

# DISTRIBUTION AND ORIGIN OF GASEOUS HYDROCARBONS AND CARBON DIOXIDE IN THE QUATERNARY SEDIMENTS AT STARUNIA PALAEOONTOLOGICAL SITE AND VICINITY (CARPATHIAN REGION, UKRAINE)

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Kotarba, M. J., Sechman, H. & Dzieniewicz, 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.

**Abstract:** Near-surface gases were investigated in Starunia, where remains of mammoth and woolly rhinoceroses were discovered at the beginning of the 20th century. Samples were collected at 30 measurement sites, from 0.8, 1.6, 2.4, 3.2 and 4.0 m depths and analysed for their molecular and isotopic compositions. Most of the methane and all higher gaseous hydrocarbons accumulated within the near-surface zone are of thermogenic origin. The distribution of thermogenic methane and higher gaseous hydrocarbons in Quaternary sediments is variable and, generally, increases with depth. Microbial methane or a mixture of microbial and thermogenic methane also occurs at the near-surface zone. The presence of hydrogen and alkenes in the near-surface gases also suggests a contribution from recent, microbial processes. Helium of crustal origin migrated through the Rinne Fault and other tectonic zones located in the study area, and was subsequently dispersed during migration through the lithologically diversified Pleistocene and Holocene sediments. The high variability of the carbon dioxide concentration and stable carbon isotope composition at various depths in the near-surface zone is caused by its polygenetic origin (thermogenic, microbial, and oxidation of hydrocarbons and Quaternary organic matter), and also by its dissolution in water and oil during migration through lithologically diversified Pleistocene and Holocene sediments. Zones of thermogenic methane occurrence within Pleistocene sediments, dominated by muds saturated with bitumen and brines, provide the most favourable environment for preservation of large extinct mammals. It is likely that during the Pleistocene winters, when thick ice and snow covered the tundra lake and swamp, zones of outflow of brines, oils, helium, and thermogenic gaseous hydrocarbons had a higher temperature, which could have resulted in melting and cracking of the ice cover and drowning of large mammals. The most favourable conditions for preservation of large, extinct mammals probably still exists in the vicinity of sampling probe sites Nos 21, 22, 23 and 36. Zones of dominance of microbial methane concentrations are less favourable sites for preservation of extinct mammals, because this methane was generated within recent swamps and also within recent descending meteoric waters which infiltrated into Pleistocene and Holocene sediments. Older Pleistocene microbial gases have already escaped to the atmosphere.

**Key words:** near-surface geochemical survey, depth gas distribution, stable carbon isotopes, gaseous hydrocarbon origin, carbon dioxide origin, Quaternary sediments, woolly rhinoceros, Starunia palaeontological site, Ukrainian Carpathians.

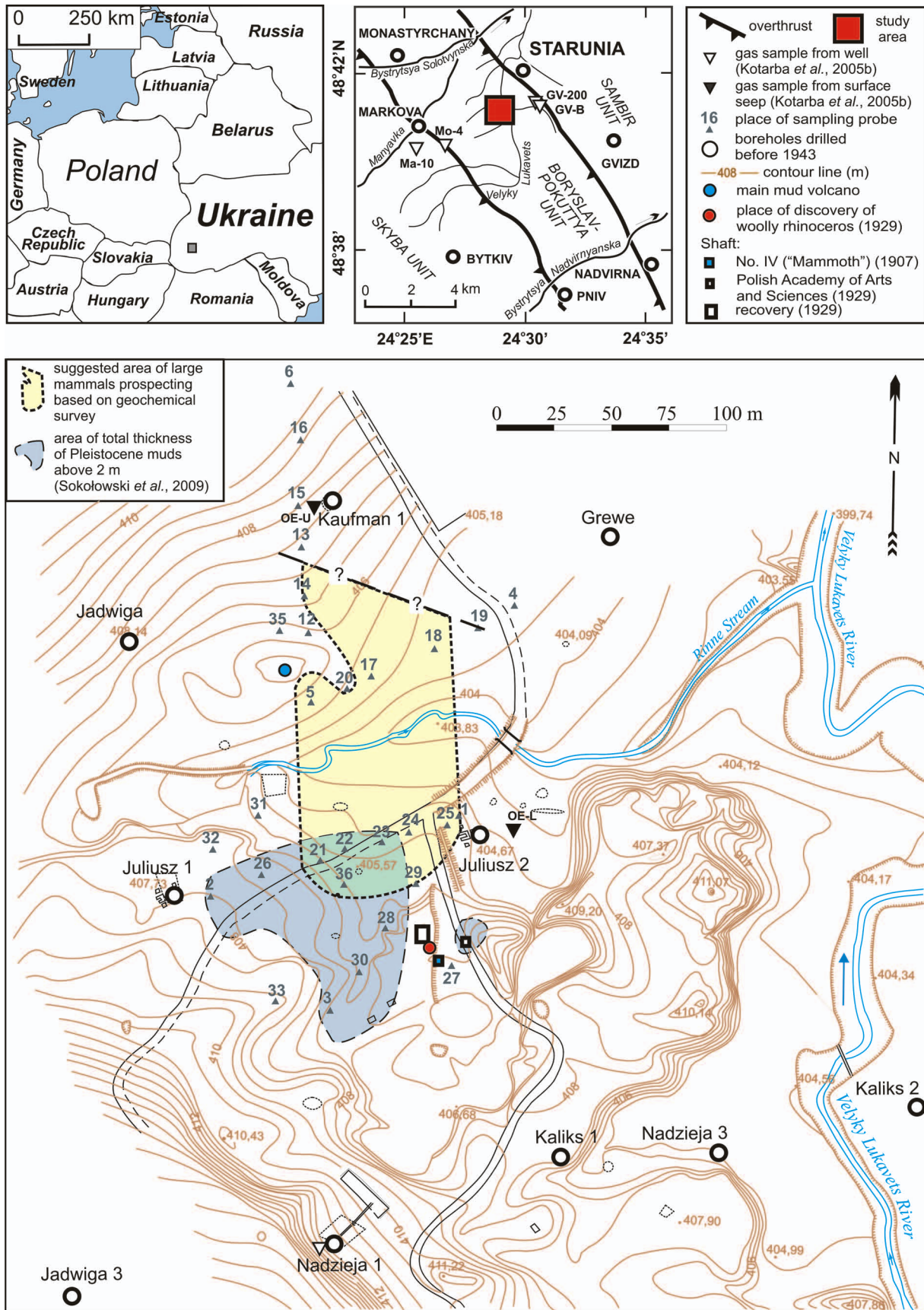
*Manuscript received 5 May 2009, accepted 10 September 2009*

## 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 rocks of the Boryslav-Pokuttya Unit of the Carpathian Foredeep Basin (Alexandrowicz, 2004, 2005; Koltun *et al.*, 2005). In 1907, remains of a mammoth and a woolly rhinoceros were found in No. 4 (then called “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).

The near-surface geochemical study down to 4.0 m depth was a part of an interdisciplinary research project fo-



**Fig. 1.** Sketch map of the Starunia area (Carpathian region, Ukraine) with the location of sampling sites. Location of gas wells and seeps after Kotarba *et al.* (2005b). Oil and gas seeps: OE-U – “upper eye”; OE-L – “lower eye”

cused on the Starunia area. During the period 2006–2009, comprehensive investigations were carried out at the Starunia palaeontological site (Kotarba, 2009). General information covering the history of petroleum exploitation in the study area, details of the geology, and the results of earlier interdisciplinary research were reported in a special monograph (Kotarba, 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).

In 2004, a preliminary soil gas geochemical survey was carried out in the area of the abandoned ozokerite mine in Starunia (Kotarba *et al.*, 2005a, 2008a), and in 2007 a detailed soil gas geochemical survey (Sechman *et al.*, 2009) was completed. 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 detailed, deeper geochemical survey. In total, 30 measurement sites were selected for the near-surface geochemical survey down to 4 m depth (Fig. 1).

The main aim of the geochemical studies is to determine where the best conditions within the Pleistocene muds exist for the preservation and conservation of specimens of other woolly rhinoceroses and/or mammoths, apart from the ones discovered in 1907 and 1929. Therefore, the direct objective of this study was to determine the isotopic composition, molecular concentration, and origin of gaseous alkanes, alkenes, carbon dioxide, hydrogen, and helium in the near-surface zone at sampling depths of 0.8, 1.6, 2.4 and 4.0 m. Links to the natural gases accumulated in deep structures of the Boryslav-Pokuttya and the Skyba units of the Carpathians and the recently generated microbial gases have also been established. Moreover, an attempt was made to determine migration routes of natural gas from deep accumulations to the surface, especially along the thrust and fault zones, and then within lithologically diversified Pleistocene and Holocene sediments.

## GEOLOGICAL SETTING AND PETROLEUM OCCURRENCE

The Ukrainian Carpathians belong to the largest petroleum provinces of Central Europe, constituting one of the oldest petroleum-producing regions in the world. Exploitation of oil and natural gas began in 1854 and 1921, respectively (Kotarba & Koltun, 2006). The ozokerite itself is a rare petroleum substance, and in the Carpathians it is only found in five sites: Boryslav, Volanka, Truskavets-Pomiarki, Dzvinych and Starunia (Alexandrowicz, 2005). The Starunia ozokerite deposit occurs in the Miocene salt-bearing Vorotyshcha beds of the Boryslav-Pokuttya Unit. This unit belongs to the internal part of the Carpathian Fore-deep Basin (Koltun *et al.*, 2005).

