon dioxide is of thermogenic origin.

Examples of changes in concentrations of methane, total C₂-C₅ alkanes, total C₂-C₄ alkenes, hydrogen and carbon dioxide referred to lithostratigraphic columns (Fig. 15) do not reveal mutual relationships. It suggests the complicated physical and biochemical processes (diffusion, effusion,

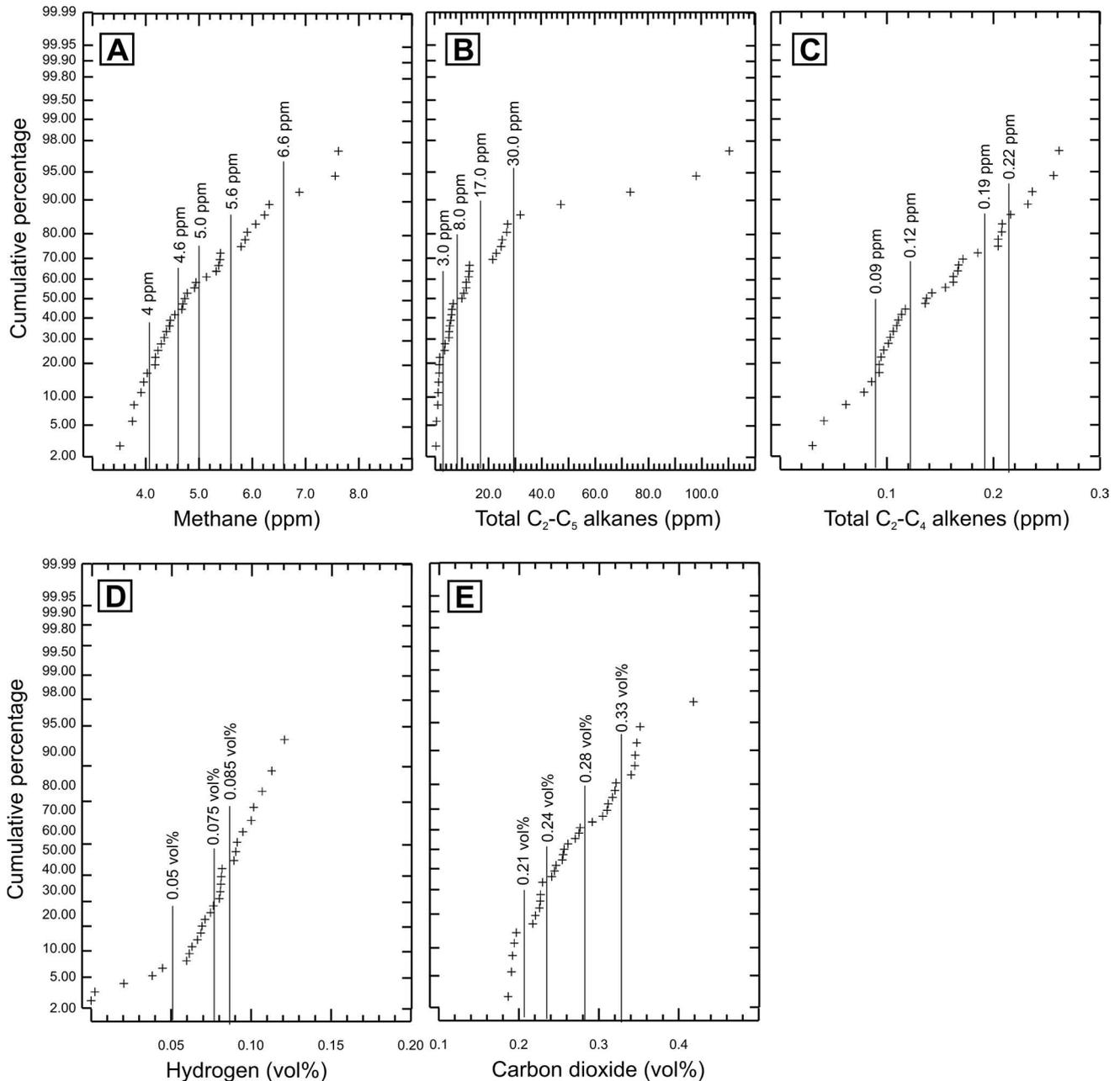


Fig. 9. Cumulative frequency diagrams of: (A) methane, (B) total C₂-C₅ alkanes, (C) total C₂-C₄ alkenes, (D) hydrogen and (E) carbon dioxide concentrations measured in adsorbed gas of core samples collected to 12 m depth

sorption, action of microorganisms) operating during the migration of hydrocarbons from deep accumulations towards the surface.

