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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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 rhinoceroses, Starunia palaeontological site, Ukrainian Carpathians.

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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 Foredrop 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-Rybyka, 2008; Sokolowski et al., 2009; Sokolowski & Stachowicz-Rybyka, 2009; Stachowicz-Rybyka 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 & Majdej, 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 & Kol tun, 2006). The ozokerite itself is a rare petroleum substance, and in the Carpathians it is only found in five sites: Boryslav, Volanka, Truskavets-Pomiariki, Dzvinyach 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 Foredeep Basin (Kol tun 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 (Sokolowski 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; Sokolowski & Stachowicz-Rybyka, 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 (Slaczka 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 & Kol tun, 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; Kol tun 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), Kol tun et al. (2005), Korin (2005), Kotarba & Stachowicz-Rybyka (2008), Kotarba et al. (2008a), Sokolowski et al. (2009), Sokolowski & Stachowicz-Rybyka (2009) and Stachowicz-Rybyka 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-
Principal statistical parameters of alkanes concentrations and hydrocarbon index for near-surface gas samples collected down to 4 m depth

<table>
<thead>
<tr>
<th>Statistical parameters</th>
<th>Unit</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>i-C₃H₁₀</th>
<th>n-C₃H₁₀</th>
<th>n-C₄H₁₀</th>
<th>i-C₅H₁₂</th>
<th>n-C₅H₁₂</th>
<th>Total C₂-C₅ alkanes</th>
<th>C₁₀C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum (vol%)</td>
<td></td>
<td>0.0003</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>2.6</td>
</tr>
<tr>
<td>Maximum (vol%)</td>
<td></td>
<td>92.2</td>
<td>2.25</td>
<td>0.40</td>
<td>0.19</td>
<td>0.26</td>
<td>0.0023</td>
<td>0.19</td>
<td>0.12</td>
<td>2.93</td>
<td>94250</td>
</tr>
<tr>
<td>Median (vol%)</td>
<td></td>
<td>0.047</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0002</td>
<td>0.0002</td>
<td>&lt;0.0000</td>
<td>0.0005</td>
<td>0.0001</td>
<td>0.0036</td>
<td>44.6</td>
</tr>
<tr>
<td>Mean (vol%)</td>
<td></td>
<td>9.91</td>
<td>0.11</td>
<td>0.031</td>
<td>0.014</td>
<td>0.017</td>
<td>0.0002</td>
<td>0.014</td>
<td>0.0063</td>
<td>0.19</td>
<td>1168</td>
</tr>
<tr>
<td>Standard deviation (vol%)</td>
<td></td>
<td>21.2</td>
<td>0.34</td>
<td>0.087</td>
<td>0.036</td>
<td>0.051</td>
<td>0.0005</td>
<td>0.038</td>
<td>0.021</td>
<td>0.53</td>
<td>8003</td>
</tr>
<tr>
<td>Number of samples *</td>
<td></td>
<td>150</td>
<td>146</td>
<td>147</td>
<td>146</td>
<td>137</td>
<td>72</td>
<td>136</td>
<td>123</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Percentage of samples (%)</td>
<td></td>
<td>100.0</td>
<td>97.3</td>
<td>98.0</td>
<td>97.3</td>
<td>91.3</td>
<td>48.0</td>
<td>90.7</td>
<td>82.0</td>
<td>100.0</td>
<td>100</td>
</tr>
</tbody>
</table>