The top surface of the Miocene Vorotyshcha beds in Starunia area, which underlie Quaternary deposits, occurs at a maximum depth of 17 metres (Sokołowski *et al.*, 2009). In the area of abandoned Starunia ozokerite mine the Quaternary sediments are mainly developed as clayey muds with

plant remains, peat, biogenic muds and peat muds (Sokołowski *et al.*, 2009; Sokołowski & Stachowicz-Rybka, 2009). Within these sediments many brine and salt water springs occur in the Starunia vicinity. These brines and salt waters migrated along the Miocene Vorotyshcha beds and infiltrated to Quaternary sediments. Miocene strata are represented by sandstone-claystone breccias with halite, potassium-salt, gypsum and calcite layers, and veins of ozokerite (Korin, 2005).

The Boryslav-Pokuttya Unit contains the main oil and gas reservoirs in the Ukrainian Carpathians. Tectonically, the unit represents a stack of superimposed nappes, each of them comprising a flysch sequence covered by molasse (Ślęczka *et al.*, 2006). The Oligocene Menilite beds occur in the top of the flysch succession and are considered to be the most important hydrocarbon source rock with relatively high organic matter content (up to 20 wt%, Kotarba & Koltun, 2006). South and southwest of the Starunia ozokerite deposit, six oil and gas fields were discovered within the Palaeogene and Neogene reservoirs of the Boryslav-Pokuttya and Skyba units (Adamenko *et al.*, 2005; Koltun *et al.*, 2005). The Miocene Vorotyshcha salt-bearing beds provide a perfect seal for hydrocarbon traps. However, these beds underwent considerable fracturing in the course of formation of the Starunia fold, during the Carpathian overthrust movements. As oil and gas were flowing from the flysch strata towards the surface and most of gaseous hydrocarbons were emitted to the atmosphere, liquid hydrocarbons saturated Quaternary sediments, and higher hydrocarbons formed veins of ozokerite. These processes continue even now, which is evidenced by oil and gas surface seeps and mud volcanoes in the Starunia area.

Details of geology and petroleum occurrence in the Starunia area were published by Alexandrowicz (2004, 2005), Koltun *et al.* (2005), Korin (2005), Kotarba & Stachowicz-Rybka (2008), Kotarba *et al.* (2008a), Sokołowski *et al.* (2009), Sokołowski & Stachowicz-Rybka (2009) and Stachowicz-Rybka *et al.* (2009), and in references therein.

## METHODS

### Field work and sampling procedure

The near-surface gas samples were collected with a measurement probe and an air-tight syringe. The free-gas sampling method was applied (Dzieniewicz & Sechman, 2001, 2002). In comparison with other methods, this procedure reflects the current dynamics of migration of gaseous components (Sokolov & Grigoriev, 1962; Philp, 1987; Tedesco, 1995). The device was subsequently modified to enable collection of samples from greater depths. A probe of 7 mm external diameter, 3 mm internal diameter and 4.5 m length was used. This probe was driven into the near-surface layers with a hammer, and gas samples were collected at the depths of 0.8, 1.6, 2.4, 3.2 and 4.0 m. In total, 150 samples of near-surface gases were taken from 30 measurement sites. The volume of a single sample ranged from 25 to 100 ml, depending on the lithology of the soils. Collected gas samples were transferred with an air-tight sy-

**Table 1**

Principal statistical parameters of alkanes concentrations and hydrocarbon index for near-surface gas samples collected down to 4 m depth

Statistical parameters	Unit	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	<i>n</i> -C <sub>4</sub> H <sub>10</sub>	<i>neo</i> -C <sub>5</sub> H <sub>12</sub>	<i>i</i> -C <sub>5</sub> H <sub>12</sub>	<i>n</i> -C <sub>5</sub> H <sub>12</sub>	Total C <sub>2</sub> -C <sub>5</sub> alkanes	C <sub>HC</sub>
Minimum	(vol%)	0.0003	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2.6
Maximum	(vol%)	92.2	2.25	0.40	0.19	0.26	0.0023	0.19	0.12	2.93	94250
Median	(vol%)	0.047	0.0004	0.0003	0.0002	0.0002	<0.0000	0.0005	0.0001	0.0036	44.6
Mean	(vol%)	9.91	0.11	0.031	0.014	0.017	0.0002	0.014	0.0063	0.19	1168
Standard deviation	(vol%)	21.2	0.34	0.087	0.036	0.051	0.0005	0.038	0.021	0.53	8003
Number of samples *		150	146	147	146	137	72	136	123	150	150
Percentage of samples	(%)	100.0	97.3	98.0	97.3	91.3	48.0	90.7	82.0	100.0	100

\* – number of samples with concentration of component above detection limit; b.d.l. – below detection limit

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

**Table 2**

Principal statistical parameters of alkenes, carbon dioxide, hydrogen and helium concentrations and carbon dioxide – methane index for near-surface gas samples collected down to 4 m depth

Statistical parameters	Unit	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	<i>I</i> -C <sub>4</sub> H <sub>8</sub>	Total C <sub>2</sub> -C <sub>4</sub> alkenes	CO <sub>2</sub>	H <sub>2</sub>	He	CDMI
Minimum	(vol%)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.108	b.d.l.	b.d.l.	1.8
Maximum	(vol%)	0.049	0.0001	0.0008	0.049	15.8	0.063	0.0048	99.8
Median	(vol%)	<0.0000	<0.0000	<0.0000	<0.0000	0.24	<0.000	<0.0000	84.8
Mean	(vol%)	0.0017	<0.0000	<0.0000	0.0017	1.26	0.005	0.0003	63.6
Standard deviation	(vol%)	0.0072	0.00001	0.00009	0.0071	2.56	0.010	0.0008	38.0
Number of samples*		98	25	52	118	150	62	20	150
Percentage of samples	(%)	65.3	16.7	34.7	78.7	100	41.3	13.3	100

\* – number of samples with concentration of component above detection limit; b.d.l. – below detection limit

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

ringe to bottles filled with a saturated NaCl solution. Samples were then transported to the AGH University of Science and Technology in Kraków, Poland, for analyses.

### Analytical methods

The molecular composition in near-surface gaseous hydrocarbons was analysed with a FISSONS Instruments GC 8160 flame-ionisation gas chromatograph. The presence and concentrations of carbon dioxide, hydrogen, helium, oxygen and nitrogen were measured using a Carlo Erba Instruments GC 6300 gas chromatograph. Details of the gas

chromatographic procedure were described in Sechman *et al.* (2009). The detection limit was equal: hydrocarbons ±0.01 ppm; hydrogen ±10 ppm, helium ±10 ppm; carbon dioxide ±0.01 vol%, oxygen ±0.01 vol%, nitrogen ±0.01 vol%.

Stable carbon isotope analyses were carried out on a Finnigan Delta Plus mass spectrometer. Stable carbon isotope data are presented in δ-notation relative to the PDB standard. The analytical precision is estimated to be about ±0.2 ‰. Methane, ethane, propane and carbon dioxide were isolated chromatographically for stable carbon isotope analyses. Methane, ethane and propane were, in turn, combusted

**Table 3**

Principal statistical parameters of stable carbon isotope composition of methane, ethane, propane and carbon dioxide for near-surface gas samples collected down to 4 m depth

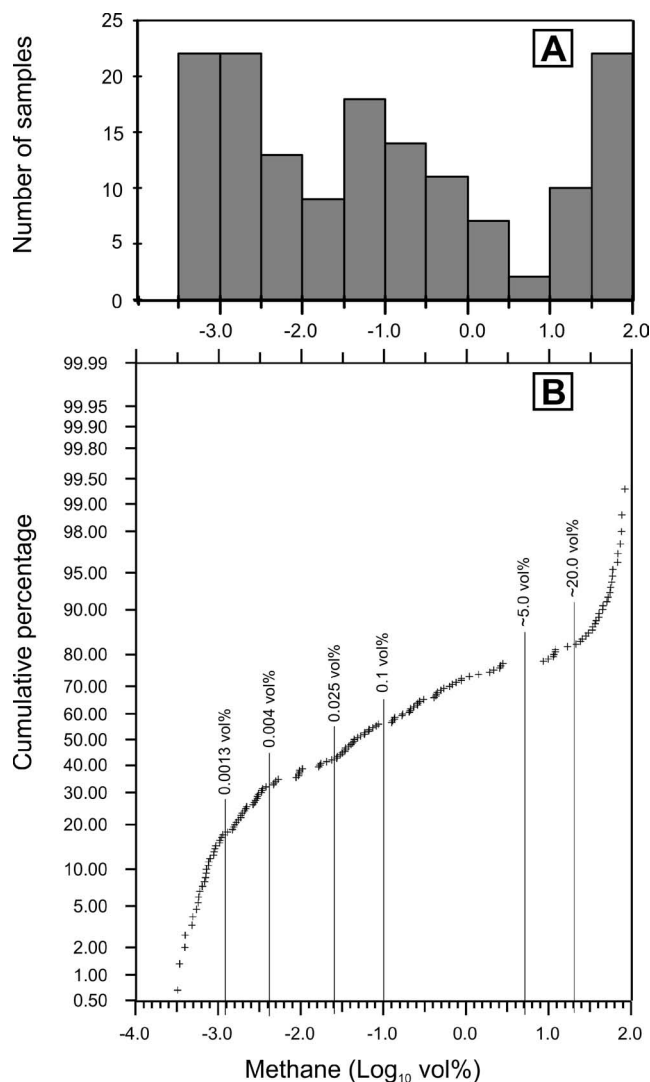
Statistical parameters	Unit	$\delta^{13}\text{C}(\text{CH}_4)$	$\delta^{13}\text{C}(\text{C}_2\text{H}_6)$	$\delta^{13}\text{C}(\text{C}_3\text{H}_8)$	$\delta^{13}\text{C}(\text{CO}_2)$
Minimum	(‰)	-64.4	-29.3	-28.2	-20.1
Maximum	(‰)	-29.1	-23.7	-22.7	24.3
Median	(‰)	-46.5	-27.4	-27.6	-15.7
Mean	(‰)	-46.8	-27.3	-27.0	-8.0
Standard deviation	(‰)	8.2	1.2	1.6	13.9
Number of samples		63	25	15	63
Percentage of samples	(%)	42.0	16.7	10.0	42.0

over hot copper oxide (850°C) and the carbon dioxide produced with the on-line system was introduced to the mass spectrometer.