CONCLUSIONS

Studies of molecular composition of gases released by thermal-vacuum degassing from cuttings and drill core samples indicate high saturation of near-surface sediments with oil. The highest concentration of alkanes occurs in Miocene strata. Migration rate of hydrocarbons from deep accumulations towards the surface along faults, fissures and fractures can be regarded as relatively high.

In the near-surface zone hydrocarbons were oxidized and dehydrogenated, which led to generation of unsaturated compounds and hydrogen. This generation was most intensive in Pleistocene sediments and in mine wastes. Increased concentrations of hydrogen may also originate from radiolysis of water at the presence of hydrocarbons.

Concentrations of carbon dioxide in adsorbed gas in relation to other analysed gases are most uniform; a slight increase is observed in mine wastes indicating more favourable conditions for oxidation of hydrocarbons.

The detected concentrations compared to the results obtained with the free gas method (Kotarba *et al.*, 2009; Sechman *et al.*, 2009) lead to a general conclusion that concentrations of alkanes, alkenes and carbon dioxide mea-

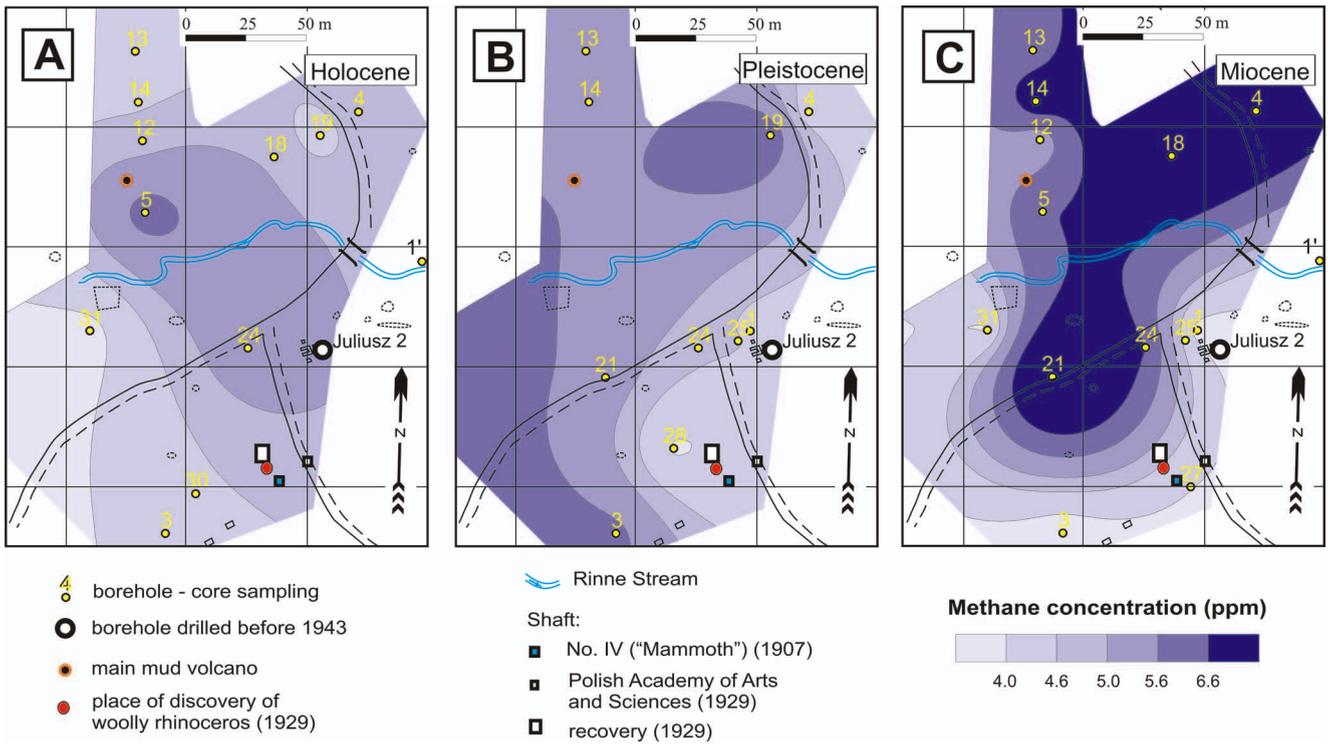


Fig. 10. Contour maps of mean values of methane concentrations in the adsorbed gas of core samples from: (A) Holocene, (B) Pleistocene, and (C) Miocene strata