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

$$C_{10C} = \frac{CH_4}{C_2H_6 + C_3H_8}$$

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

<table>
<thead>
<tr>
<th>Statistical parameters</th>
<th>Unit</th>
<th>C₂H₄</th>
<th>C₃H₆</th>
<th>i-C₄H₈</th>
<th>Total C₂-C₄ alkenes</th>
<th>CO₂</th>
<th>H₂</th>
<th>He</th>
<th>CDMI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum (vol%)</td>
<td></td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>0.108</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>1.8</td>
</tr>
<tr>
<td>Maximum (vol%)</td>
<td></td>
<td>0.049</td>
<td>0.0001</td>
<td>0.0008</td>
<td>0.049</td>
<td>15.8</td>
<td>0.063</td>
<td>0.0048</td>
<td>99.8</td>
</tr>
<tr>
<td>Median (vol%)</td>
<td></td>
<td>&lt;0.0000</td>
<td>&lt;0.0000</td>
<td>&lt;0.0000</td>
<td>&lt;0.0000</td>
<td>0.24</td>
<td>&lt;0.0000</td>
<td>&lt;0.0000</td>
<td>84.8</td>
</tr>
<tr>
<td>Mean (vol%)</td>
<td></td>
<td>0.0017</td>
<td>&lt;0.0000</td>
<td>&lt;0.0000</td>
<td>0.0017</td>
<td>1.26</td>
<td>0.005</td>
<td>0.0003</td>
<td>63.6</td>
</tr>
<tr>
<td>Standard deviation (vol%)</td>
<td></td>
<td>0.0072</td>
<td>0.00001</td>
<td>0.00009</td>
<td>0.0071</td>
<td>2.56</td>
<td>0.010</td>
<td>0.0008</td>
<td>38.0</td>
</tr>
<tr>
<td>Number of samples*</td>
<td></td>
<td>98</td>
<td>25</td>
<td>52</td>
<td>118</td>
<td>150</td>
<td>62</td>
<td>20</td>
<td>150</td>
</tr>
<tr>
<td>Percentage of samples (%)</td>
<td></td>
<td>65.3</td>
<td>16.7</td>
<td>34.7</td>
<td>78.7</td>
<td>100</td>
<td>41.3</td>
<td>13.3</td>
<td>100</td>
</tr>
</tbody>
</table>

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

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

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 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.
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 (C\text{HC}) [C\text{HC} = CH\text{4}/(C\text{2}H\text{6} + C\text{3}H\text{8})] and carbon dioxide methane (CDMI) [CDMI = [CO\text{2}/(CO\text{2} + CH\text{4})] 100 (%)] gas indices of analysed gases vary within the following ranges (Tables 1 to 3): CH\text{4} from 0.0003 vol% to 92.2 vol% (mean 9.91 vol%), total C\text{2}-C\text{5} alkanes from 0 to 2.93 vol% (mean 0.191 vol%), of which C\text{2}H\text{6} from 0 to 2.25 vol% (mean 0.108 vol%), C\text{3}H\text{8} from 0 to 0.403 vol% (mean 0.031 vol%), i-C\text{4}H\text{10} from 0 to 0.192 vol% (mean 0.014 vol%), n-C\text{4}H\text{10} from 0 to 0.262 vol% (mean 0.017 vol%), neo-C\text{5}H\text{12} from 0 to 0.0023 vol% (mean 0.0002 vol%), i-C\text{5}H\text{12} from 0 to 0.187 vol% (mean 0.014 vol%) and n-C\text{5}H\text{12} from 0 to 0.119 vol% (mean 0.0063 vol%), total C\text{2}-C\text{4} alkenes from 0 to 0.049 vol% (average 0.0017 vol%), CO\text{2} from 0.108 to 15.8 vol% (mean 1.26 vol%), H\text{2} from 0 to 0.0627 vol% (mean 0.0051 vol%), He from 0 to 0.0048 vol% (mean 0.0003 vol%), hydrocarbon (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), δ\text{13}C(CH\text{4}) from -64.4 to -29.1‰, δ\text{13}C(C\text{2}H\text{6}) from -29.3 to -23.7‰, δ\text{13}C(C\text{3}H\text{8}) from -28.2 to -22.7‰ and δ\text{13}C(CO\text{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%.

The same statistical procedure reveals the following boundary values for total C\text{2}-C\text{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

