

SURFACE GEOCHEMICAL SURVEY AT STARUNIA PALAEOLOGICAL SITE AND VICINITY (CARPATHIAN REGION, UKRAINE)

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Sechman, H., Kotarba, M. J. & Dzieniewicz, M., 2009. Surface geochemical survey at Starunia palaeontological site and vicinity (Carpathian region, Ukraine). *Annales Societatis Geologorum Poloniae*, 79: 375–390.

Abstract: A surface geochemical survey was carried out in an abandoned ozokerite mine in Starunia, where remnants of a mammoth and three woolly rhinoceroses and one almost completely preserved rhinoceros carcass were found in 1907 and 1929. In total, 689 measurement sites were defined within the selected 300×350 m rectangle (*ca.* 10.5 ha). The analysed soil gases vary in their molecular and isotopic compositions. Several zones with anomalous methane concentrations over 10 vol% were identified in the study area. These anomalous concentrations correlate well with total C₂-C₅ alkane anomalies (over 1 vol%). The zones with carbon dioxide concentrations over 15 vol% are generally shifted SW of those, where the methane and the sum of C₂-C₅ alkanes anomalies were identified. High helium concentrations of crustal origin (over 0.001 vol%) are clustered near fault zones. In a majority of cases methane is of thermogenic origin, migrating to the near-surface zone from deep-seated accumulations. Microbial methane, or methane with a high microbial component, is genetically related to recent swamps. The high variability of concentrations of gaseous components together with the highly variable isotopic composition of individual gases in the soil, indicate their thermogenic and/or microbial origin, and point to the lithological diversity of Quaternary sediments in the study area. Several zones with thermogenic gaseous hydrocarbons and helium were delineated. It is likely that during the Pleistocene winters, under a thick ice and snow cover, the tundra lake and swamp zones around outflows of brines, oil, helium and thermogenic gases had a higher temperature, which resulted in melting and cracking of the ice cover. These sites would be more prospective for future search of well-preserved large vertebrates.

Key words: surface geochemical survey, stable carbon isotopes, methane origin, gaseous hydrocarbon C₂-C₅ origin, carbon dioxide origin, woolly rhinoceros, Starunia, Carpathian region, Ukraine.

Manuscript received 4 May 2009, accepted 1 October 2009

INTRODUCTION

A surface geochemical survey was a part of an interdisciplinary research project focused on the study of the Starunia area. During the period 2006–2009, comprehensive investigations were carried out in an abandoned ozokerite (earth wax) mine in Starunia (Kotarba, 2009), about 130 kilometres southeast of Lviv, Ukraine (Fig. 1). Remnants of a mammoth and woolly rhinoceros were discovered in 1907 in this place. Furthermore, one nearly completely preserved rhinoceros carcass (called “second woolly rhinoceros”) and remnants of two other woolly rhinoceroses were found in 1929. The discovery of large Pleistocene mammals at the Starunia ozokerite mine was a spectacular scientific event on a world scale. An unique combination of oil and brine within the Pleistocene clayey mud, into which the animals had sunk, resulted in almost perfect preservation of these specimens.

General information on the history of the Starunia discoveries and the results of earlier research, including a reconnaissance surface geochemical survey carried out in the area in 2004, are discussed in a special monograph devoted to Starunia (Kotarba, 2005). Based on the results of the preliminary surface survey (Dzieniewicz *et al.*, 2005; Kotarba *et al.*, 2005a, 2008b), a detailed surface geochemical survey was carried out over an area of about 10.5 ha using a rectangular measurement grid.

The main aim of the current study was to identify potential sites within the Pleistocene muds favouring the preservation and conservation of specimens of other woolly rhinoceroses and/or mammoths. Therefore, a high-resolution survey of concentration and isotopic composition of soil gases at a depth of about 1.2 m was undertaken. Measured mixing ratios of gaseous alkanes, alkenes, carbon dioxide,

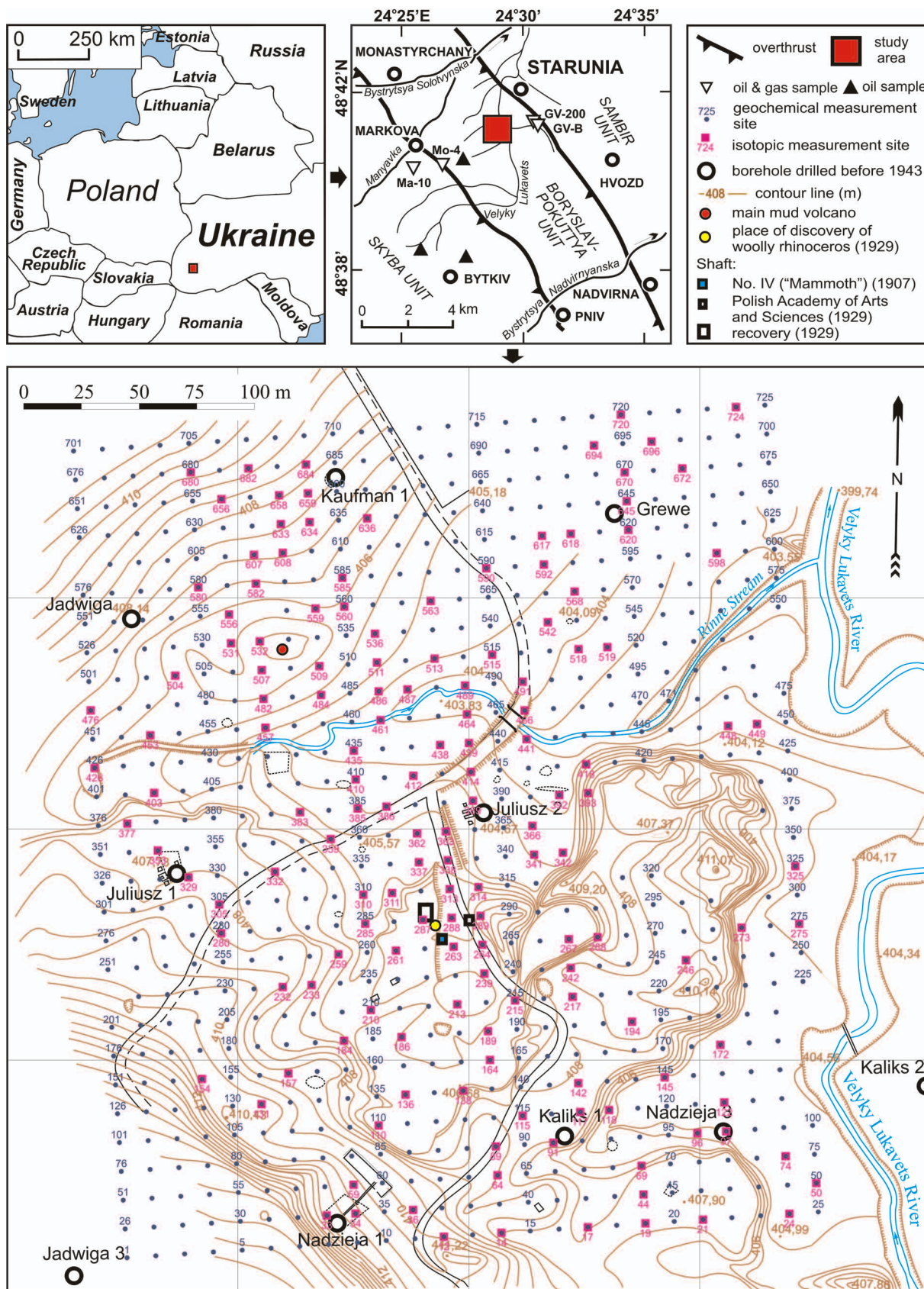


Fig. 1. Sketch map of the Starunia study area (Carpathian region, Ukraine) showing the location of surface geochemical survey. Deep wells for oil and gas exploitation are also shown (Kotarba et al., 2005b)

hydrogen and helium, and relations between these components, as well as stable carbon isotope composition of methane, ethane, propane and carbon dioxide, allowed us to investigate the origin and genetic connections between the soil gases, the natural gases accumulated in deep structures and the recently generated microbial gases. Moreover, an attempt was made to determine the extent of migration of natural gas from deep accumulations to the surface, especially along the thrust and fault zones.