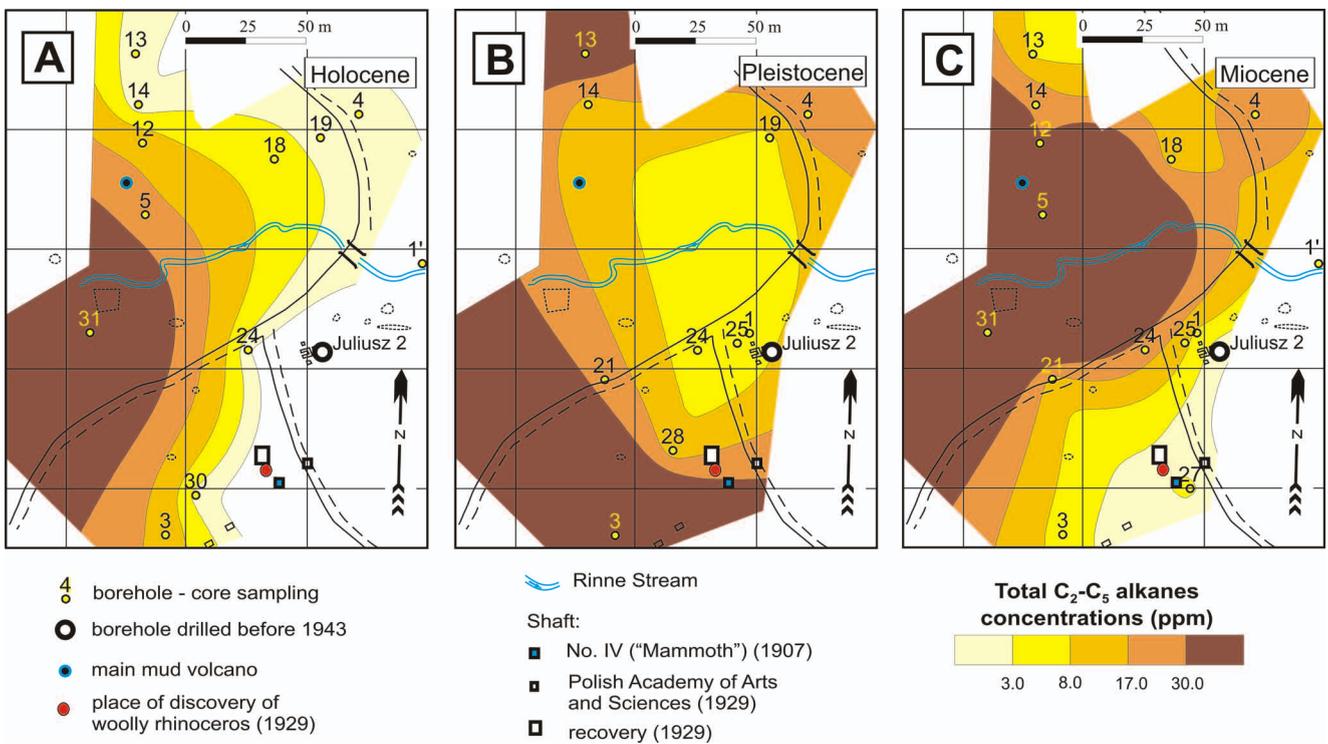


Fig. 11. Contour maps of mean values of total C₂-C₅ alkanes concentrations in the adsorbed gas of core samples from: (A) Holocene, (B) Pleistocene, and (C) Miocene strata

