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BITUMEN AND SALT CONTENTS WITHIN THE QUATERNARY SEDIMENTS AT STARUNIA PALAEONTOLOGICAL SITE AND VICINITY (CARPATHIAN REGION, UKRAINE)

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Abstract: Geochemical studies were conducted on bitumen and salts saturating the Pleistocene and Holocene sediments from an abandoned ozokerite mine in Starunia. This location is noted for the discovery of remnants of a mammoth and three woolly rhinoceroses in 1907, and a nearly completely preserved rhinoceros carcass in 1929. The bitumen (oil) and brines (chloride ions) were preserving agents for the large Pleistocene mammals. The main mass of organic carbon hosted in the Pleistocene muds is related to bitumen originating from oil migrating from deep accumulations within the Boryslav-Pokuttya Unit. The highest analysed bitumen content is 9.26 wt%. The chloride ion content, originating from highly concentrated brines ascending from the salt-bearing Miocene Vorotyshcha beds, vary from 0 to 4.66 wt% but this usually does not exceed 1 wt%. The natural pathways of underground fluids (oil, gas and water) migration within the Quaternary sediments were disturbed by intensive ozokerite mining operations run between the last three decades of the 19th century and 1960. Therefore, the present preservation and conservation conditions of large, extinct mammals' remains can be different from those prevailing during the Pleistocene, when the mammals were buried. Taking into consideration the contents of the remaining preservatives: chloride and bitumen, the most favourable zone for fossils conservation and preservation is located close to boreholes Nos 22, 23, 28 and 36N, where the thickness of Pleistocene muds exceeds 2 metres. Generally, the spatial distributions of bitumen and chloride ion contents within the Holocene sediments and salt-bearing Miocene Vorotyshcha beds are very similar to those in the Pleistocene sediments.

Key words: bitumen content, chloride ion content, Pleistocene, Holocene, Starunia palaeontological site, Carpathian region, Ukraine.

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INTRODUCTION

Geochemical studies of bitumen and chloride ion saturating both the Pleistocene and Holocene sediments were a part of an interdisciplinary research project focused on 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), where remains of a mammoth, three woolly rhinoceroses, and a nearly-completely preserved rhinoceros carcass were found in 1907 and 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 accumulated within the Pleistocene clayey muds, into which the animals had sunk, resulted in near perfect preservation of these fossils.

The main aim of these geochemical studies was to check where the best conditions exist within the Pleistocene muds that favour the preservation and conservation of extinct, Pleistocene mammals. Geochemical studies focused on evaluation of total organic matter (TOC) (both bitumen and macrofossils) and salt contents, as well as on preliminary evaluation of the influence of secondary processes (*e.g.* oxidation and biodegradation) on organic matter in the Pleistocene and Holocene sediments. The methods applied were: Rock-Eval pyrolysis, qualitative analysis of bitumen (fraction composition – saturated hydrocarbons, aromatic hydrocarbons and resins) and chloride ion analyses. As both the bitumen (oil) and salt (chloride ion) were conserving factors for these fossils, special attention was paid to the Pleistocene muds.