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 at five sites: Boryslav, Volanka, Truskavets-Pomiarki, Dzvinyach, and Starunia (Alexandrowicz, 2005). At the end of the 19th century and in first half of the 20th century, ozokerite was exploited in the Starunia area from the Miocene salt-bearing Vorotyshcha beds of the Boryslav-Pokuttya Unit of the Carpathian Foredeep Basin (Alexandrowicz, 2004, 2005; Koltun *et al.*, 2005).

The top surface of the Miocene Vorotyshcha beds in Starunia, underlying Quaternary deposits, occurs at a maximum depth of 17 metres (Sokołowski *et al.*, 2009). In the area of the abandoned Starunia ozokerite mine, Quaternary sediments mainly contain 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. Miocene strata contain sandstone-claystone breccia with halite, potassium-salt, gypsum and calcite layers, and veins of ozokerite (Korin, 2005).

The Boryslav-Pokuttya Unit is the main oil and gas reservoir in the Ukrainian Carpathians. Tectonically, the unit represents a stack of superimposed nappes, each of them comprising a flysch sequence covered by molasse strata. 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).

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 surface geochemical survey was carried out within a rectangular, 300×350 m area using regular, 12.5×12.5 m measurement grid. In this pattern, 725 measurement sites were determined, of which 689 were sampled (Fig. 1). The specific free-gas sampling method that was used (Sokolov & Grigoriev, 1962; Philp, 1987; Tedesco, 1995) was developed at the Department of Fossil Fuels, AGH University of Science and Technology in Kraków (Dzieniewicz & Sechman, 2001, 2002). The target sampling depth was 1.2 metres, however, on-site lithological variability resulted in actual sampling depths from 1.1 to 1.3 metres.

A special geochemical probe was applied together with gas-tight syringe and sample vessel. The probe was driven down to the sampling depth, then soil atmosphere was collected with the gas-tight syringe. The gas sample was injected into a vessel completely filled with the analytically pure saturated solution of NaCl and then transported to the laboratory. The sampling procedure ensured “sterile” sampling of soil gases, free of contamination from the atmospheric air (Dzieniewicz & Sechman, 2001, 2002; Sechman & Dzieniewicz, 2007).

Analytical methods

The molecular composition of gaseous hydrocarbons in soil gases was analysed with the FISSONS Instruments GC 8160 flame-ionisation gas chromatograph under the following conditions: metallic column of internal diameter 4 millimetres and length 1.3 metre filled with activated alumina (mesh 100/120); carrier gas flow rate 60 ml/min (helium); programmed temperature of thermostat: 90°C for 3 min; temperature increase from 90 to 200°C (30°C/min) and held at 200°C for 3 min; temperature of FID detector 270°C; temperature of injection chamber 120°C; volume of the analysed sample 1 ml.

The concentrations (mixing ratios) of carbon dioxide, hydrogen and helium were measured using a Carlo Erba Instruments GC 6300 gas chromatograph equipped with a TCD detector. Carbon dioxide was detected under the following conditions: metallic column 2.5 metres long filled with the HAYSEP Q 80/100 mesh; carrier gas flow 30 ml/min (argon), temperature of thermostat – 65°C (constant), temperature of TCD detector (base – 60°C, filament – 180°C). Hydrogen and helium were detected under the following conditions: metallic column 2.5 metres long filled with molecular sieve 5A 80/100 mesh; carrier gas flow 16 ml/min (argon), temperature of thermostat – 65°C (constant), temperature of TCD detector (base – 60°C, filament – 180°C), volume of analysed sample, 2 ml (VALCO dosage valve).

Both the FID and TCD readings were processed with the PeakSimple software. The gas chromatograph was calibrated with the gas standards “Scott II” from Supelco and Alltech. The precision of concentration (mixing ratio) measurements was equal: ±0.01 ppm for hydrocarbons; ±10 ppm for hydrogen, ±10 ppm helium, and ±0.01 vol% for carbon dioxide.

Table 1

Principal statistical parameters of alkanes concentrations and hydrocarbon index for soil gas samples

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	(vol%)	0.0001	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.6
Maximum	(vol%)	82.6	2.6	0.407	0.2018	0.2515	0.0332	0.1763	0.1148	3.21	404990.6
Median	(vol%)	0.0553	0.0002	0.0001	0.0001	0.0001	0.0	0.0002	0.0	0.0015	55.2
Mean	(vol%)	8.06	0.0894	0.0177	0.0099	0.0066	0.0002	0.0073	0.0017	0.133	2545.5
Stand. dev.	(vol%)	16.8	0.284	0.0563	0.0270	0.0273	0.0013	0.0238	0.0108	0.396	26087.7
Number of samples *		689	652	663	622	615	404	636	371	687	685
Percentage of samples	(%)	100.0	94.6	96.2	90.3	89.3	58.6	92.3	53.8	99.7	99.4

* – number of samples with concentration of the given component over detection limit; stand. dev. – standard deviation; 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 soil gas samples

Statistical parameters	Unit	C ₂ H ₄	C ₃ H ₆	<i>l</i> -C ₄ H ₈	Total C ₂ -C ₄ alkenes	CO ₂	H ₂	He	CDMI
Minimum	(vol%)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.01	b.d.l.	b.d.l.	0.7
Maximum	(vol%)	0.335	0.0167	0.1110	0.4627	15.52	0.066	0.0156	100.0
Median	(vol%)	0.0000	0.0000	0.0000	0.0000	0.69	0.0	0.0000	90.5
Mean	(vol%)	0.0061	0.0001	0.0007	0.0068	1.98	0.004	0.0005	67.1
Stand. dev.	(vol%)	0.0315	0.0013	0.0065	0.0370	2.60	0.008	0.0014	37.2
Number of samples*		420	138	145	510	689	300	126	689
Percentage of samples	(%)	61.0	20.0	21.0	74.0	100.0	43.5	18.3	100.0

* – number of samples with concentration of the given component over detection limit; stand. dev. – standard deviation; b.d.l. – below detection limit

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

Stable carbon isotope analyses were carried out with a Finnigan Delta Plus mass spectrometer. The stable carbon isotope data are presented in the δ -notation relative to the VPDB standard. The analytical precision is estimated to be $\pm 0.2\%$. Methane, ethane, propane and carbon dioxide were isolated chromatographically for carbon isotope analysis. Methane, ethane and propane were combusted over hot copper oxide (850°C) and the carbon dioxide was introduced to the mass spectrometer.

Statistical procedure

For the measured concentrations of gaseous hydrocarbons, helium, hydrogen, carbon dioxide and the results of isotopic analyses [$\delta^{13}C(CH_4)$, $\delta^{13}C(C_2H_6)$, $\delta^{13}C(C_3H_8)$, $\delta^{13}C(CO_2)$] basic statistical parameters are determined.

Qualitative evaluation of the measured methane, total alkanes C₂-C₅, carbon dioxide and helium concentrations

was based on histograms and probability plots. In each plot the boundary between distinctive subsets of data was marked for each studied set of concentration. Determination of concentration boundaries was guided by visible changes of the slope of cumulative probability curves. The determined subset limits were taken as contour spacing in distribution maps of methane, total C₂-C₅ alkanes and carbon dioxide concentrations. Due to the insufficient number of measurement sites, in which helium concentrations exceeded the detection limit, changes in concentration of this gas are displayed as circles of relevant diameters.

Correlations between methane and total C₂-C₅ alkanes, methane and helium, total C₂-C₅ alkanes and helium, methane and carbon dioxide, total C₂-C₅ alkanes and carbon dioxide concentrations were analysed. Scatter-plots were made and correlation coefficients R² calculated for these pairs. Directional correlations between changes of concentrations of the analysed components were investigated.

Table 3

Principal statistical parameters of stable carbon isotope composition of methane, ethane, propane and carbon dioxide for soil gas samples

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	(‰)	-84.6	-29.4	-28.4	-29.2
Maximum	(‰)	-29.9	-23.6	-22.9	22.9
Median	(‰)	-49.4	-26.7	-25.3	-17.3
Mean	(‰)	-51.2	-26.6	-25.7	-13.4
Stand. dev.	(‰)	10.5	1.1	1.7	11.6
Number of samples		147	83	21	150
Percentage of samples	(%)	21.3	12.0	3.0	21.8

Stand. dev. – standard deviation

These correlations illustrate the percentage of congruent and non-congruent changes of the measured concentrations.