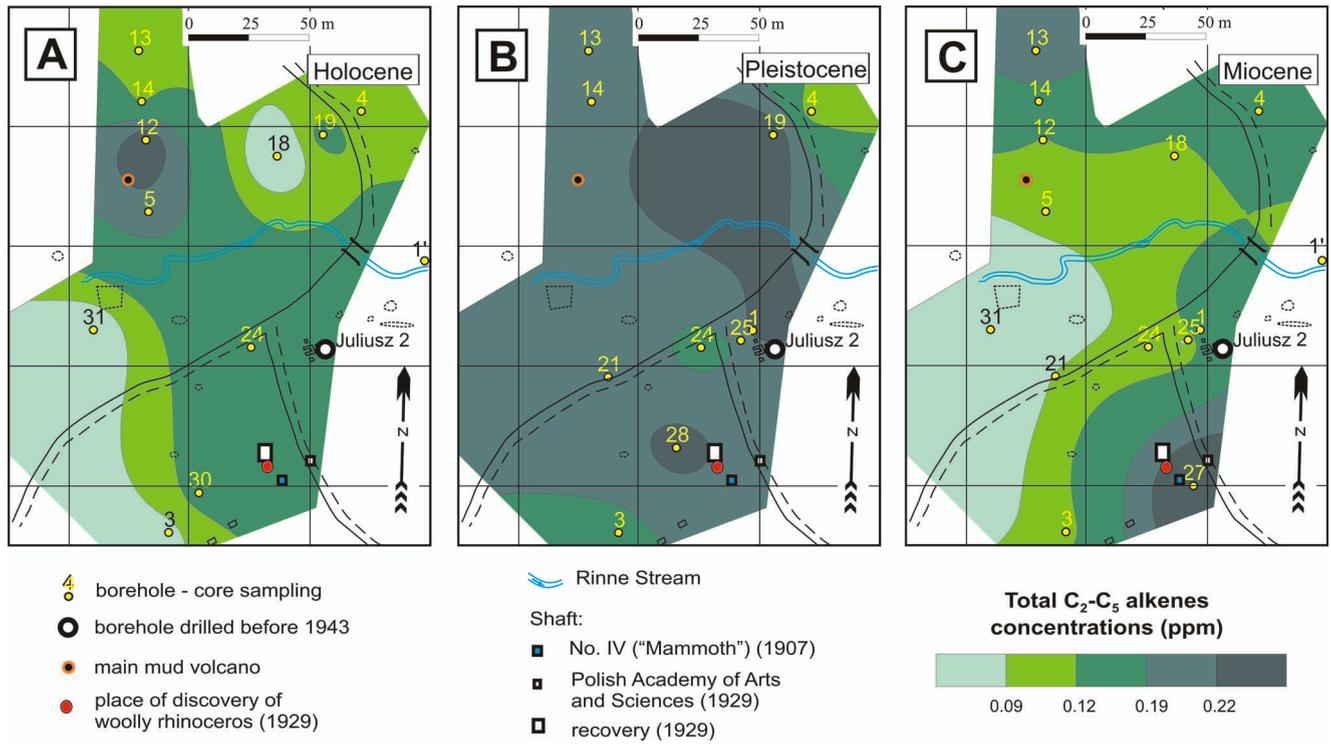


Fig. 12. Contour maps of mean values of total C₂-C₄ alkenes concentrations in the adsorbed gas of core samples from: (A) Holocene, (B) Pleistocene, and (C) Miocene strata