## RESULTS

The analysed near-surface gases collected from 0.8, 1.6, 2.4, 3.2 and 4.0 m sampling depths are variable in their molecular and isotopic compositions. Molecular and isotopic compositions, and hydrocarbon ( $\text{C}_{\text{HC}}$ ) [ $\text{C}_{\text{HC}} = \text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$ ] and carbon dioxide methane (CDMI) { $\text{CDMI} = [\text{CO}_2/(\text{CO}_2 + \text{CH}_4)] 100 (\%)$ } gas indices of analysed gases vary within the following ranges (Tables 1 to 3):  $\text{CH}_4$  from 0.0003 vol% to 92.2 vol% (mean 9.91 vol%), total  $\text{C}_2$ - $\text{C}_5$  alkanes from 0 to 2.93 vol% (mean 0.191 vol%), of which  $\text{C}_2\text{H}_6$  from 0 to 2.25 vol% (mean 0.108 vol%),  $\text{C}_3\text{H}_8$  from 0 to 0.403 vol% (mean 0.031 vol%), *i*- $\text{C}_4\text{H}_{10}$  from 0 to 0.192 vol% (mean 0.014 vol%), *n*- $\text{C}_4\text{H}_{10}$  from 0 to 0.262 vol% (mean 0.017 vol%), *neo*- $\text{C}_5\text{H}_{12}$  from 0 to 0.0023 vol% (mean 0.0002 vol%), *i*- $\text{C}_5\text{H}_{12}$  from 0 to 0.187 vol% (mean 0.014 vol%) and *n*- $\text{C}_5\text{H}_{12}$  from 0 to 0.119 vol% (mean 0.0063 vol%), total  $\text{C}_2$ - $\text{C}_4$  alkenes from 0 to 0.049 vol% (average 0.0017 vol%),  $\text{CO}_2$  from 0.108 to 15.8 vol% (mean 1.26 vol%),  $\text{H}_2$  from 0 to 0.0627 vol% (mean 0.0051 vol%), He from 0 to 0.0048 vol% (mean 0.0003 vol%), hydrocarbon ( $\text{C}_{\text{HC}}$ ) index from 2.6 to 94,252 (mean 1,168), carbon dioxide methane (CDMI) index from 1.8 to 99.8 (mean 63.8),  $\delta^{13}\text{C}(\text{CH}_4)$  from -64.4 to -29.1‰,  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  from -29.3 to -23.7‰,  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  from -28.2 to -22.7‰ and  $\delta^{13}\text{C}(\text{CO}_2)$  from -20.1 to 24.3‰.

A histogram of methane concentration reveals a polymodal pattern (Fig. 2A). Several subsets can be distinguished with boundary values confirmed by the cumulative probability plot (Fig. 2B). These are: <0.0013 vol%, 0.0013 to 0.004 vol%, 0.004 to 0.025 vol%, 0.025 to 0.1 vol%, 0.1 to 5 vol%, 5 to 20.0 vol%, and over 20.0 vol%.



**Fig. 2.** (A) Histogram and (B) cumulative frequency diagram of methane concentrations

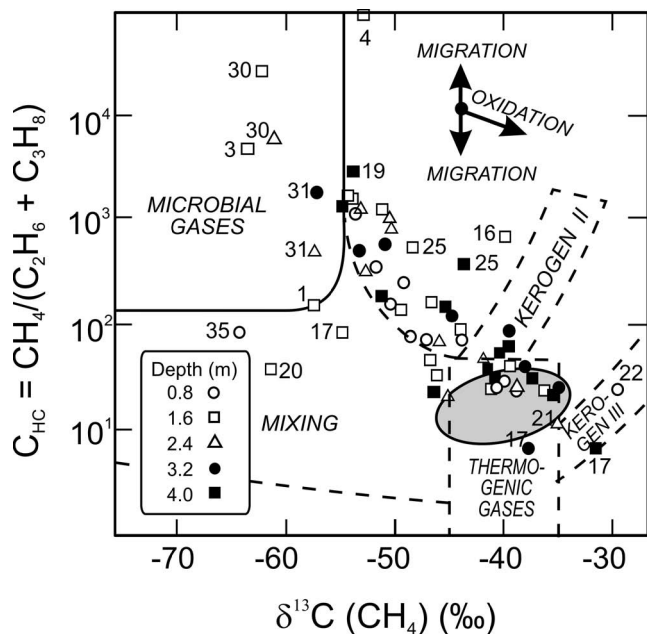
The same statistical procedure reveals the following boundary values for total  $\text{C}_2$ - $\text{C}_5$  alkanes: 0 to 0.000028 vol%, 0.000028 to 0.00025 vol%, 0.00025 to 0.0028 vol%, 0.0028 to 0.035 vol%, 0.035 to 2.5 vol% and over 2.5 vol%, and for carbon dioxide: <0.23 vol%, 0.23 to 0.35 vol%, 0.35 to 0.63 vol%, 0.63 to 3.2 vol%, 3.2 to 3.7 vol% and over 3.7 vol%, respectively.

## DISCUSSION

The occurrence and origin of gaseous hydrocarbons, hydrogen, helium and carbon dioxide as well as the influence of mixing and secondary processes on molecular and stable carbon isotope compositions are discussed below.

### Hydrocarbons

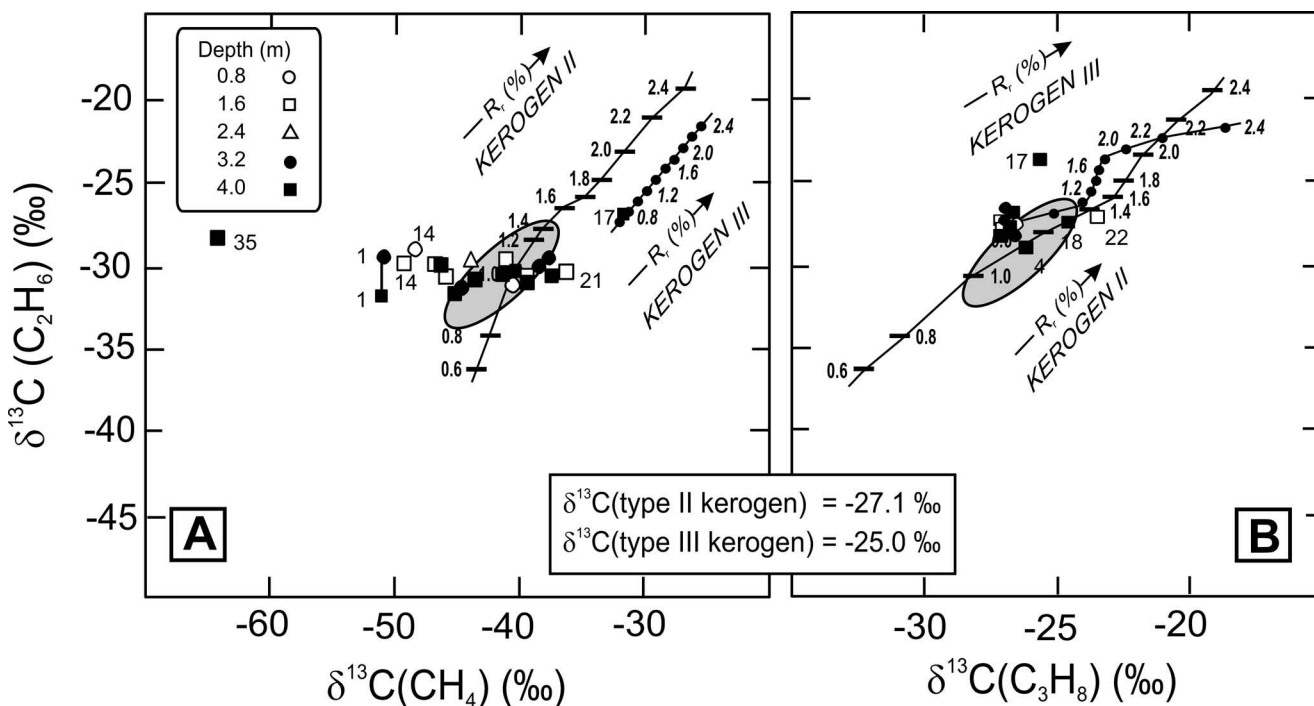
For the identification of the origin of analysed hydrocarbon gases, the genetic diagrams (Figs 3, 4) described by