RESULTS AND DISCUSSION

The analysed soil gases vary in their molecular composition, and hydrocarbon (C_{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) {CDMI = [$\text{CO}_2/(\text{CO}_2 + \text{CH}_4)$] 100 (%)} gas indices. The molecular composition of the main analysed gases varies within the following ranges (Tables 1, 2): CH_4 from 0.0001 to 82.6 vol% (average 8.06 vol% for 689 samples), sum of $\text{C}_2\text{-C}_5$ alkanes from 0 to 3.21 vol% (average 0.133 vol%), sum of $\text{C}_2\text{-C}_4$ alkenes from 0 to 0.463 vol% (average 0.0068 vol%), CO_2 from 0.01 to 15.5 vol% (average 1.98 vol%), H_2 from 0 to 0.066 vol% (average 0.004 vol%), He from 0 to 0.0156 vol%, hydrocarbon (C_{HC}) index from 55.1 to 404,991, and carbon dioxide methane (CDMI) index from 0.7 to 100.

The analysed soil gases are also variable in their carbon isotope composition. Stable carbon isotope ratios vary within the following ranges (Table 3): $\delta^{13}\text{C}(\text{CH}_4)$ from -84.6 to -29.9‰, $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$ from -29.4 to -23.6‰, $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$ from -28.4 to -22.9‰, and $\delta^{13}\text{C}(\text{CO}_2)$ from -29.2 to 22.9‰.

The distribution of methane concentration is multimodal (Fig. 2A, B). Six subsets can be distinguished: 0.0001 to 0.0016 vol%, 0.0016 to 0.015 vol%, 0.015 to 0.25 vol%, 0.25 to 1.78 vol%, 1.78 to 20.0 vol%, and over 20.0 vol%.

The distribution of total $\text{C}_2\text{-C}_5$ alkanes concentrations is bimodal (Fig. 3A). However, the distribution plot reveals more than 7 subsets (Fig. 3B). The subset limits are: 0 to 0.00005 vol%, 0.00005 to 0.00032 vol%, 0.00032 to 0.01 vol%, 0.01 to 0.1 vol%, 0.1 to 0.32 %, 0.32 to 2.0 vol%, and more than 2.0 vol%.

The spatial distributions of measured methane (Fig. 4) and total $\text{C}_2\text{-C}_5$ alkanes concentrations (Fig. 5) reveal a complex picture. Anomalous concentrations of methane

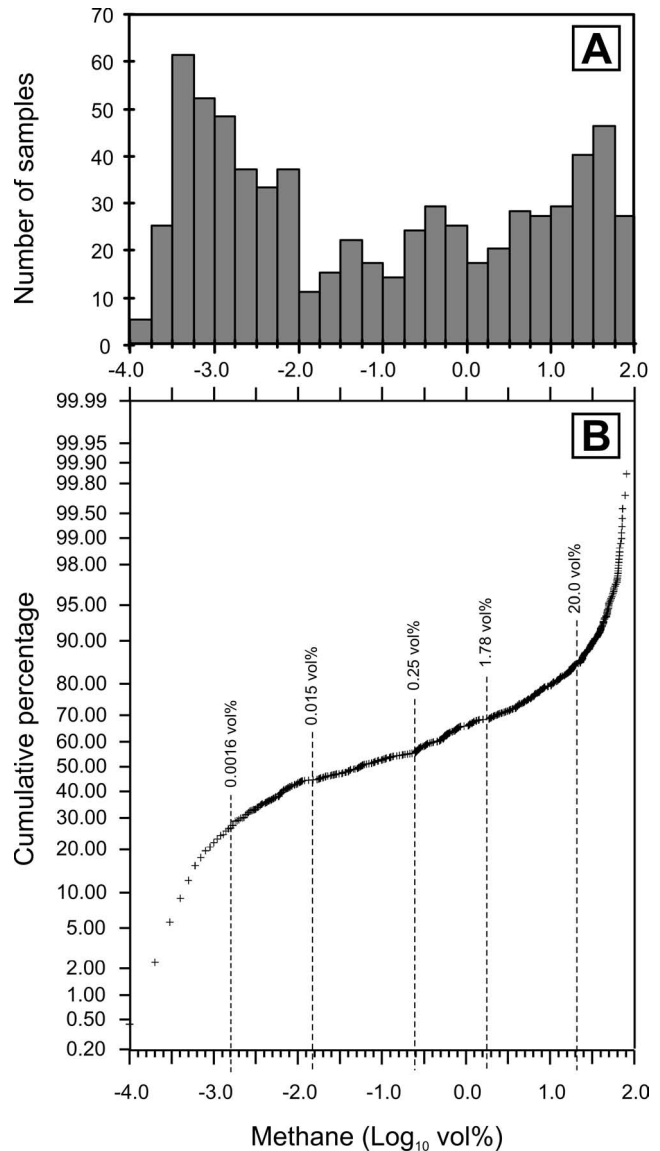


Fig. 2. (A) Histogram and (B) cumulative frequency diagram of methane concentration

(>0.25 vol.%) occupy about 30% of the measurement area and form an irregular pattern, extending from SSE to NNW (Fig. 4). The largest areas of reduced methane concentration occur in the SW and NE parts of the study area. The distribution of the sum of $\text{C}_2\text{-C}_5$ alkane concentrations (Fig. 5) is similar to that of methane. This is confirmed by the correlation of their concentrations (Fig. 6A), and also the high congruence of the trends of their changes (Fig. 7A).

Stable carbon isotope analyses of methane, ethane and propane in soil gases (Table 3) reveal that methane from a majority of analysed sampling sites (Figs 8, 9A, 10) and ethane and propane from all analysed sampling sites (Fig. 9B) are thermogenic in origin and migrated to the near-surface zone from deep-seated accumulations. A population of gas samples from deep accumulations and gases from two surface oil seeps are also displayed in the genetic diagrams (Figs 8, 9A, B) (Kotarba *et al.*, 2005b). Deep gases accumulated in both the Oligocene and Eocene reservoirs as well as

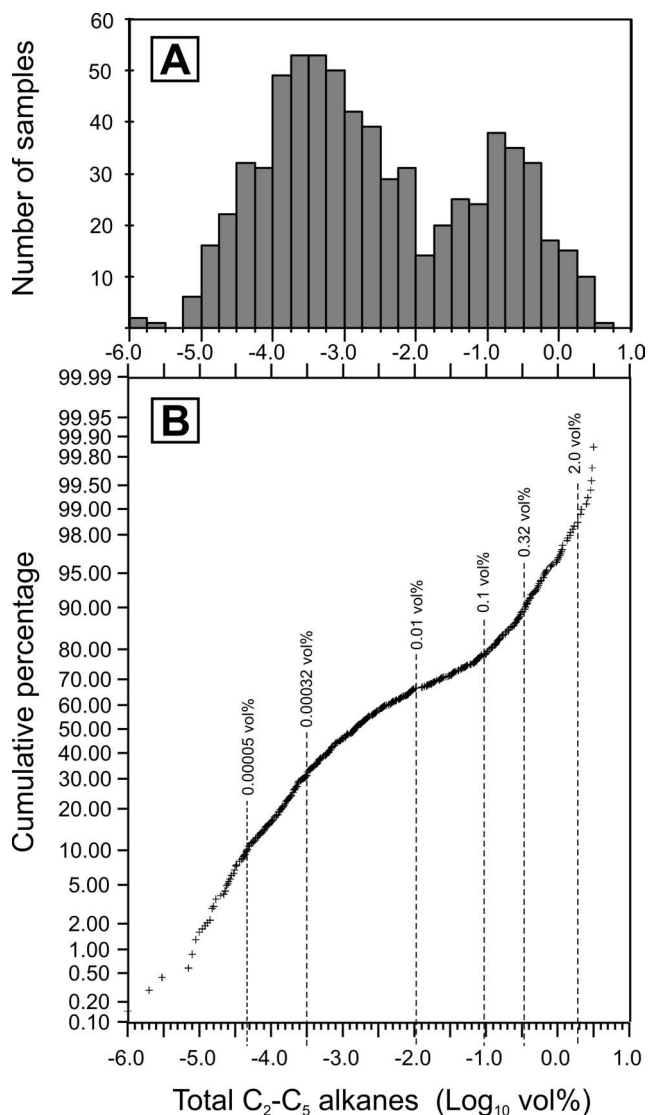


Fig. 3. (A) Histogram and (B) cumulative frequency diagram of total C₂-C₅ alkanes concentration

gases associated with two surface oil seeps in the Starunia area were generated mainly by low-temperature thermogenic processes (“oil window”) at a maturity level of 0.8 to 1.0% on the vitrinite reflectance scale under the assumption that mixed type II/III kerogen occurs (Figs 8, 9A, B).