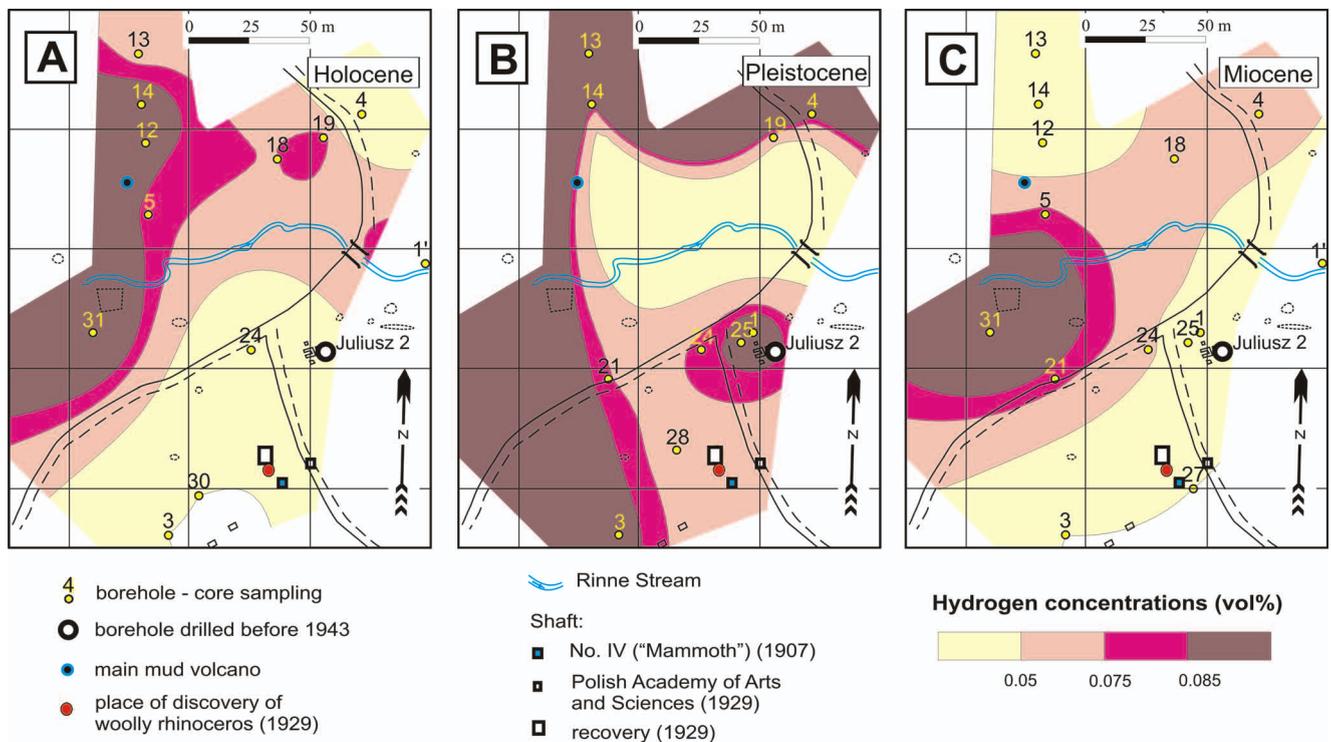


Fig. 13. Contour maps of mean values of hydrogen concentrations in the adsorbed gas of core samples from: (A) Holocene, (B) Pleistocene, and (C) Miocene strata

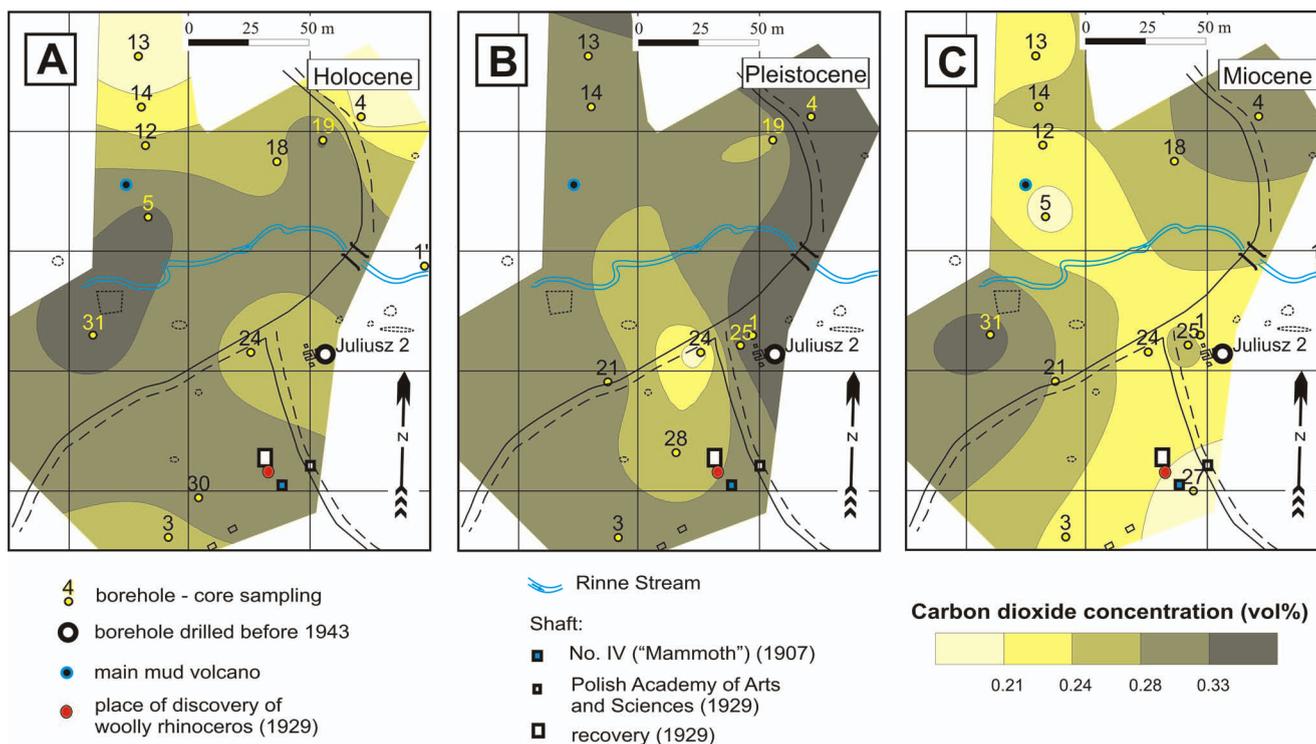


Fig. 14. Contour maps of mean values of carbon dioxide concentrations in the adsorbed gas of core samples from: (A) Holocene, (B) Pleistocene, and (C) Miocene strata

sured in gas desorbed from rock samples are lower and that the number of anomalous concentrations is also lower than those measured in the free gas. However, hydrogen concentrations are higher in adsorbed gas than in free gas (Kotarba *et al.*, 2009; Sechman *et al.*, 2009). It indicates that no additional effects from recent (*e.g.* microbial) processes were detected with the adsorbed gas method. Hence, the obtained results reflect the effects of an earlier saturation of rocks with ascending hydrocarbons and other components. The final effect results from complicated sorption processes within the rock formations. In authors' opinion, the more comprehensive interpretation of the results of geochemical survey carried out with the adsorbed gas method will be possible after comparative analysis of the results and relationships obtained with the free gas and the adsorbed gas methods.