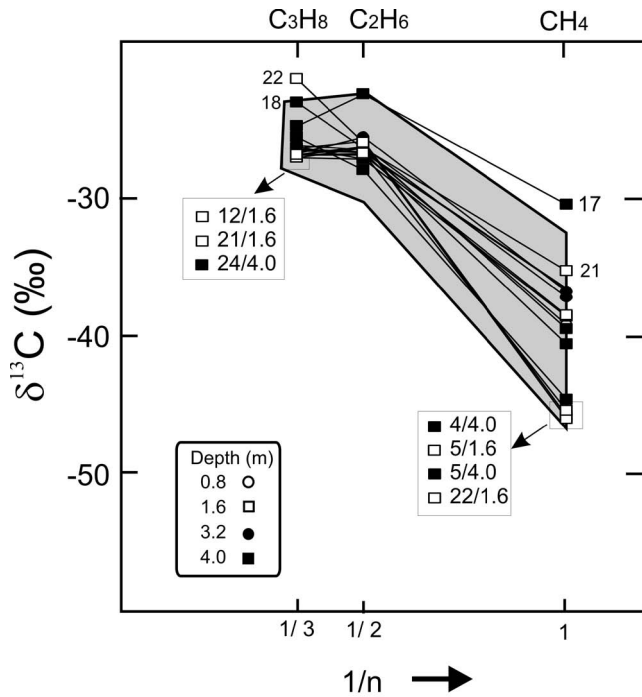
**Fig. 3.** Hydrocarbon index ( $C_{HC}$ ) versus  $\delta^{13}C(CH_4)$  for near-surface gases at the selected sampling depths. Compositional fields after Whiticar (1994). Shaded area represents gas from deep accumulations and surface seeps at the Starunia palaeontological site and surrounding area after Kotarba *et al.* (2005b)

Berner and Faber (1996), Schoell (1988), Whiticar (1994), and Whiticar *et al.* (1986) were used. An important implication for the interpretation is that a linear relationship of methane, ethane and propane carbon isotopes (Fig. 5) with their reciprocal carbon number is not an exclusive indicator of a natural gas from a single source as sometimes assumed (*e.g.*, Chung *et al.*, 1988; Rooney *et al.*, 1995). Zou *et al.* (2007) and Kotarba *et al.* (2009a) suggest that a “dogleg” trend, exemplified by relatively  $^{13}C$  depleted methane and enriched propane compared to ethane, in this type of plot is a result of a natural gas that was not generated from a single source rock or that underwent post-generation alteration (*e.g.*, secondary gas cracking, microbial oxidation, thermochemical sulphate reduction). Moreover, relatively more and more  $^{13}C$  depleted methane to ethane can be applied to evaluation of mixing proportion between microbial methane and thermogenic gases (Kotarba & Lewan, 2004; Kotarba *et al.*, 2009a).

Stable carbon isotope analyses of methane, ethane and propane from the near-surface zone (Table 3 and Figs 3, 4) reveal that both ethane and propane, at all analysed sampling sites and at different depths, and methane at majority of these sites are of thermogenic origin and migrated to the near-surface zone from deep-seated accumulations (Fig. 5). Populations of gases from deep accumulations and gases from two oil seeps (Kotarba *et al.*, 2005b) are also displayed in the genetic diagrams (Figs 3–5). It appears that deep gases, which have accumulated in Oligocene and Eocene reservoirs, as well as gases from oil seeps, were generated by both low- and high-temperature thermogenic processes



**Fig. 4.**  $\delta^{13}C(C_2H_6)$  versus (A)  $\delta^{13}C(CH_4)$  and (B)  $\delta^{13}C(C_3H_8)$  for near-surface gases at the selected sampling depths. Position of vitrinite reflectance curves for Type II and III kerogens after Berner and Faber (1996). Curves were shifted based on average values of  $\delta^{13}C = -27.1$  ‰ for type II, IIS and I/II kerogens, and  $\delta^{13}C$  values =  $-25.0$  ‰ for type III kerogen from the Menilite Shales in the Carpathians (Curtis *et al.*, 2004). Shaded area represents gas from deep accumulations and seeps at the Starunia palaeontological site and surrounding area after Kotarba *et al.* (2005b)



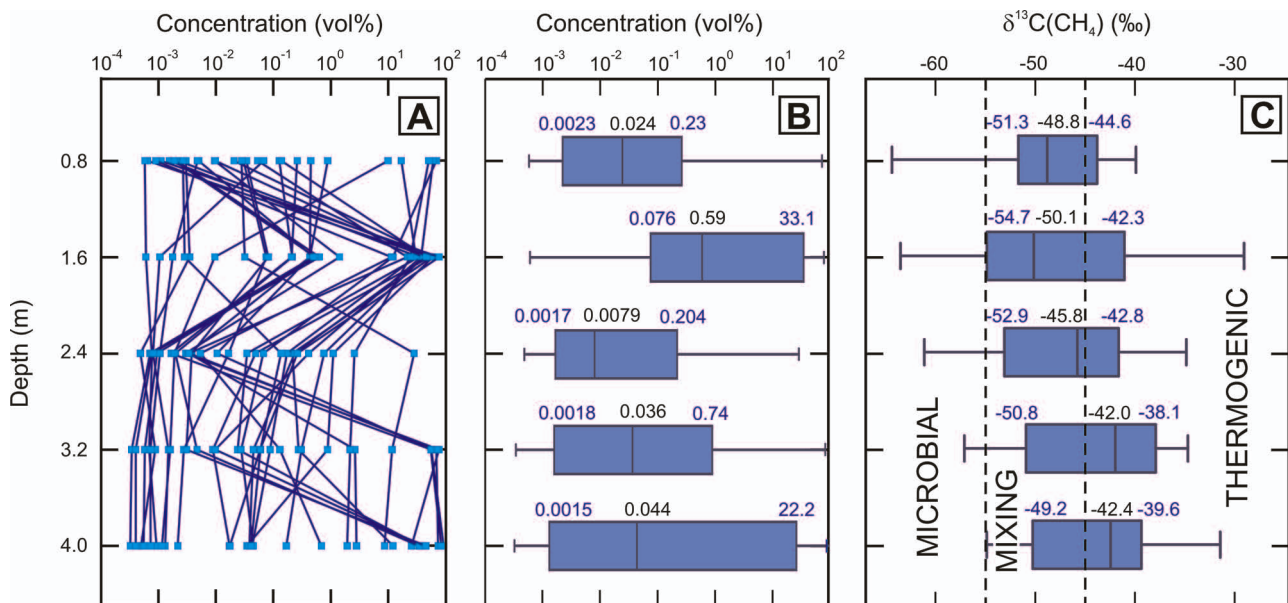
**Fig. 5.** Stable carbon isotope composition of methane, ethane and propane from near-surface gas samples collected at sites Nos 4, 5, 12, 14, 17, 18, 21, 22, 23 and 24, from 0.8, 1.6, 3.2 and 4.0 m depths. Structure of the graph after Rooney *et al.* (1995). Shaded area represents gas from deep accumulations and seeps at the Starunia palaeontological site and surrounding area after Kotarba *et al.* (2005b)

(“oil window”) (Kotarba *et al.*, 2005b) at the maturity level 0.7 to 0.9% on vitrinite reflectance scale, based on the assumption that mixed type II/III kerogen is present.

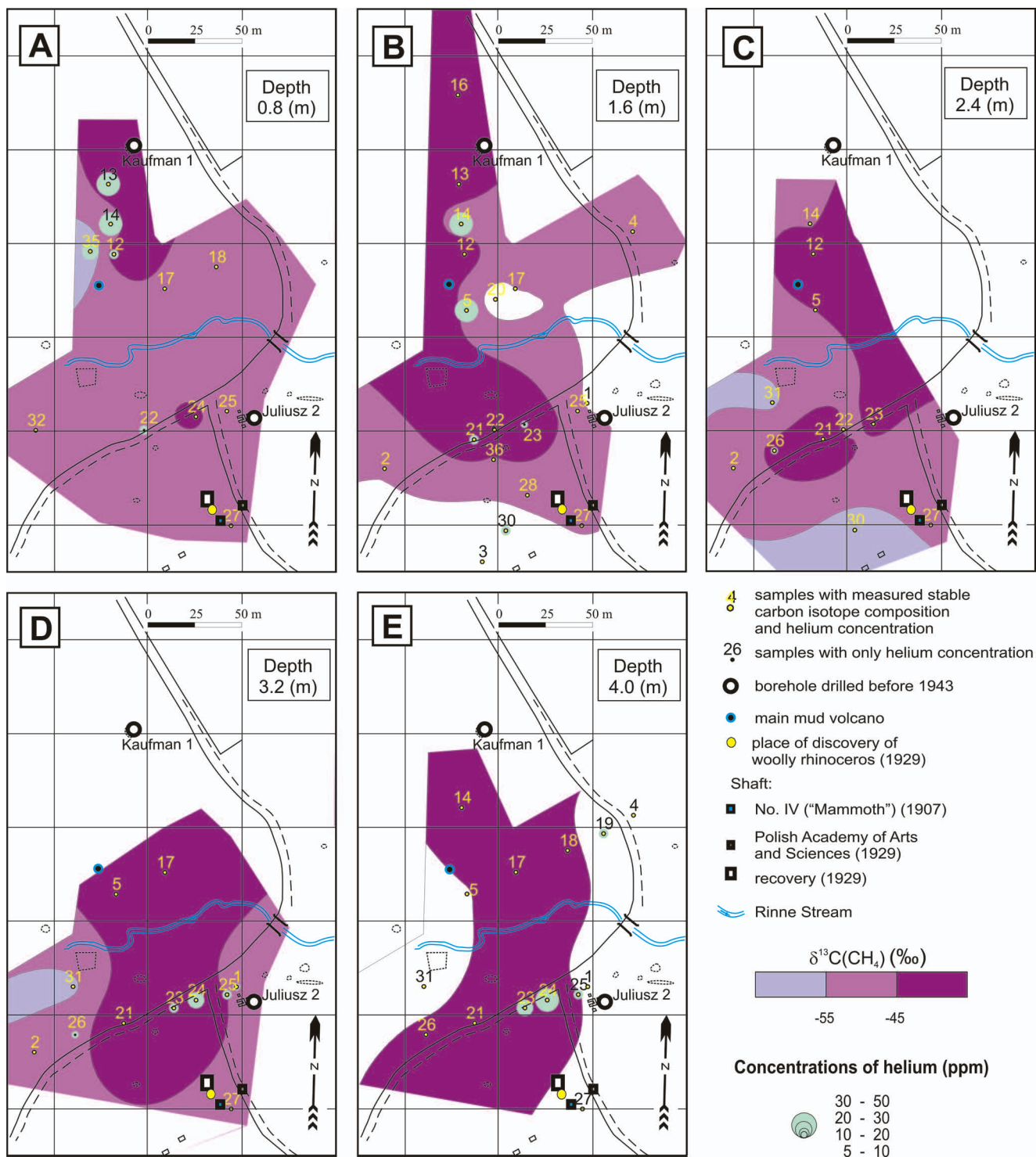
In the near-surface gases, practically all of the ethane,