In places, where $\delta^{13}\text{C}$ -values of methane are less than -55‰ (Figs 8, 9A, 10) microbial methane or a mixture of microbial and thermogenic methane occurs. The presence of hydrogen and alkenes in the soil gases also suggests a contribution from microbial processes (Table 2). Large quantities of microbial methane were generated within the Quaternary sediments of the Starunia area, as documented by depleted (“anomalous”) $\delta^{13}\text{C}$ -values in methane, below -55‰ (Fig. 10). Unlike the sites of helium and thermogenic (hydrocarbons and carbon dioxide) gases fluxes, such locations would be less likely sites for future discovery of well-preserved, extinct mammals because microbial methane was generated locally, in recent swamps.

The distribution of helium concentrations is monomodal, asymmetric, positively skewed with anomalous tail (Fig. 11A). From the probability plot the following concentration ranges were determined: 0 to 0.003 vol%, 0.003 to 0.006 vol%, 0.006 to 0.008 vol% and over 0.008 vol% (Fig. 11B). Generally, the increased helium concentrations follow those of methane (Fig. 4) and higher C₂-C₅ alkanes (Fig. 5). This is confirmed by the relatively high similarity of changes of methane and helium as well as the total C₂-C₅ alkanes and helium concentrations (Fig. 7). The low correlation between the analysed components (Fig. 6B, C) points to different origins for alkanes and helium. Increased helium concentrations occur mainly in the central and northern parts of the study area, where helium and thermogenic gaseous hydrocarbons migrate along the Rinne fault and other tectonic zones and within lithologically differentiated Pleistocene sediments. Helium is generally of crustal origin with more than 99.2% radiogenic ^4He , but an appreciable amount of ^3He is probably derived from the upper mantle (Kotarba & Nagao, 2008).

The distribution of carbon dioxide concentrations is multimodal (Fig. 12A). The limits of the concentration subsets are determined from the probability plot: 0.01 to 0.1 vol%, 0.1 to 0.22 vol%, 0.22 to 0.4 vol%, 0.4 to 2.0 vol%, 2.0 to 6.0 vol%, and over 6.0 vol% (Fig. 12B). Changes in carbon dioxide concentrations (Fig. 13) generally correspond to those of methane (Fig. 4) and total C₂-C₅ alkanes (Fig. 5), but detailed patterns are complicated. Concentrations of CO₂ form irregular, highly fragmented fields. Concentrations over 2 vol% cluster in both the central and south-eastern parts of the study area. The similarity of distribution of alkanes and carbon dioxide concentrations is confirmed by the congruent trends of their changes. For methane, the degree of congruence with carbon dioxide may reach even 70%, and in the case of total C₂-C₅ alkanes almost 67% (Fig. 7). The presence of anomalous carbon dioxide concentrations at the same measuring sites, where higher concentrations of methane homologues were detected, may suggest its endogenic origin. However, the lack of correlation in scatter plots (Fig. 6D, E) between alkanes and carbon dioxide concentration suggests another source of the latter.

The stable carbon isotope composition of carbon dioxide (Figs 14, 15) suggest a variety of origins: thermogenic (most frequent), recent microbial processes, and secondary microbial oxidation of hydrocarbons.

The values of pH and chloride concentrations in the ground waters are variable (Kotarba *et al.*, 2009). Because of the metabolism of methane bacteria (methanogens), which depends on these conditions (Woltemate *et al.*, 1984; Zhang & Chen, 1985), detailed identification of sites where microbial methane occurs, may help to identify places unfavourable to burial and preservation of Pleistocene vertebrates. Locally, in recent swamps, high quantities of microbial methane were generated. The Quaternary sediments of the Starunia study area mainly contain clayey muds with plant remnants, peats, biogenic muds, peat muds, sands, and gravels (Sokołowski *et al.*, 2009; Sokołowski & Stachowicz-Rybka, 2009). In the area of the abandoned ozokerite mine, apart from oil and gas also brines occur, which are ge-

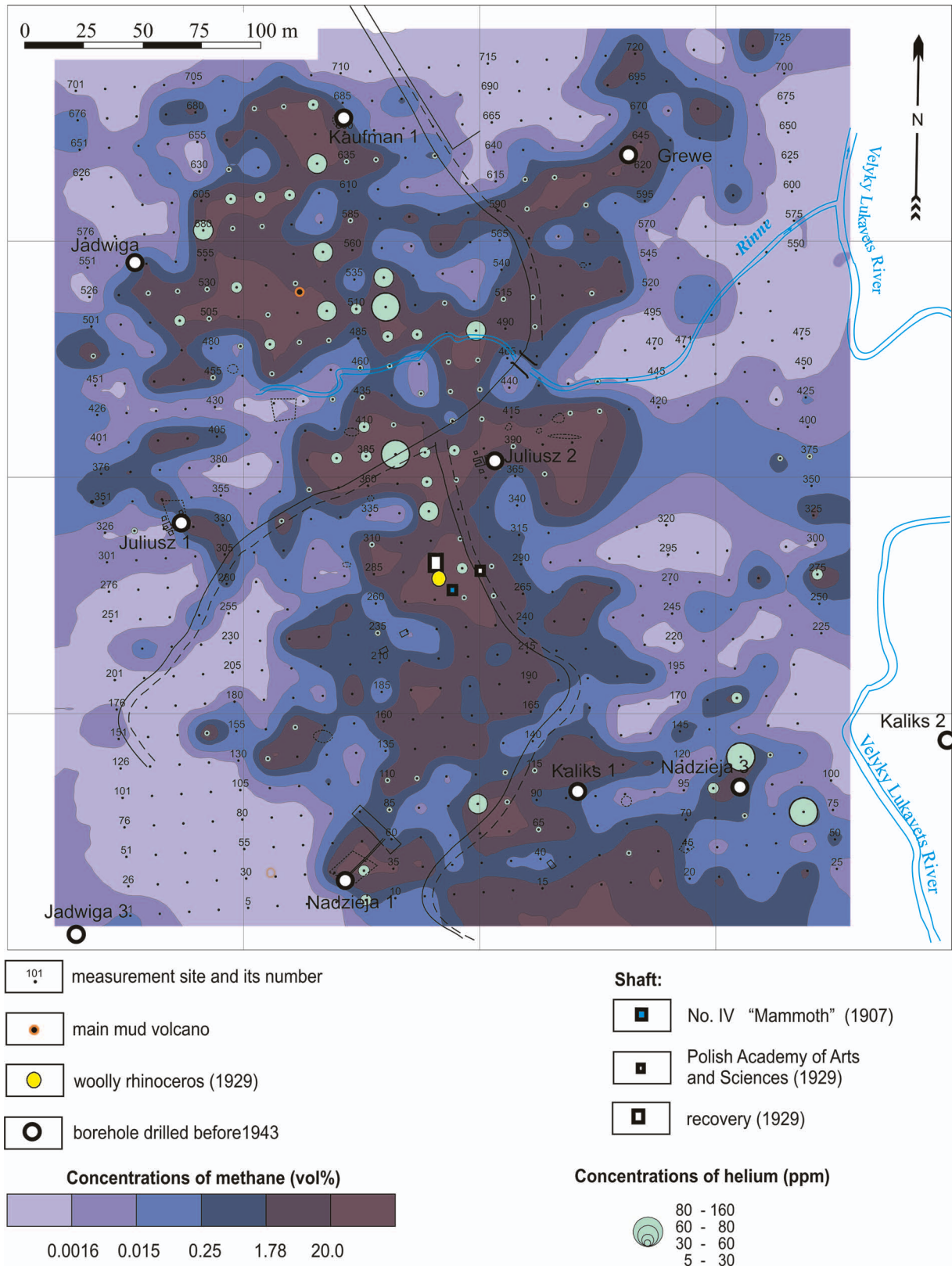


Fig. 4. Contour map of methane mixing ratios and locations of anomalous helium concentrations measured in soil gas samples