Acknowledgements

Financial support from the Ministry of Science and Higher Education (grant No. 139/UKR/2006/01) is kindly acknowledged. Review comments and suggestions by Zenon Kłapyta and Maciej Manecki of the AGH University of Science and Technology in Kraków were very helpful. We would like to express our gratitude to Mark Pawlewicz of the U.S. Geological Survey in Denver for his critical comments, which improved this paper.

Table 8

Results of stable carbon isotope composition of adsorbed gas of core samples from near-surface geological strata

No. of boreholes	Depth (m)	Stratigraphy	$\delta^{13}\text{C}(\text{CO}_2)$ (‰)
1	2.0	Pleistocene	-10.8
4	6.0	Miocene	-12.3
5	2.0	Holocene	-10.4
13	2.0	Pleistocene	-10.3
21	2.0	Pleistocene	-10.4
25	2.0	Pleistocene	-11.0
28	8.0	Pleistocene	-10.5
31	4.0	Holocene	-13.5

REFERENCES

- Alexandrowicz, S. W., 2004. Starunia and the Quaternary research in the tradition and initiatives of the Polish Academy of Arts and Sciences. (In Polish, English summary). *Studia i materiały do dziejów Polskiej Akademii Umiejętności*. Polska Akademia Umiejętności, Kraków, 3, 261 pp.
- Alexandrowicz, S. W., 2005. The history of Starunia – a palaeontologic site and old ozokerite mine. In: Kotarba, M. J. (ed.), *Polish and Ukrainian studies (2004–2005) at Starunia – the area of discoveries of woolly rhinoceroses*. Polish Geological Institute and Society of Research on Environmental Changes "Geosphere", Warszawa–Kraków: 21–38.
- Hawkes, H. E., 1972. Free hydrogen in genesis of petroleum.