propane, and methane with  $\delta^{13}\text{C}$ -values higher than  $-45\text{‰}$  (Figs 3–5, 6C) are of thermogenic origin. It is apparent (Fig. 6C), that the distribution of thermogenic methane in Quaternary sediments is variable and generally increases with depth. At the sites where  $\delta^{13}\text{C}$ -values of methane are lower than  $-45\text{‰}$  (Figs 3–5, 6C, 7) microbial methane or a mixture of microbial and thermogenic methanes occur. Microbial methane was generated within Quaternary sediments of the Starunia area, as documented by anomalous  $\delta^{13}\text{C}$ -values of methane below  $-55\text{‰}$  (Figs 3, 7). The near-surface gases sampled at different depths at sites Nos 1, 3, 14, 17, 20, 30, 31 and 35 (Figs 3, 7) reveal high microbial component. Sometimes, an isotopic shift towards heavier  $\delta^{13}\text{C}$  values (Fig. 3) can be caused not only by genetic effects but also by secondary oxidation of microbial and/or thermogenic methane (Whiticar & Faber, 1986; Woltemate *et al.*, 1984). Some inaccuracies in the classification of the analysed gases in genetic diagrams (Figs 3, 4) can be caused by the influence of various secondary processes (oxidation, biodegradation, etc.) on molecular and/or isotope compositions (Table 3).

Wide ranges of methane and total  $\text{C}_2\text{--C}_5$  alkanes concentrations of the analysed gases and considerably higher mean values compared to medians for measured hydrocarbon concentrations (Tab. 4, Figs 6A, B, 8A, B) indicate the presence of a large number of anomalous values in the 4 m sample depth interval. The diversity of changes in hydrocarbon concentrations at different depths points to the anisotropy of the near-surface zone. The remaining relationships, apart from genetic and secondary processes, may suggest the influence of other factors: lithological variability of Quaternary sediments (Sokołowski *et al.*, 2009), their saturation with bitumen (Kotarba *et al.*, 2009b), as well as moisture content and the action of microorganisms (Barabasz *et al.*, 2009).



**Fig. 6.** (A) Changes of methane concentrations, (B) distribution of methane concentrations displayed in the form of box plots, and (C) its stable carbon isotope composition at selected sampling depths. Blue numbers indicate lower and upper quartiles, while black number corresponds to median



**Fig. 7.** Contour maps of  $\delta^{13}\text{C}(\text{CH}_4)$  values at the selected sampling depths: (A) 0.8, (B) 1.6, (C) 2.4, (D) 3.2, and (E) 4.0 m

Taking into account the migration of gases from deep accumulations towards the surface, a general increase in concentration with depth should be expected (increasing dispersion towards the surface). For methane, the highest inter-quartile range, an indicator of the variability of an analyzed parameter, was found at a sampling depth of 1.6 m (Fig. 6B). This implies that at this particular depth methane is derived from a mixture of thermogenic and microbial

sources. For total  $\text{C}_2\text{-C}_5$  alkanes the highest inter-quartile range was observed at a sampling depth of 4.0 m (Fig. 8B). The values of the contour lines in the maps of the distribution of methane and total  $\text{C}_2\text{-C}_5$  alkane concentrations for different sampling depths (Figs 9, 10) were determined based on a statistical procedure. For example, a histogram and cumulative frequency distribution for methane are presented in Fig. 2. The lateral distribution of methane and total



**Table 4**

Principal statistical parameters of methane, alkanes and alkenes concentrations of 150 near-surface gas samples collected from the depths: 0.8, 1.6, 2.4, 3.2 and 4 m

Depth (m)	Methane (vol %)			Total C <sub>2</sub> -C <sub>5</sub> alkanes (vol%)			Total C <sub>2</sub> -C <sub>4</sub> alkenes (vol%)		
	Maximum	Mean	Median	Maximum	Mean	Median	Maximum	Mean	Median
0.8	68.6	6.95	0.024	2.93	0.18	0.0026	0.012	0.0008	<0.0000
1.6	77.1	17.0	0.59	2.41	0.29	0.0058	0.046	0.0032	<0.0000
2.4	28.3	1.14	0.0079	0.088	0.0091	0.0008	0.0008	0.0001	<0.0000
3.2	76.4	9.18	0.036	2.15	0.14	0.0024	0.045	0.0015	<0.0000
4.0	92.2	15.3	0.044	2.85	0.34	0.0099	0.049	0.0028	<0.0000

C<sub>2</sub>-C<sub>5</sub> alkane concentrations shows a complicated pattern. Qualitatively, areas of increased methane concentration correspond to those of increased total C<sub>2</sub>-C<sub>5</sub> alkanes (Figs 9, 10). This is particularly visible for the sampling depth of 4.0 m (Figs 9E, 10E). Such relationships indicate that most of the gaseous hydrocarbons originate from deep sources.

### Hydrogen

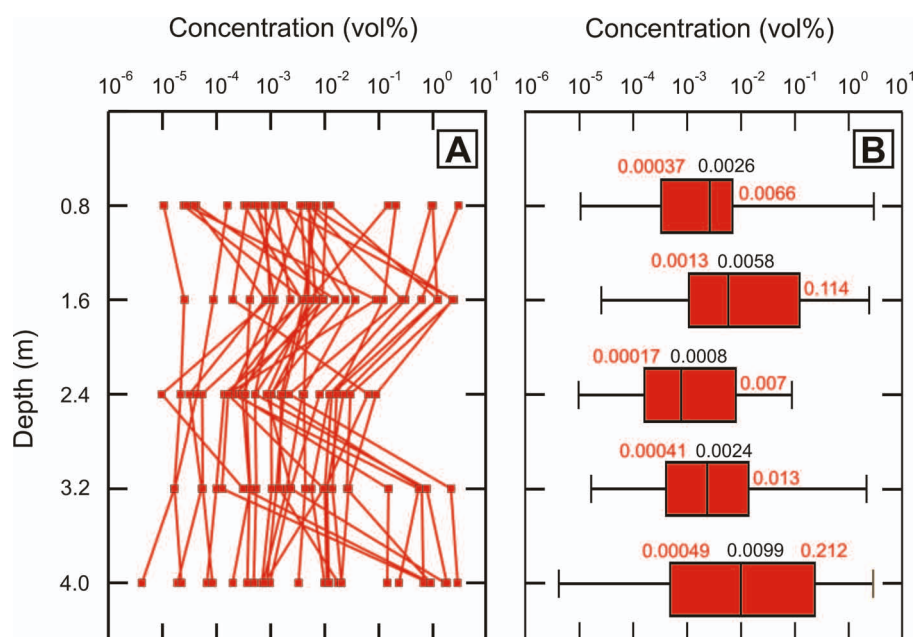
Hydrogen concentrations in the near-surface gases vary from 0.00 to 0.063 vol% (Tables 2 and 5). Natural hydrogen is generated by various biogenic and abiogenic processes: microbial fermentation of sedimentary organic matter, microbial carbon dioxide reduction, thermal decomposition of sedimentary organic matter, hydrolysis, water radiolysis (dissociation of water molecules bombarded by alpha particles), and natural nuclear reactions (Zobell, 1947; Zinger, 1962; Hawkes, 1972; Dubessy *et al.*, 1988; Whitaric *et al.*, 1986; Savary & Pagel, 1997). Hydrogen is a very reactive and mobile gas, so its retention in petroleum traps and in

sedimentary rocks is rather ephemeral. Thus, its presence in natural gases indicates that it is either recently generated in secondary reactions within the reservoir and/or in the adjacent source beds, or it is ascending from deep-seated sources (Hunt, 1996).