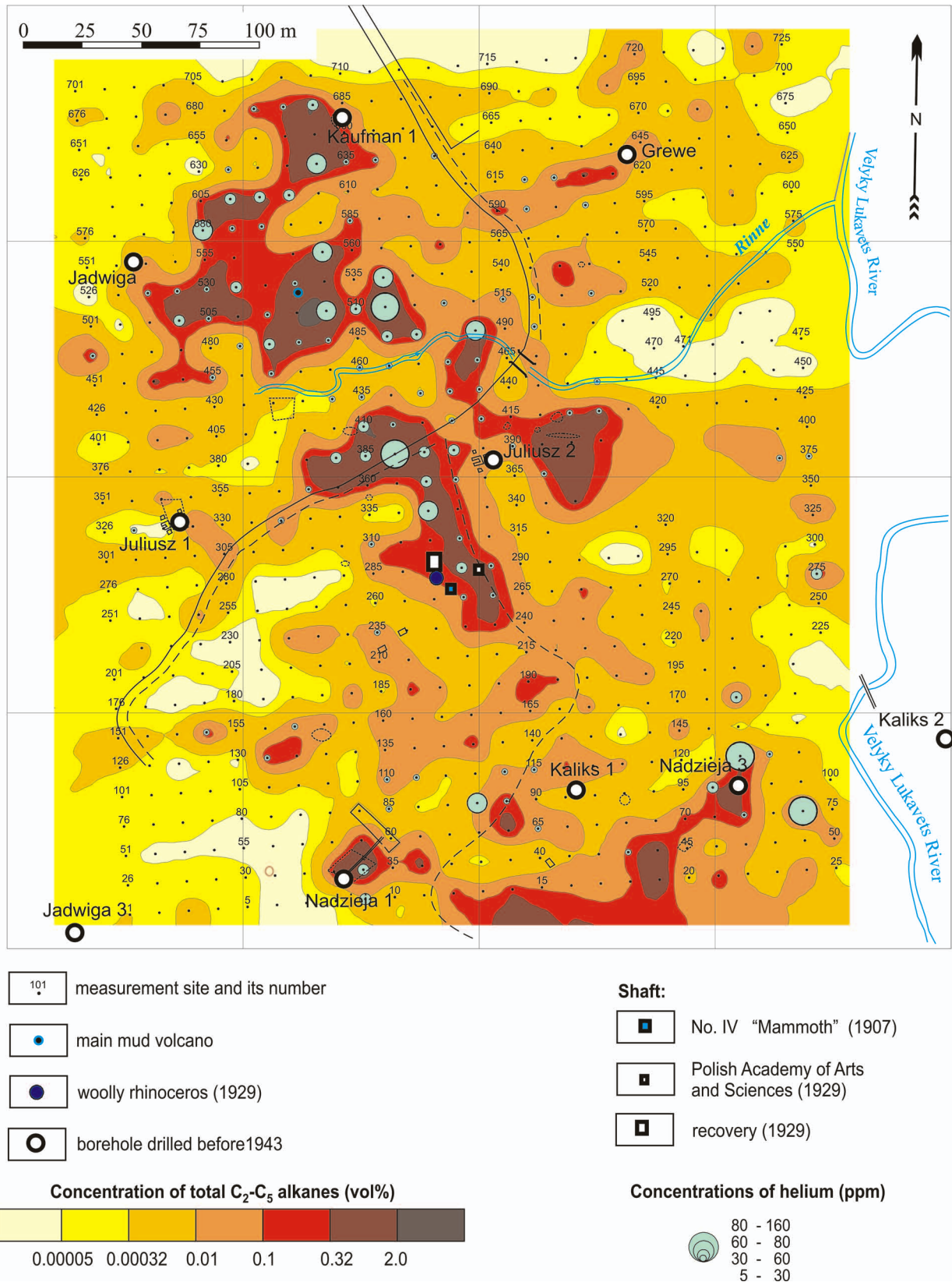


Fig. 5. Contour map of total C₂-C₅ alkanes measured in soil gas samples and location of anomalous helium concentrations measured in soil gas samples

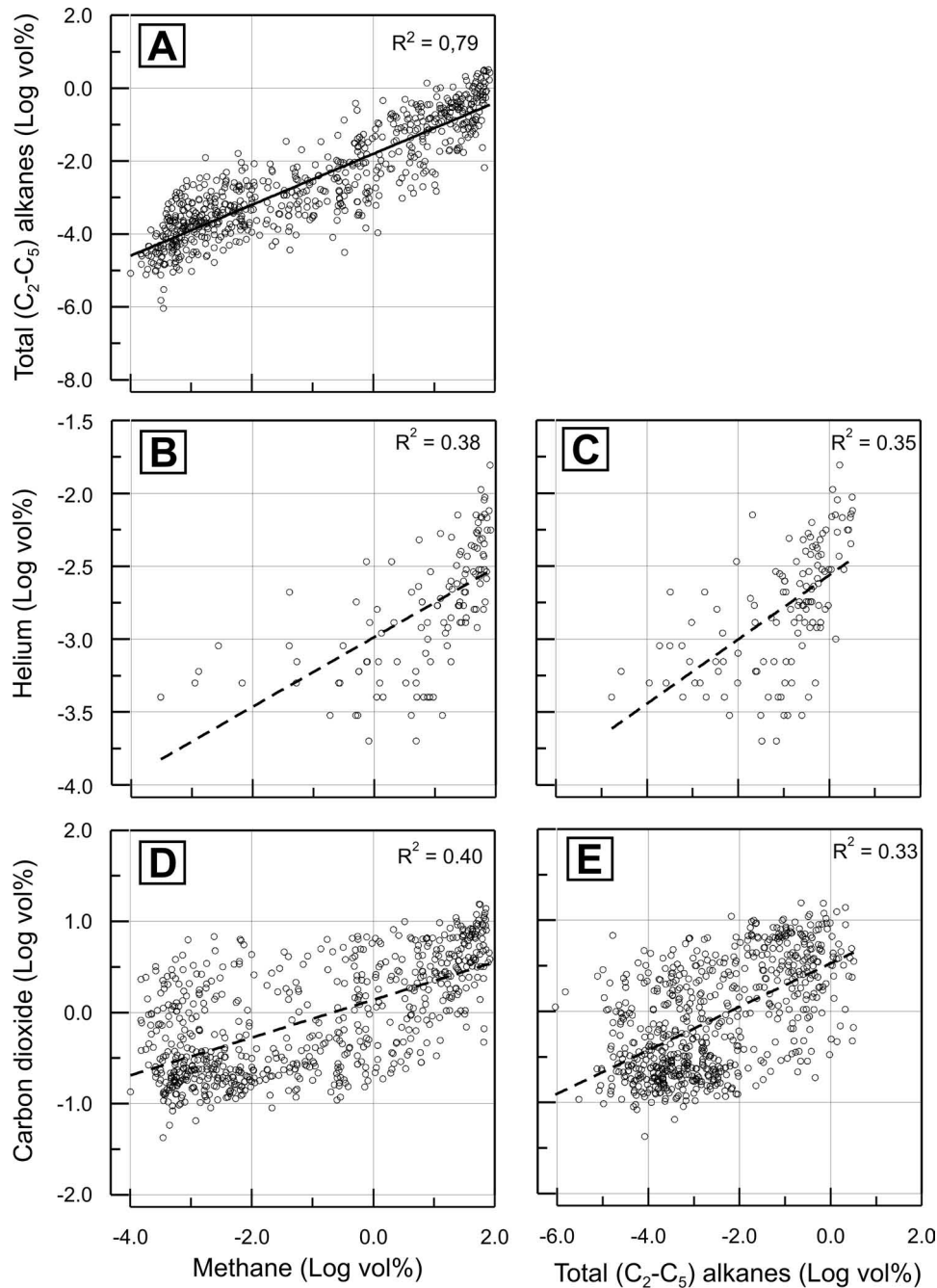


Fig. 6. Scatter-plots of: (A) methane versus total C₂-C₅ alkanes, (B) methane versus helium, (C) total C₂-C₅ alkanes versus helium, (D) methane versus carbon dioxide, and (E) total C₂-C₅ alkanes versus carbon dioxide concentrations

netically related to the underlying Miocene Vorotyshcha salt-bearing beds (Duliński *et al.*, 2005; Korin, 2005). The redox environment within the Quaternary sediments is diversified.

The distributions of the mixing ratios 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, number approximately 500 (Kotarba & Stachowicz-Rybka, 2008; Kotarba, 2009) in the study area (Fig. 1). Such sites can provide additional migration routes for ascending gases.