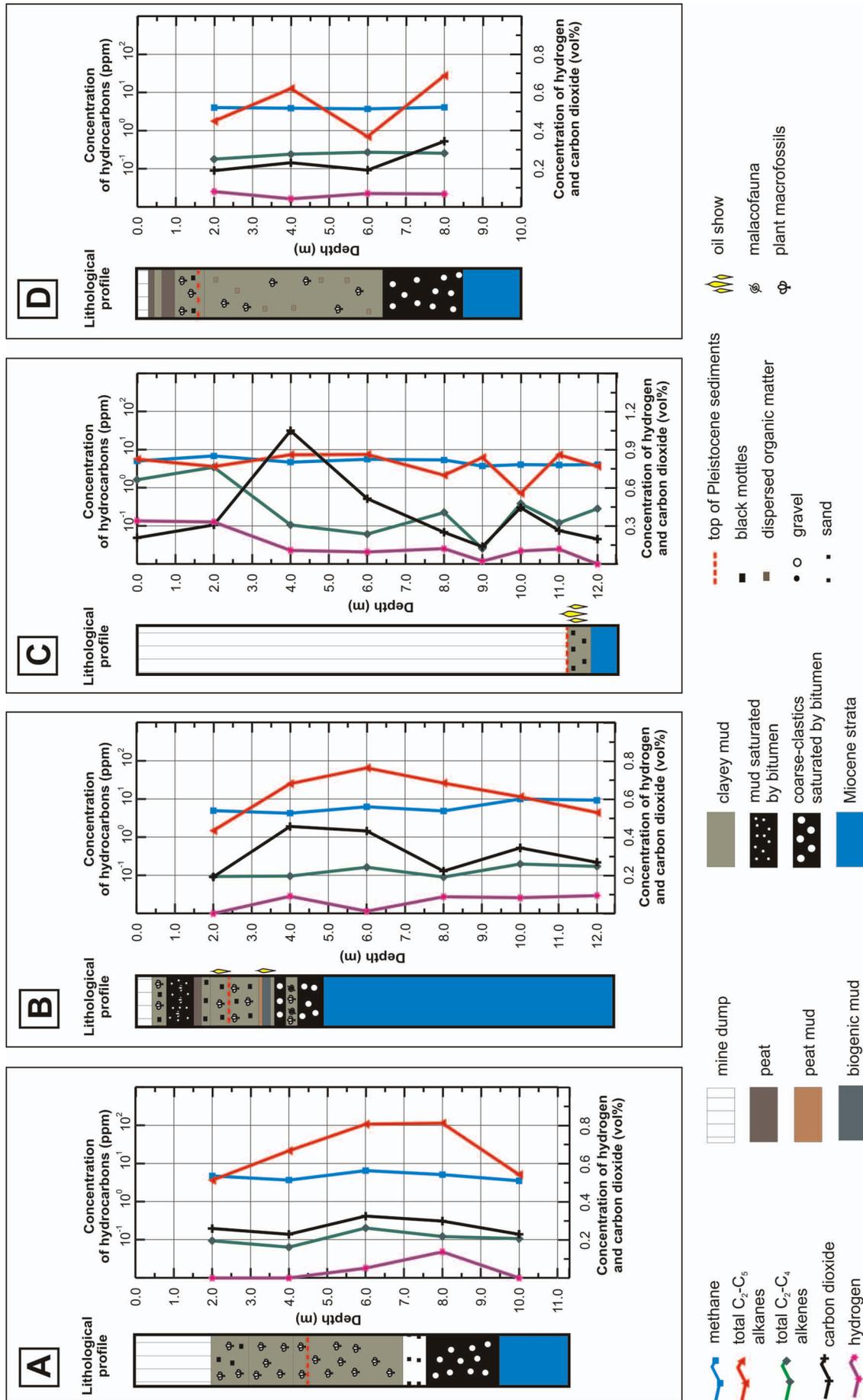


Fig. 15. Changes in methane, total C₂-C₆ alkanes, total C₇-C₄ alkenes, hydrogen and carbon dioxide concentrations in profiles of boreholes (A) No. 3, (B) No. 4, (C) No. 27, and (D) No. 28