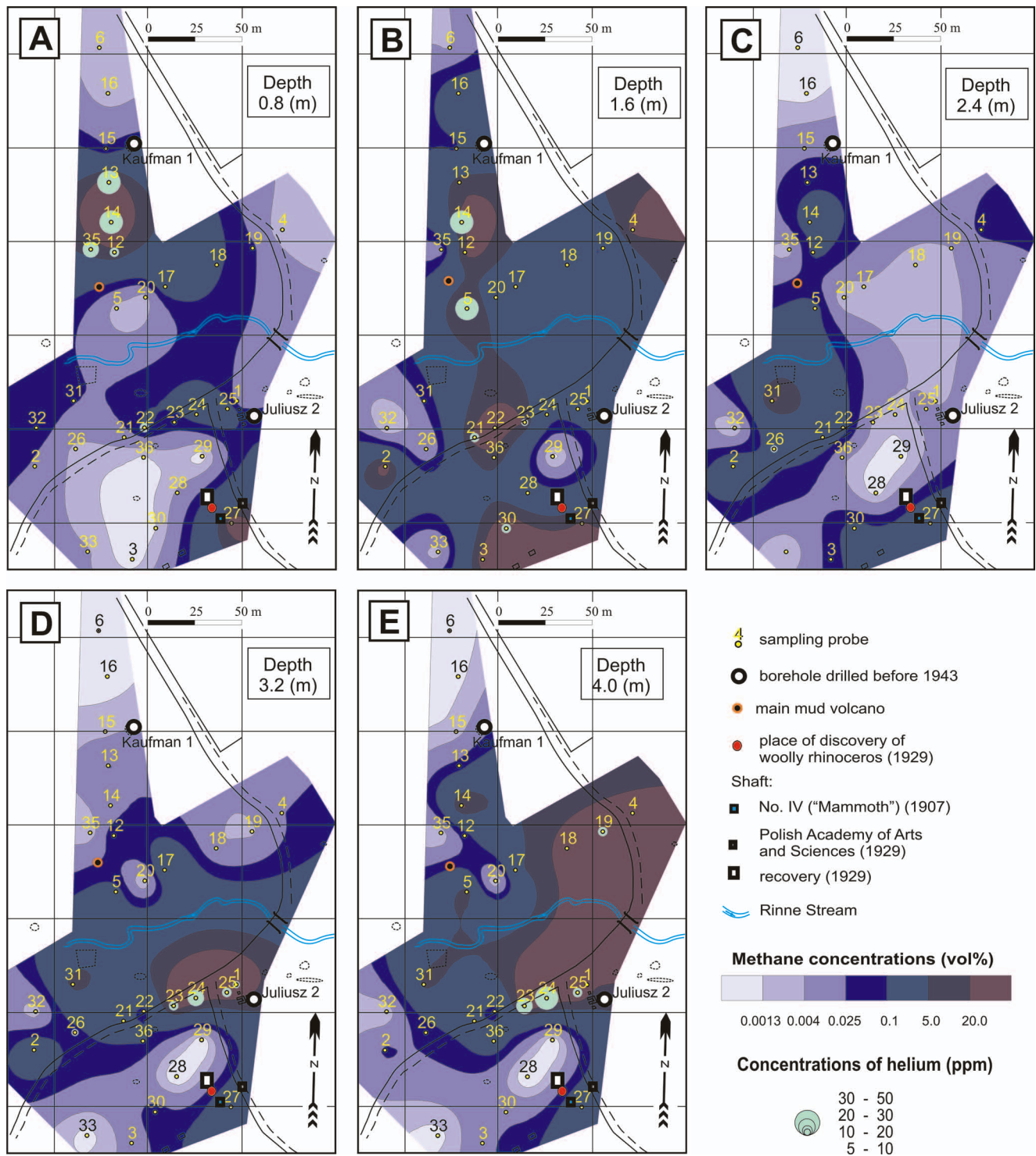
In Pleistocene and Holocene sediments considerable quantities of methanogenic and methylotrophic bacteria were found (Barabasz *et al.*, 2009). Therefore, it seems very probable that the presence of hydrogen within the near-surface zone of the Starunia area is related to microbial processes. The presence of alkenes in the near-surface gases (Tables 2 and 4) also suggests a contribution from microbial reactions.

### Helium

Helium concentrations vary from 0.00 to 0.0048 vol% (Table 5). Generally, increased helium concentrations follow those of methane (Fig. 6) and higher C<sub>2</sub>-C<sub>5</sub> alkanes (Fig. 7), and in most cases its elevated ("anomalous") con-



**Fig. 8.** (A) Changes of total C<sub>2</sub>-C<sub>5</sub> alkanes concentrations and (B) distribution of total C<sub>2</sub>-C<sub>5</sub> alkanes concentrations displayed in the form of box plots at selected sampling depths. Red numbers indicate lower and upper quartiles, while black number corresponds to median

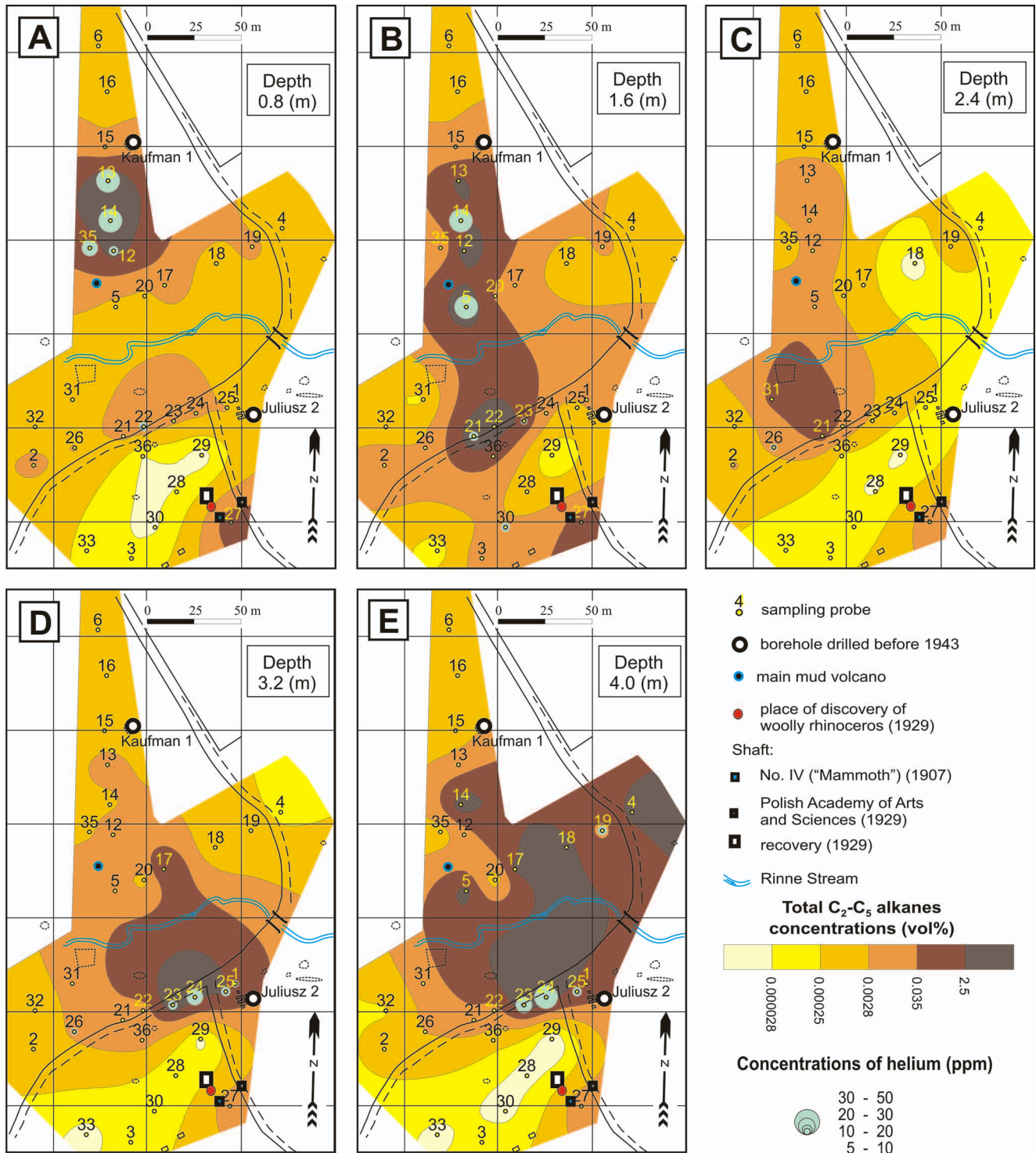


**Fig. 9.** Contour maps of methane concentration at the selected sampling depths: (A) 0.8, (B) 1.6, (C) 2.4, (D) 3.2, and (E) 4.0 m

centration is connected with the thermogenic gases (Fig. 11). Helium is generally of crustal origin, and only an insignificant amount is derived probably from the upper mantle (Kotarba & Nagao, 2008). Helium and thermogenic gaseous hydrocarbons migrated upwards along the Rinne Fault and other tectonic zones in the study area, and then within lithologically diversified Pleistocene and Holocene sediments (Sechman *et al.*, 2009).

### Carbon dioxide

Carbon dioxide which occurs in the natural gases of deep accumulations and "upper oil eye" (OE-U) seep (Fig. 11) was generated by thermogenic processes (Kotarba *et al.*, 2005b). However, carbon dioxide from the "lower oil eye" (OE-L) surface seep and from various sampling depths of the near-surface zone is isotopically very heavy [ $\delta^{13}\text{C}(\text{CO}_2)$



**Fig. 10.** Contour maps of total C<sub>2</sub>-C<sub>5</sub> alkanes concentration at the near-surface zone at sampling depths: (A) 0.8, (B) 1.6, (C) 2.4, (D) 3.2, and (E) 4.0 m

up to 24.3‰] (Table 3, Fig. 11). This isotopic effect is most probably connected with microbial processes and/or isotope fractionation caused by dissolution of carbon dioxide in water and oil during migration. The high variability of stable carbon isotope composition of carbon dioxide at various depths in the near-surface zone (Figs 12, 13C) could be caused by the following factors: separate occurrence of thermogenic and microbial carbon dioxide, mixing of these

gases, secondary oxidation of hydrocarbons, as well as carbon dioxide dissolution in water and oil during migration through lithologically diversified Pleistocene and Holocene sediments.

The contour map of carbon dioxide concentration for different depths (Fig. 14) is based on the same statistical procedure as the contour maps for methane and total C<sub>2</sub>-C<sub>5</sub> alkanes (Figs 7, 9).