CONCLUSIONS

The wide range of concentrations of the analysed gases, the presence of several populations of three analysed gaseous components (methane, total C₂-C₅ alkanes and carbon dioxide), as well as variable carbon isotope ratios of methane, ethane, propane and carbon dioxide point to multiple origins and a complex history of migration of these gases to and within the near-surface zone. In the majority of the investigated sites, methane is of thermogenic origin and it migrated to the near-surface zone from deep accumulations.

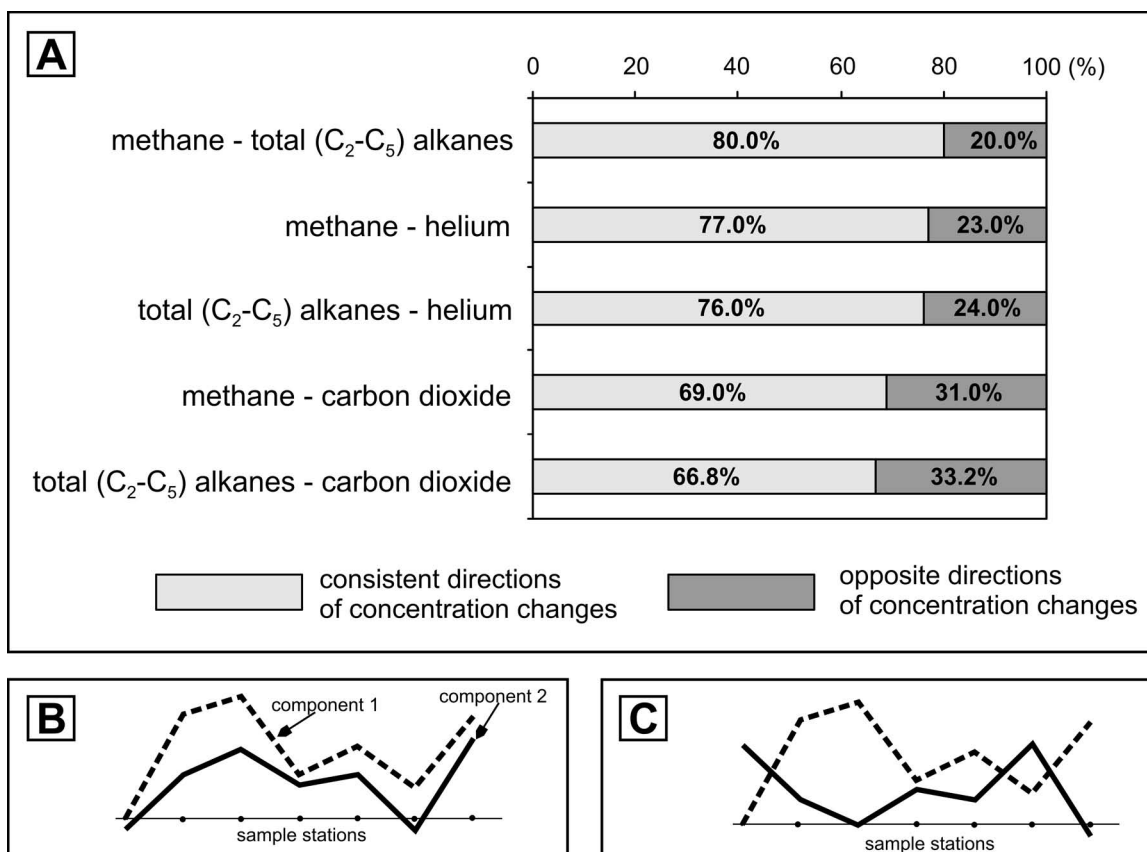


Fig. 7. Results of directional correlations between measured components

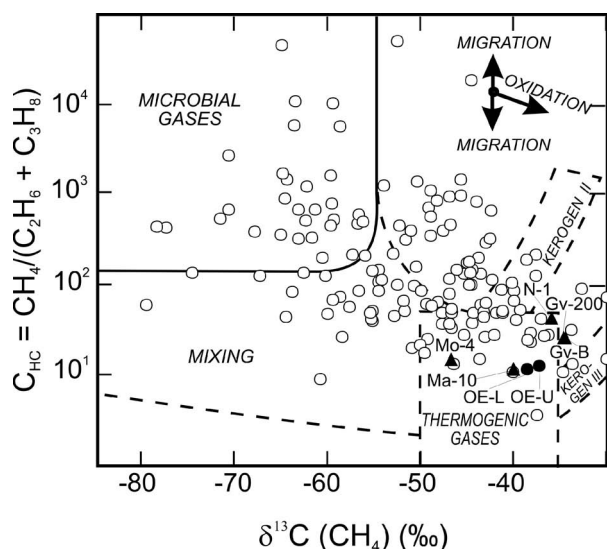


Fig. 8. Hydrocarbon index (C_{HC}) versus $\delta^{13}C(CH_4)$ for soil gases. Included for comparison natural gases from deeper accumulations and surface seeps from Kotarba *et al.* (2005b). Compositional fields after Whiticar (1994). See Fig. 1 for locations and sample key of natural gases from deep accumulations and surface seeps. Explanations of symbols as in Fig. 9

Either the microbial methane or the thermogenic methane mixed with a high contribution of microbial component occurs at a few measurement sites only.

Carbon dioxide most frequently is of thermogenic origin, but only sometimes is recent microbial origin or a product of secondary microbial oxidation of hydrocarbons.

High helium concentrations (over 0.001 vol%) occur near the fault zones and within lithologically differentiated Pleistocene sediments. Helium is generally of crustal origin.

Sites with anomalous (high) concentrations of methane and total C₂-C₅ alkanes may suggest the existence of a Pleistocene water reservoir ("palaeoswamp"), which probably developed over fault zones and may have had a rectangular (350 per 150 m) shape and NW-SE trend. The herbivorous mammals migrating in search of food and water might have been trapped in such places and drowned in the clayey matter saturated with brine and oil. It seems possible that during the Pleistocene tundra winters, when a thick ice and snow cover was resting on the tundra "palaeoswamp", the seeps of brine, oil, helium and thermogenic gases had a higher temperature, which resulted in melting and cracking of the ice cover. Identification of several sites within the "palaeoswamp", where thermogenic gaseous hydrocarbons, carbon dioxide and helium occur may lead to the discovery of zones favourable for burial and preservation of Pleistocene extinct mammals.

Large quantities of microbial methane were generated within the Quaternary sediments of the Starunia area. Unlike the sites of significant fluxes of helium and thermo-