- American Association of Petroleum Geologists Bulletin*, 56: 2268–2277.
- Karčev, A. A., Tabasaranskiy, Z. M., Subbota, M. I. & Mogilevskiy, G. A., 1954. *Geokhimi-cheskiye metody poiskov i razvedki neftianyykh i gazovykh mestorozhdeniy*. (In Russian). Gostoptekhizdat, Moskva, 430 pp.
- Koltun, Y. V., Adamenko, O. M., Kotarba, M. J., Dudok, I. V., Pavluk, M. I., Burzewski, W. & Stelmakh, O. R., 2005. Geological setting and petroleum occurrence of the Starunia area, fore-Carpathian region, Ukraine. In: Kotarba, M. J. (ed.), *Polish and Ukrainian studies (2004–2005) at Starunia – the area of discoveries of woolly rhinoceroses*. Polish Geological Institute and Society of Research on Environmental Changes “Geosphere”, Warszawa–Kraków: 61–78.
- Kotarba, M. J., 2002. Composition and origin of hydrocarbons saturating the remnants of woolly rhinoceros from Starunia, the Ukrainian Carpathians. (In Polish, English summary). *Przeгляд Geologiczny*, 50: 531–534.
- Kotarba, M. J. (ed.), 2005. *Polish and Ukrainian geological studies (2004–2005) at Starunia – the area of discoveries of woolly rhinoceroses*. Polish Geological Institute and Society of Research on Environmental Changes “Geosphere”, Warszawa–Kraków, 218 pp.
- Kotarba, M. J., 2009. Interdisciplinary studies at Starunia palaeontological site and vicinity (Carpathian region, Ukraine) in the years 2006–2009: Previous discoveries and research, purposes, results and perspectives. *Annales Societatis Geologorum Poloniae*, 79: 219–241.
- Kotarba, M. J., Alexandrowicz, S. W. & Stachowicz-Rybka, R., 2008a. Historia i program dalszych badań geologicznych na obszarze byłej kopalni ozokerytu i stanowiska paleontologicznego w Staruni. (In Polish). *Przeгляд Geologiczny*, 56: 34–441.
- Kotarba, M. J., Dzieńiewicz, M., Mościcki, W. J. & Sechman, H., 2008b. Unique Quaternary environment for discoveries of woolly rhinoceroses in Starunia, fore-Carpathian region, Ukraine: Geochemical and geoelectric studies. *Geology*, 36: 567–570.
- Kotarba, M. J., Dzieńiewicz, M. & Sechman, H., 2005. Geochemical survey, molecular and isotopic compositions, and genetic identification of near-surface gases from the Starunia area, fore-Carpathian region, Ukraine. In: Kotarba, M. J. (ed.), *Polish and Ukrainian studies (2004–2005) at Starunia – the area of discoveries of woolly rhinoceroses*. Polish Geological Institute and Society of Research on Environmental Changes “Geosphere”, Warszawa–Kraków: 157–174.
- Kotarba, M. J. & Stachowicz-Rybka, R., 2008. Wyjątkowe stanowisko paleontologiczne i środowisko osadów plejstoceńskich, w których znaleziono nosorożce włochate w Staruni (Karpaty Wschodnie). (In Polish). *Przeгляд Geologiczny*, 56: 442–452.
- Kotarba, M. J., Sechman, H. & Dzieńiewicz, M., 2009. Distribution and origin of gaseous hydrocarbons and carbon dioxide in the Quaternary sediments at Starunia palaeontological site and vicinity (Carpathian region, Ukraine). *Annales Societatis Geologorum Poloniae*, 79: 403–419.
- Kubiak, H. & Drygant, D. M., 2005. The Starunia collections in Lviv and Kraków natural history museums and history of palaeontological studies. In: Kotarba, M. J. (ed.), *Polish and Ukrainian studies (2004–2005) at Starunia – the area of discoveries of woolly rhinoceroses*. Polish Geological Institute and Society of Research on Environmental Changes “Geosphere”, Warszawa–Kraków: 37–44.
- Lundegard, P. D., Sweeney, R. E. & Ririe, G. T., 2000. Soil gas methane at petroleum contaminated sites: forensic determination of origin and source. *Environmental Forensics*, 1: 3–10.
- Morrison, R. T. & Boyd, R. N., 1983. *Study guide to organic chemistry*. Allyn and Bacon, Boston, 745 pp.
- Mościcki, W. J., 2009. Characterization of near-surface sediments based on combined geoelectric studies at Starunia palaeontological site and vicinity (Carpathian region, Ukraine). *Annales Societatis Geologorum Poloniae*, 79: 333–342.
- Porzucek, S. & Madej, J., 2009a. Recognition of geological structures at Starunia palaeontological site and vicinity (Carpathian region, Ukraine) based on gravity surveys. *Annales Societatis Geologorum Poloniae*, 79: 357–363.
- Porzucek, S. & Madej, J., 2009b. Detection of near-surface geological heterogeneity at Starunia palaeontological site and vicinity (Carpathian region, Ukraine) based on microgravity survey. *Annales Societatis Geologorum Poloniae*, 79: 365–374.
- Saunders, D. F., Burson, K. R. & Thompson, C. K., 1999. Model for hydrocarbon microseepage and related near-surface alterations. *American Association of Petroleum Geologists Bulletin*, 83, 1: 170–184.
- Sechman, H. & Dzieńiewicz, M., 2007. Influence of soil moisture on the results of surface geochemical survey applied to petroleum exploration. *Journal of Petroleum Science and Engineering*, 56, 4: 267–282.
- Sechman, H., Kotarba, M. J. & Dzieńiewicz, M., 2009. Surface geochemical survey at Starunia palaeontological site and vicinity (Carpathian region, Ukraine). *Annales Societatis Geologorum Poloniae*, 79: 375–390.
- Sokołowski, T. & Stachowicz-Rybka, R., 2009. Chronostratigraphy and changes of environment of Late Pleistocene and Holocene at Starunia palaeontological site and vicinity (Carpathian region, Ukraine). *Annales Societatis Geologorum Poloniae*, 79: 315–331.
- Sokołowski, T., Stachowicz-Rybka, R. & Woronko, B., 2009. Upper Pleistocene and Holocene deposits at Starunia palaeontological site and vicinity (Carpathian region, Ukraine). *Annales Societatis Geologorum Poloniae*, 79: 255–278.
- Stachowicz-Rybka, R., Granoszewski, W. & Hrynowiecka-Czmielewska, A., 2009. Quaternary environmental changes at Starunia palaeontological site and vicinity (Carpathian region, Ukraine) based on palaeobotanical studies. *Annales Societatis Geologorum Poloniae*, 79: 279–288.
- Starobiniec, I. S., 1986. *Gazokhimicheskije pokazateli neftegazonosti i prognoz sostava uglevodorodnykh skoplenij*. (In Russian). Izdatelstvo Niedra, Moskva, 200 pp.
- Whiticar, M. J. & Faber, E., 1986. Methane oxidation in sediment and water column environments – isotope evidence. *Organic Geochemistry*, 11: 759–768.
- Whiticar, M. J., Faber, E. & Schoell, M., 1986. Biogenic methane formation in marine and Freshwater environments: CO₂ reduction vs. acetate fermentation – isotope evidence. *Geochimica et Cosmochimica Acta*, 50: 693–709.