<table>
<thead>
<tr>
<th>Statistical parameters</th>
<th>Unit</th>
<th>Minimum (%)</th>
<th>Maximum (%)</th>
<th>Median (%)</th>
<th>Mean (%)</th>
<th>Standard deviation (%)</th>
<th>Number of samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ\text{13}C(CH\text{4})</td>
<td>‰</td>
<td>-64.4</td>
<td>-29.1</td>
<td>-46.5</td>
<td>-46.8</td>
<td>8.2</td>
<td>63</td>
</tr>
<tr>
<td>δ\text{13}C(C\text{2}H\text{6})</td>
<td>‰</td>
<td>-29.3</td>
<td>-23.7</td>
<td>-27.4</td>
<td>-27.3</td>
<td>1.2</td>
<td>25</td>
</tr>
<tr>
<td>δ\text{13}C(C\text{3}H\text{8})</td>
<td>‰</td>
<td>-28.2</td>
<td>-22.7</td>
<td>-27.6</td>
<td>-27.0</td>
<td>1.6</td>
<td>15</td>
</tr>
<tr>
<td>δ\text{13}C(C\text{4}H\text{10})</td>
<td>‰</td>
<td>-20.1</td>
<td>24.3</td>
<td>-15.7</td>
<td>-8.0</td>
<td>13.9</td>
<td>63</td>
</tr>
</tbody>
</table>

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.
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, thermo-chemical 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.

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**Fig. 3.** Hydrocarbon index (C$_{12}$) versus $^{13}$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)

**Fig. 4.** $^{13}$C(C$_2$H$_6$) versus (A) $^{13}$C(CH$_4$) and (B) $^{13}$C(C$_3$H$_8$) 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 $^{13}$C = –27.1 ‰ for type II, IIS and I/II kerogens, and $^{13}$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)
Oil win dow” (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 δ13C-values higher than −45‰ (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 δ13C-values of methane are lower than −45‰ (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 δ13C-values of methane below −55‰ (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 δ13C 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 C2-C5 alkanes concentrations of the analysed gases and considerably higher mean values compared to 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. 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,

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
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 C2-C5 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 C2-C5 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
C$_2$-C$_5$ alkane concentrations shows a complicated pattern. Qualitatively, areas of increased methane concentration correspond to those of increased total C$_2$-C$_5$ 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; Whiticar 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$_2$-C$_5$ alkanes (Fig. 7), and in most cases its elevated ("anomalous") con-

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### 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

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Methane (vol %)</th>
<th>Total C$_2$-C$_5$ alkanes (vol%)</th>
<th>Total C$_2$-C$_4$ alkenes (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
<td>Mean</td>
<td>Median</td>
</tr>
<tr>
<td>0.8</td>
<td>68.6</td>
<td>6.95</td>
<td>0.024</td>
</tr>
<tr>
<td>1.6</td>
<td>77.1</td>
<td>17.0</td>
<td>0.59</td>
</tr>
<tr>
<td>2.4</td>
<td>28.3</td>
<td>1.14</td>
<td>0.0079</td>
</tr>
<tr>
<td>3.2</td>
<td>76.4</td>
<td>9.18</td>
<td>0.036</td>
</tr>
<tr>
<td>4.0</td>
<td>92.2</td>
<td>15.3</td>
<td>0.044</td>
</tr>
</tbody>
</table>

---

![Fig. 8](image)

**Fig. 8.** (A) Changes of total C$_2$-C$_5$ alkanes concentrations and (B) distribution of total C$_2$-C$_5$ 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 concentration.
Centralization 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 \(\delta^{13}C(CO_2)\).
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 C2-C5 alkanes (Figs 7, 9).
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 C2-C5 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.

### Table 5

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Carbon dioxide (vol%)</th>
<th>Hydrogen (vol%)</th>
<th>Helium (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
<td>Mean</td>
<td>Median</td>
</tr>
<tr>
<td>0.8</td>
<td>7.99</td>
<td>1.02</td>
<td>0.24</td>
</tr>
<tr>
<td>1.6</td>
<td>15.8</td>
<td>2.49</td>
<td>0.47</td>
</tr>
<tr>
<td>2.4</td>
<td>4.65</td>
<td>0.41</td>
<td>0.22</td>
</tr>
<tr>
<td>3.2</td>
<td>12.0</td>
<td>1.18</td>
<td>0.23</td>
</tr>
<tr>
<td>4.0</td>
<td>11.8</td>
<td>1.73</td>
<td>0.28</td>
</tr>
</tbody>
</table>

### 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 (Soko³owski 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 recultiivated shafts, the existing and recultiivated dug-wells and old boreholes, which number approximately 500 in the study area (Kotarba...
& 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 C₂-C₅ 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...
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.

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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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