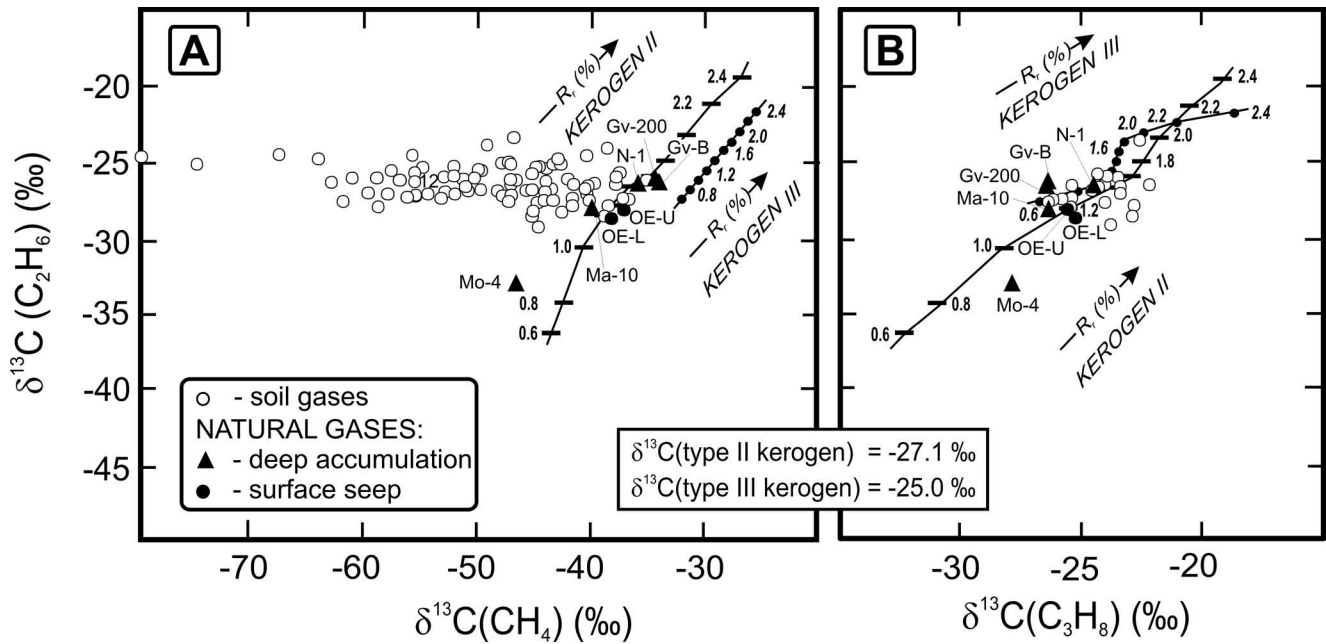


Fig. 9. $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$ versus (A) $\delta^{13}\text{C}(\text{CH}_4)$ and (B) $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$ for soil gases. Included for comparison are values for natural gases from deeper accumulations and surface seeps (Kotarba *et al.*, 2005b). Position of vitrinite reflectance curves for Type II and III kerogen after Berner and Faber (1996). Curves were shifted based on average of $\delta^{13}\text{C}$ values = -27.1‰ for type II, IIS and I/II kerogens and $\delta^{13}\text{C}$ values = -25.0‰ for type III kerogen from the Menilite Shales in the Carpathians (Curtis *et al.*, 2004)

genic gases (hydrocarbons and carbon dioxide), such locations would be less likely locations for future discovery of well-preserved large vertebrates because microbial methane was generated locally, in recent swamps. Moreover, microbial methane generated from Pleistocene swamps escaped to the atmosphere.

The distributions of the measured mixing ratios of the analysed gases can be significantly influenced by fault zones and lithologically differentiated Pleistocene sediments as well as by numerous closed and recultivated shafts, existing and recultivated dug-wells and old boreholes. Such sites provide additional migration routes for ascending, thermogenic and microbial gases.

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 Rózański 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 for his 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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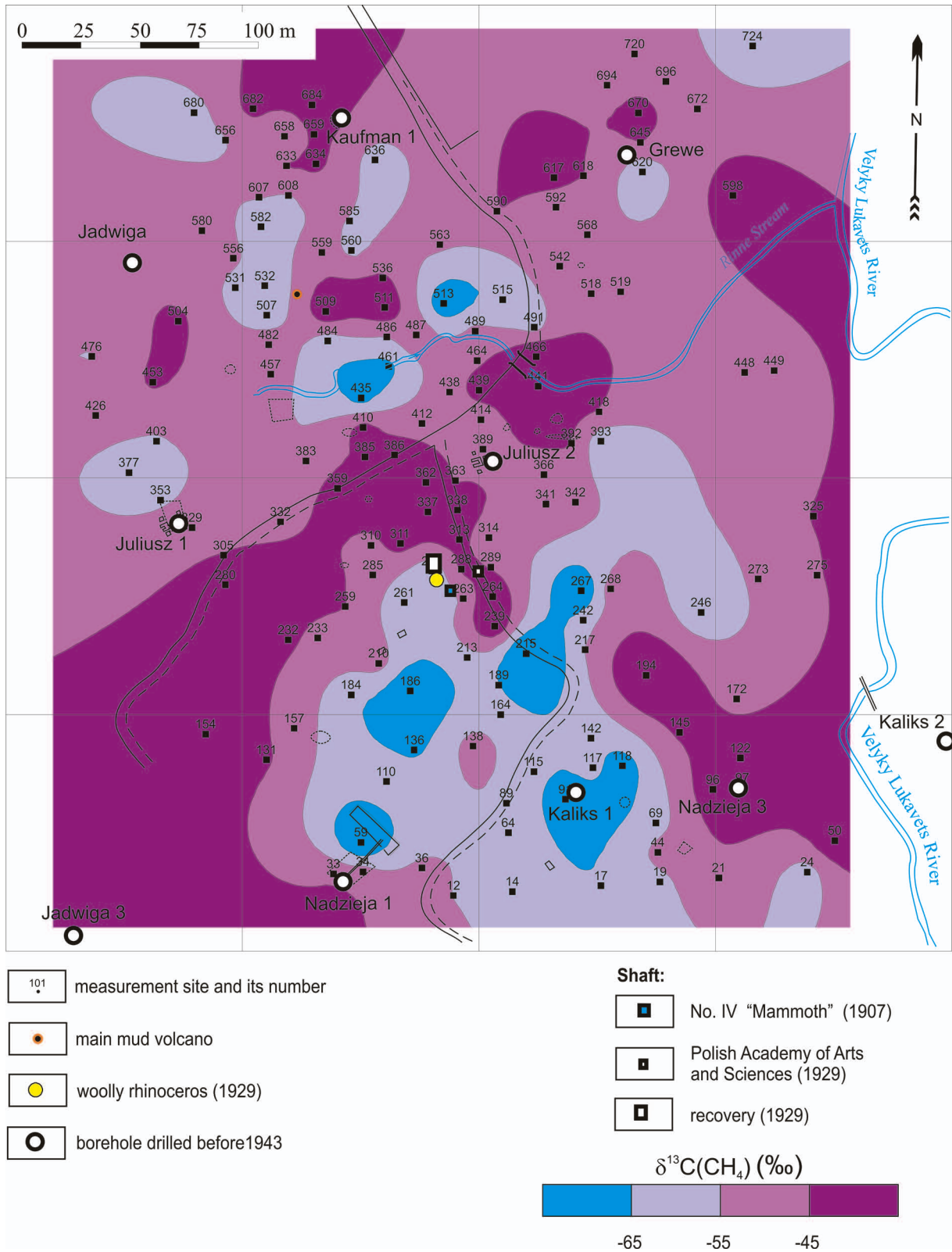


Fig. 10. Contour map of $\delta^{13}\text{C}(\text{CH}_4)$ values of soil gas samples

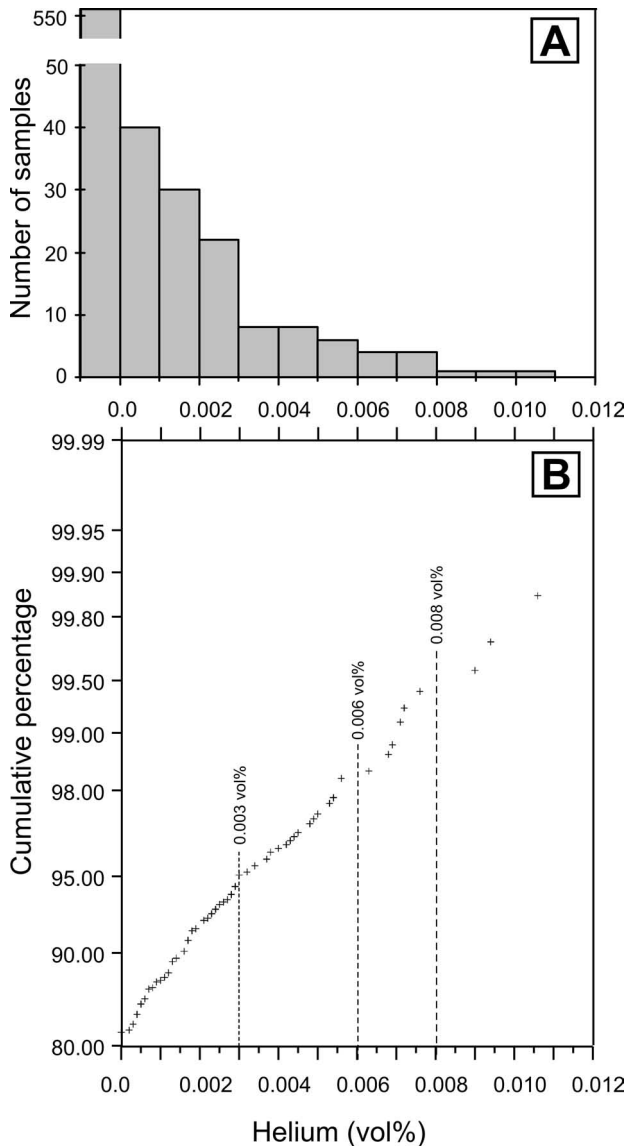


Fig. 11. (A) Histogram and (B) cumulative frequency diagram of helium concentrations