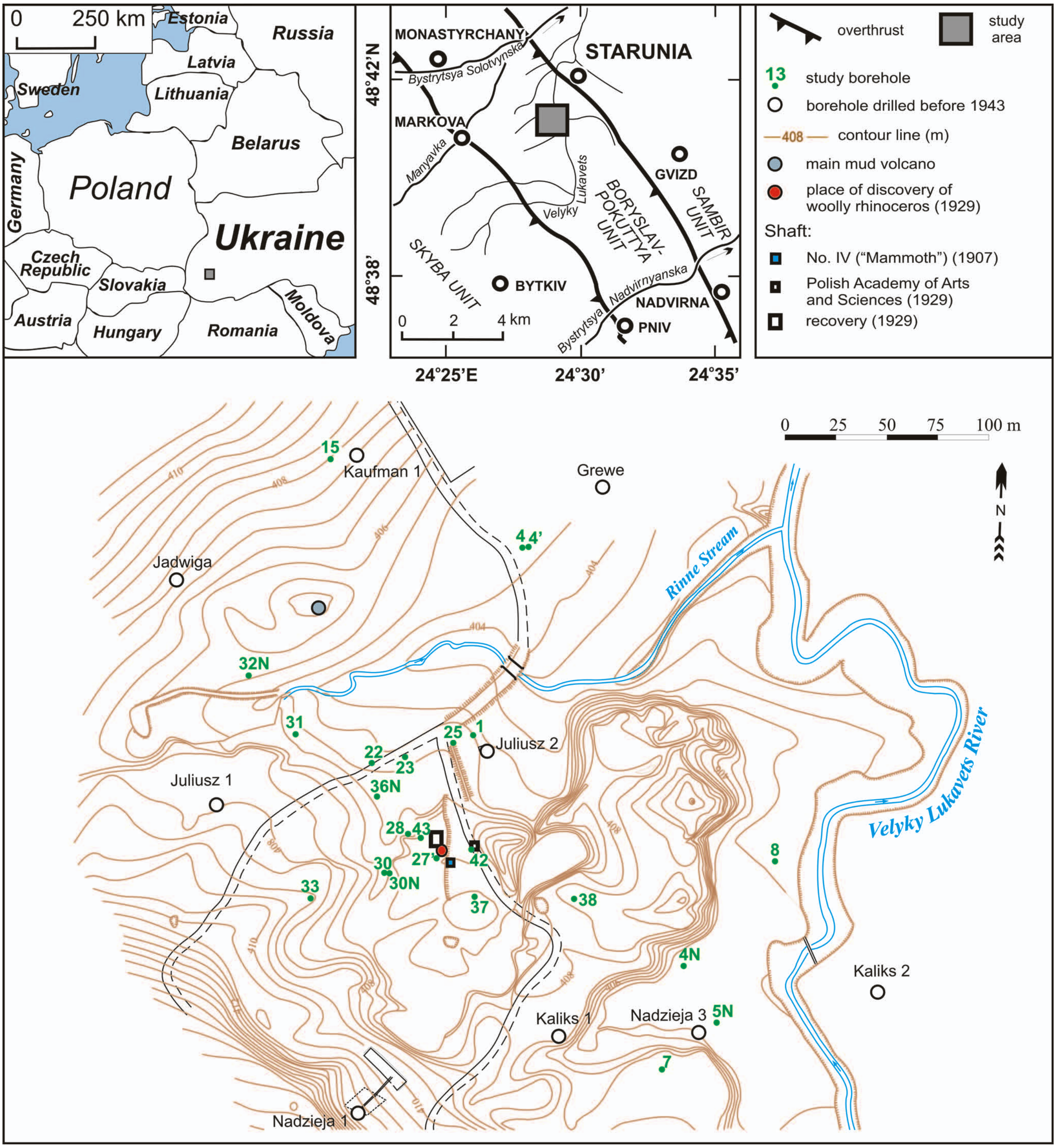


Fig. 1. Sketch map of the Starunia palaeontological site and surrounding area (Carpathian region, Ukraine) showing the location of boreholes drilled for geochemical studies

General information on the history of geological studies and petroleum exploitation in the Starunia area and the results of earlier interdisciplinary research are contained in a special monograph devoted to Starunia (Kotarba, ed., 2005).

At the end of the 19th century and in the first half of the 20th century ozokerite was exploited in the Starunia area from the Boryslav-Pokuttya Unit of the Carpathian Foredeep Basin (Alexandrowicz, 2004, 2005; Koltun *et al.*, 2005). In 1907, the remains of a mammoth and woolly rhinoceros were found in shaft No. 4 (since then known as the "Mammoth shaft") of the ozokerite mine, at depths of 12.5 m and 17.6 m, respectively. In 1929, an unique, fully preserved woolly rhinoceros body was found in a special shaft of the Polish Academy of Arts and Sciences, at 12.5 m depth, in Quaternary sediments saturated with oil and brine (Kotarba, 2002; Alexandrowicz, 2005).