**Table 5**

Principal statistical parameters of carbon dioxide, hydrogen and helium concentrations measured in 150 near-surface gas samples collected from the depths: 0.8, 1.6, 2.4, 3.2 and 4 m

Depth (m)	Carbon dioxide (vol%)			Hydrogen (vol%)			Helium (vol%)		
	Maximum	Mean	Median	Maximum	Mean	Median	Maximum	Mean	Median
0.8	7.99	1.02	0.24	0.016	0.0033	<0.000	0.0048	0.0004	<0.000
1.6	15.8	2.49	0.47	0.017	0.0044	0.003	0.0040	0.0004	<0.000
2.4	4.65	0.41	0.22	0.053	0.0037	<0.000	0.0005	<0.0000	<0.000
3.2	12.0	1.18	0.23	0.063	0.0068	<0.000	0.0024	0.0002	<0.000
4.0	11.8	1.73	0.28	0.056	0.0074	<0.000	0.0033	0.0003	<0.000

The vertical distribution of carbon dioxide concentration (Table 5, Figs 13, 14) shows relationships that are similar to those for methane (Figs 4, 6) and total C<sub>2</sub>-C<sub>5</sub> alkanes (Figs 5, 7) concentrations. A distinct increase in carbon dioxide concentration was identified at sampling depth 1.6 m (Figs 13A, B, 14B). These complicated depth variations in concentration and stable isotope composition of carbon dioxide also indicate both the multiple origins of this component of the analysed gases and the influence of secondary processes.

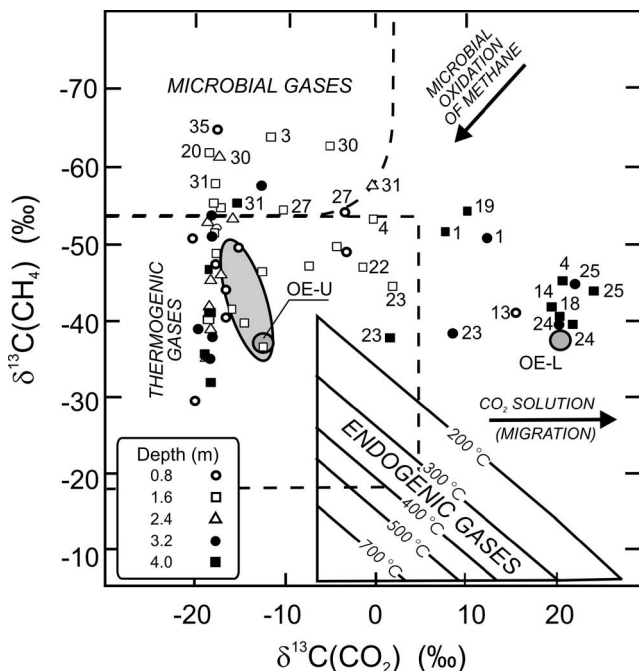
### Origin of near-surface gases and sites of preservation of extinct large mammals

Zones of higher thermogenic methane concentration together with Pleistocene sediments dominated by clayey muds highly saturated with bitumen and brines (Kotarba *et al.*, 2009b) seem to be the most favourable environment for preservation of large mammal fossils.

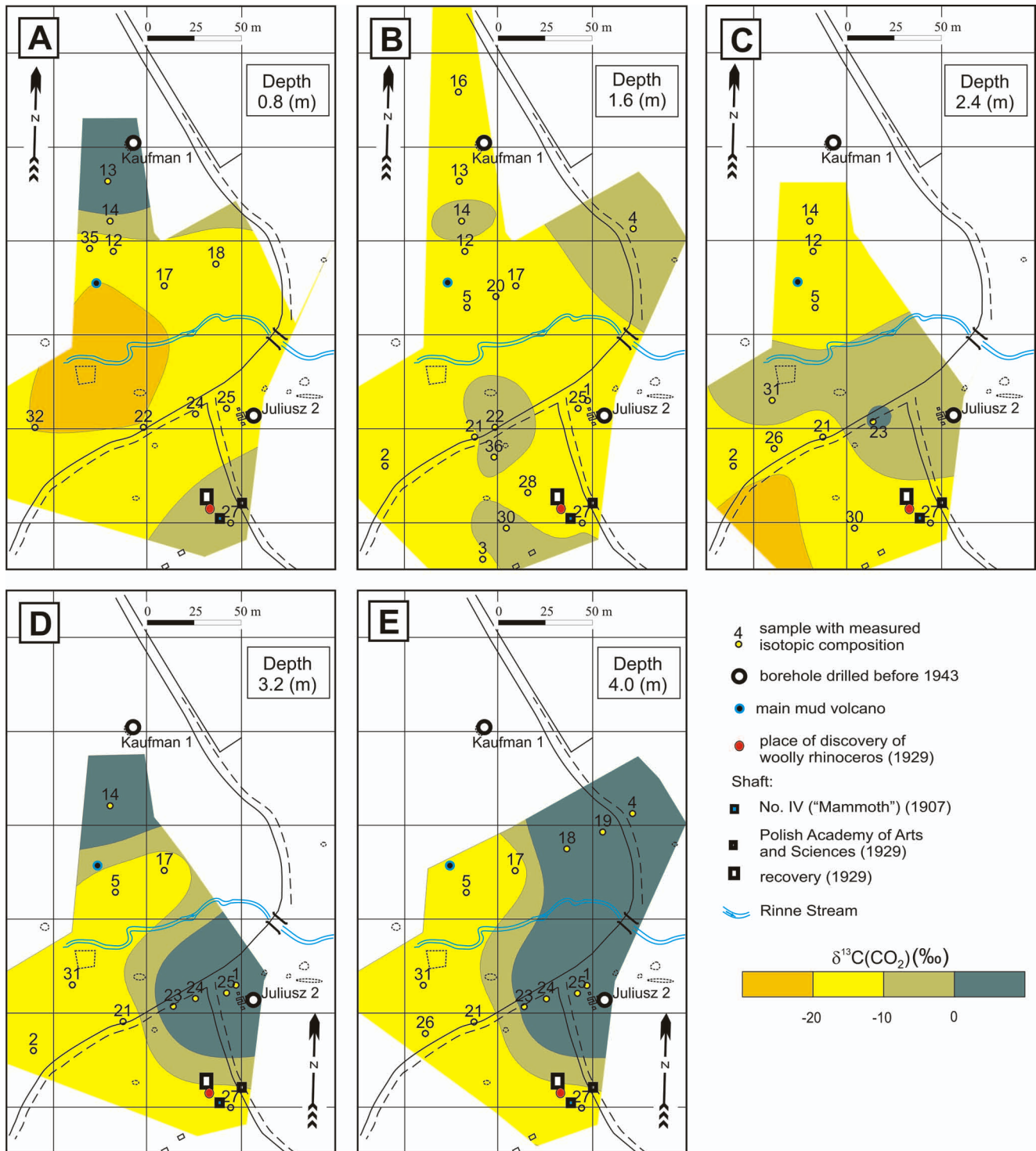
It is likely that during the Pleistocene tundra winters, when thick ice and snow covered the tundra "palaeo-swamp", the areas where the outflows of brines, oils, helium, and thermogenic gaseous hydrocarbons took place were characterized by higher temperatures, which resulted in melting and cracking of ice and snow and drowning of large mammals (Kotarba *et al.*, 2008b).

Chloride ion content in the Quaternary sediments is also variable (Kotarba *et al.*, 2009b). Because the metabolism of methane bacteria (methanogens) depends on these factors (Woltemate *et al.*, 1984; Zhang & Chen, 1985), detailed identification of such sites may help to identify the sites unfavourable for burial and preservation of Pleistocene vertebrate fossils. Zones of microbial methane's occurrence within Pleistocene sediments would be less promising sites for future discovery of well-preserved, large, extinct mammals. The older Pleistocene and Holocene microbial gases have already escaped to the atmosphere. Microbial methane recently detected in the near-surface zone was generated locally, in recent swamps and in recent descending meteoric waters which infiltrated Pleistocene and Holocene sediments. Molecular and isotopic compositions of analysed gases accumulated in the Quaternary sediments in the near-surface zone enabled the determination of the area of large mammals prospecting (yellow zone in Fig. 1). Bearing in mind the lithological criteria, where the total thickness of Pleistocene muds exceeds 2 meters (Sokolowski *et al.*, 2009), the most favourable conditions for preservation of large, extinct mammals still exist in the vicinity of sampling probe sites Nos 21, 22, 23 and 36 (Fig. 1).