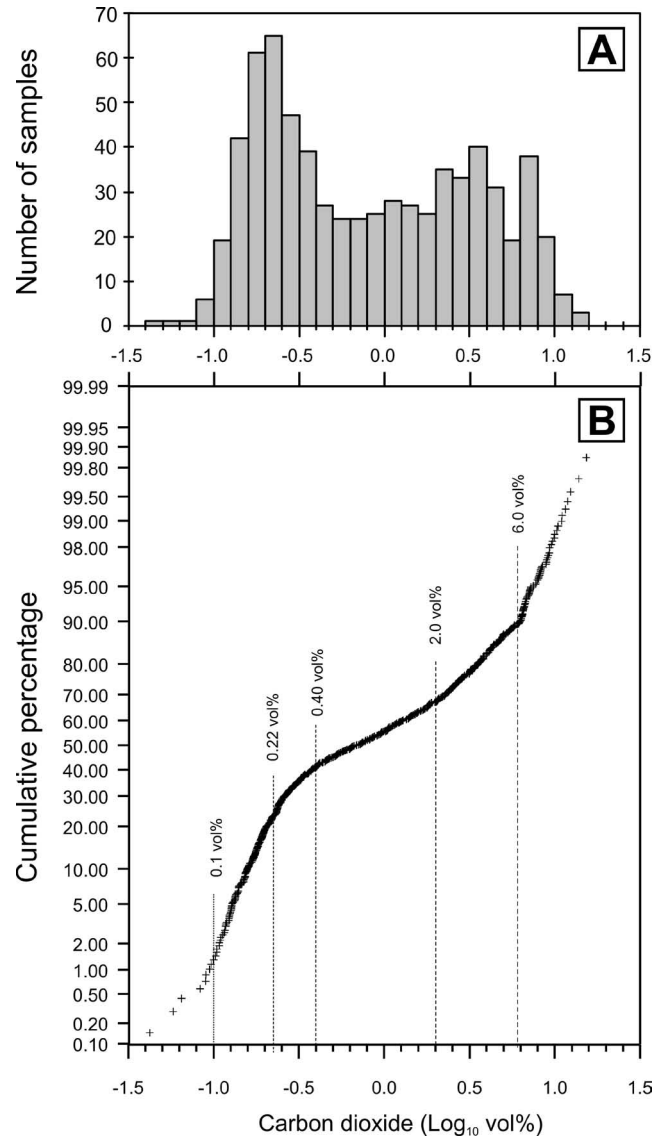


Fig. 12. (A) Histogram and (B) cumulative frequency diagram of carbon dioxide concentrations

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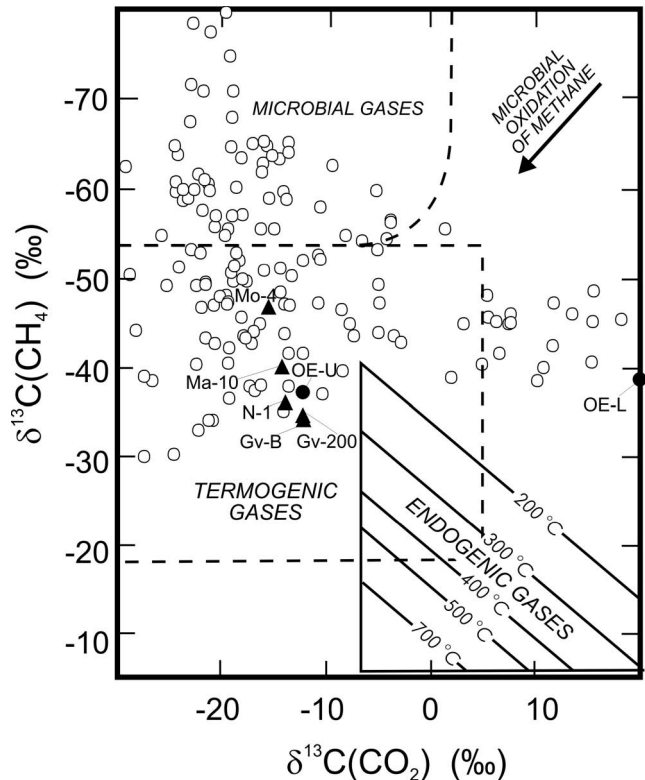


Fig. 14. $\delta^{13}\text{C}(\text{CH}_4)$ versus $\delta^{13}\text{C}(\text{CO}_2)$ for near surface gases. Included for comparison natural gases from deeper accumulations and surface seeps (Kotarba *et al.*, 2005b). Compositional fields modified from Gutsalo and Plotnikov (1981) and Kotarba (1988). Explanations of symbols as in Fig. 9

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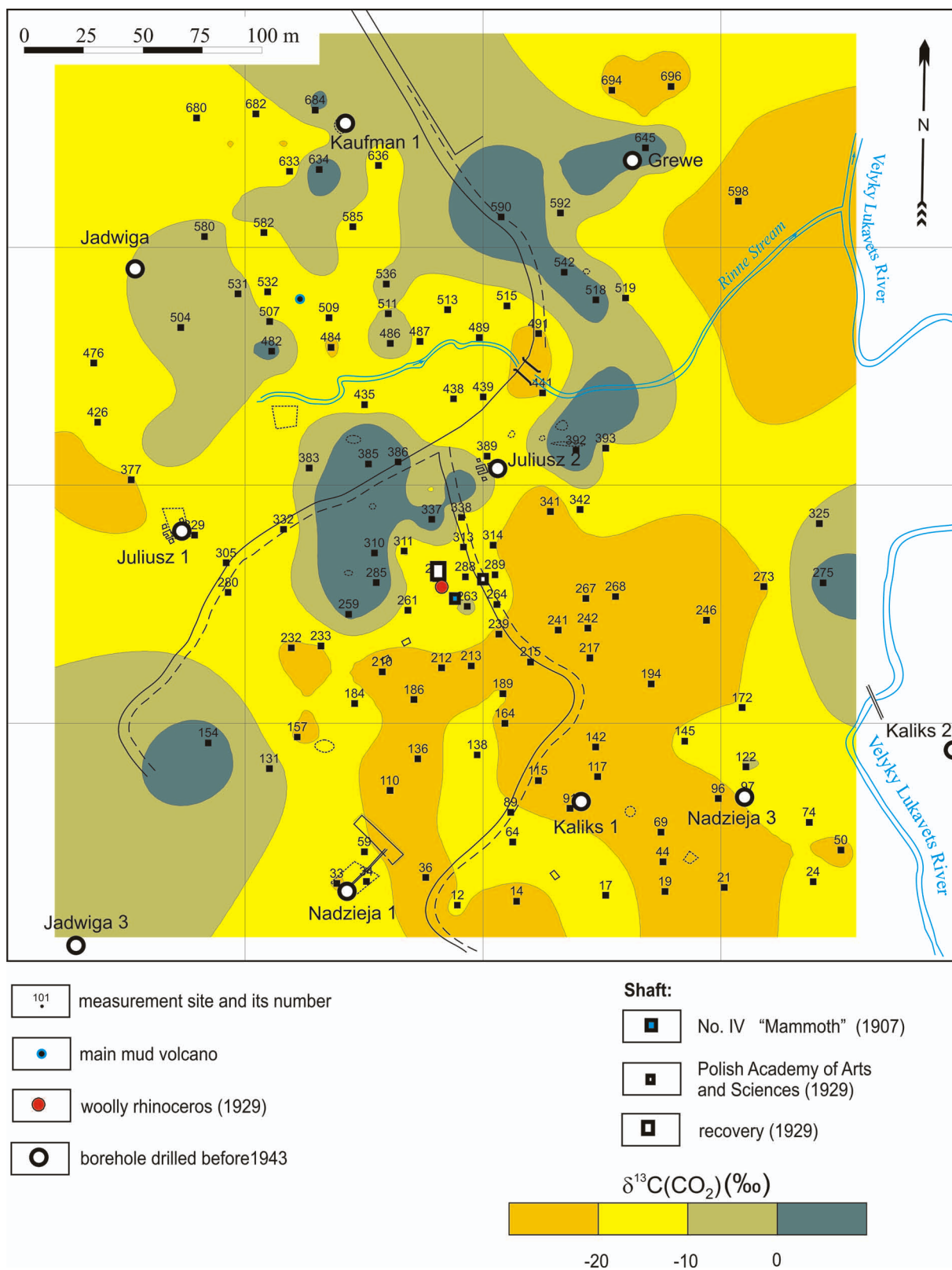


Fig. 15. Contour map of $\delta^{13}\text{C}(\text{CO}_2)$ values of soil gas samples

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