However, it must be emphasized that spatial distributions of concentrations of the analysed gases can be strongly affected by a high number of closed and recultivated shafts, the existing and recultivated dug-wells and old boreholes, which number approximately 500 in the study area (Kotarba



**Fig. 11.**  $\delta^{13}\text{C}(\text{CH}_4)$  versus  $\delta^{13}\text{C}(\text{CO}_2)$  for near-surface gases from five sampling depths between 0.8 and 4.0 m. Compositional fields modified from Gutsalo and Plotnikov (1981) and Kotarba (1988). Shaded area represents gas from deep accumulations, "upper oil eye" (OE-U) and "lower oil eye" (OE-L) seeps at the Starunia palaeontological site and the surrounding area after Kotarba *et al.* (2005b)



**Fig. 12.** Contour maps of  $\delta^{13}\text{C}(\text{CO}_2)$  values at the selected sampling depths: (A) 0.8, (B) 1.6, (C) 2.4, (D) 3.2, and (E) 4.0 m

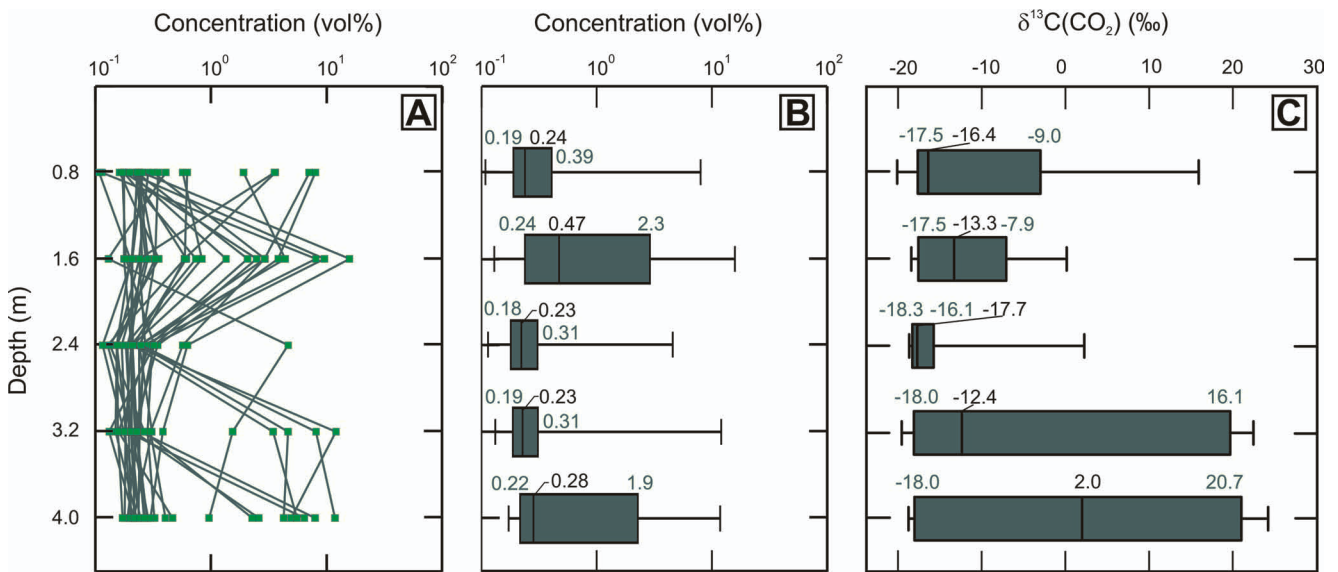
& Stachowicz-Rybka, 2008; Kotarba, 2009). Such sites can be located at additional migration routes for ascending gases as well as descending meteoric waters and microbial gases.

## CONCLUSIONS

The results of molecular and isotopic analyses of near-surface gases down to 4.0 m of depth in the Starunia

area were used for establishing the most favourable zone for preservation of large, extinct mammals within the Pleistocene sediments.

Highly variable concentrations of methane (up to 92.2 vol%), total  $\text{C}_2\text{-C}_5$  alkanes (up to 2.93 vol%) and carbon dioxide (up to 15.8 vol%), identified at different depths, indicate a diversified origin of the analysed gases and the influence of secondary processes (oxidation, biodegradation, etc.). A major part of the methane and all of the higher gaseous hydrocarbons accumulated within the near-surface



**Fig. 13.** (A) Changes of carbon dioxide concentrations, (B) distribution of carbon dioxide displayed as box plots, and (C) stable carbon isotope composition of carbon dioxide at various sampling depths. Green numbers indicate lower and upper quartiles, while black number corresponds to median

zone are of thermogenic origin. The distribution of thermogenic methane and higher gaseous hydrocarbons in Quaternary sediments varies and, generally, increases with depth. Helium of crustal origin migrated along the Rinne Fault and through other tectonic zones in the study area, and was subsequently dispersed during migration through the lithologically diversified Pleistocene and Holocene sediments. Carbon dioxide has a polygenetic origin: thermogenic, microbial, and generated by oxidation of microbial methane and/or thermogenic hydrocarbons. Apart from genetic factors, the high variability of carbon dioxide concentration observed at various depths was caused by its dissolution in water and oil during migration through lithologically diversified Pleistocene and Holocene sediments.

Zones of thermogenic methane accumulations within Pleistocene sediments dominated by clayey muds highly saturated with bitumen and brines are the most favourable preservation sites for large, extinct mammals. It is likely that during the Pleistocene tundra winters thick ice and snow covered the tundra lake and swamp areas. Only in locations, where outflows of brines, oils, helium and thermogenic gaseous hydrocarbons took place, due to higher temperature, would melting and cracking of ice and snow and drowning of large mammals possibly have occurred. Bearing in mind the geochemical and lithological criteria, the most favourable conditions for the preservation of large, extinct mammals still exist in the vicinity of sampling probe sites Nos 21, 22, 23 and 36.

Zones of the occurrence of microbial methane within Pleistocene sediments would be less favourable for future discovery of well-preserved, large, extinct mammals because this methane was generated within the recent swamps and also in recent descending meteoric waters, which infiltrated Pleistocene and Holocene sediments. The older Pleistocene and Holocene microbial gases have already escaped to the atmosphere. Moreover, distribution of the analysed

gases within the near-surface zone can be significantly influenced not only by fault zones and lithologically diversified Pleistocene sediments, but also by numerous, closed and recultivated shafts, by the existing and recultivated dug-wells and by old boreholes. Such sites can determine additional migration routes for ascending gases, descending meteoric waters and microbial gases, and the secondary processes taking place then may negatively affect the preservation of organic matter.

#### 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 Andrzej Zuber of the Polish Geological Institute in Kraków and Kazimierz Różański of the AGH University of Science and Technology in Kraków were very helpful. We would like to express our gratitude to Geoffrey S. Ellis of the U.S. Geological Survey in Denver and Jan Golonka of the AGH University of Science and Technology in Kraków for their critical comments, which improved this paper. Analytical isotope work by Tomasz Kowalski from the AGH University of Science and Technology in Kraków is gratefully acknowledged.

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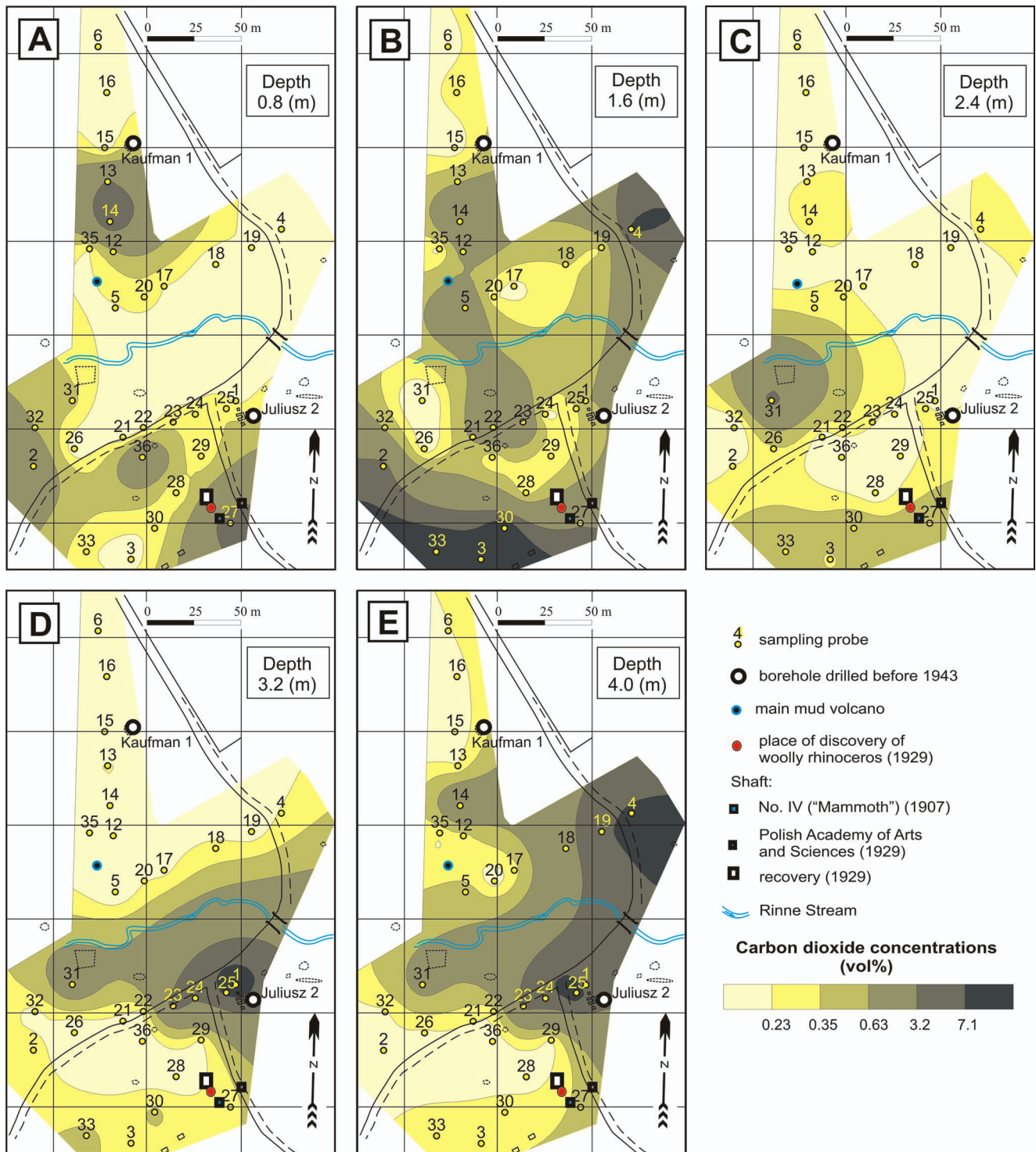


Fig. 14. Contour maps of carbon dioxide concentration at the selected sampling depths: (A) 0.8, (B) 1.6, (C) 2.4, (D) 3.2, and (E) 4.0 m

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