Organic matter contained in the Pleistocene and Holocene sediments has two sources: syngenetic (plant macrofossils, malacofauna; Stachowicz-Rybka *et al.*, 2009) and epigenetic (oil ascending from deep structures of the Boryslav-Pokuttya Nappe and saturating Quaternary sediments; Kotarba, 2002; Kotarba *et al.*, 2005a, 2009a) ones. Salts precipitated within Quaternary sediments originated from brines which migrated from the salt-bearing Vorotyshcha beds (Korin, 2005; Duliński *et al.*, 2005). Genetic correlation between bitumen hosted in Quaternary sediments from the Starunia area and oil from deep accumulations of the Boryslav-Pokuttya and Skyba units was made by Kotarba *et al.* (2009a). Inflow of oil and thermogenic gases from these deep accumulations to the Quaternary sediments, and the development of microbial and secondary geochemical processes (oxidation and biodegradation) within sediments from the Starunia area were discussed by Kotarba *et al.* (2005b, 2008b, 2009b), Sechman *et al.* (2009) and Barabasz *et al.* (2009).

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). Ozokerite is a rare petroleum substance. In the Carpathians it is known from only five sites: Boryslav, Volanka, Truskavets-Pomiarki, Dzvinyach, and Starunia (Alexandrowicz, 2005).

In the area of the abandoned Starunia ozokerite mine, the Quaternary sediments of the Velyky Lukavets River valley are developed as clayey muds with plant remains, peat, biogenic muds, and peat muds (Sokołowski *et al.*, 2009; Sokołowski & Stachowicz-Rybka, 2009). Details of the 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), Stachowicz-Rybka *et al.* (2009), and in references therein.

The top of the salt-bearing Lower Miocene Vorotyshcha beds in the Starunia area, which underlie Quaternary deposits, occurs at a maximum depth of 17 metres (Sokołowski *et al.*, 2009). The Miocene strata are sandstone-claystone breccias with halite, potassium-salt, gypsum and calcite layers, and veins of ozokerite (Korin, 2005). Within these sediments many brine and salt water springs occur in the vicinity of Starunia. 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 the flysch sequence covered by molasse (Ślączka *et al.*, 2006). The Oligocene Menilite beds occur in the top of the flysch succession in the outer part of the unit. They 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 nappes (Adamenko *et al.*, 2005; Koltun *et al.*, 2005). The Miocene Vorotyshcha salt-bearing beds provide perfect sealing of hydrocarbon traps in the Boryslav-Pokuttya Unit. 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 stable hydrocarbons formed veins of ozokerite. These processes continue even now, which can be seen in the examples of oil and gas surface seeps and mud volcanoes in the Starunia area.

METHODS

Sampling procedure

For geochemical study of bitumen and chloride contents, 101 core samples were collected from the Quaternary sediments: of these, 55 samples from the Pleistocene strata and 46 from the Holocene sediments. The latter sediments were sampled intensively because during sampling of the Holocene–Pleistocene boundary this boundary had not been determined in boreholes. For comparison, 5 core samples of the salt-bearing Lower Miocene Vorotyshcha beds and 7 samples of mine wastes were collected, as well. The location of sampled wells is shown in Fig. 1. Lithology of each sample was described. The Pleistocene sediment samples comprised several lithologies: peat (4 samples), peat muds (2), biogenic muds (6), clayey muds (41), and muds saturated with bitumen (2). The Holocene samples comprised: peat (4 samples), peat muds (7), biogenic muds (1), clayey muds (27), muds saturated with bitumen (6), and gravel (1). Detailed description of lithology is presented in Sokołowski *et al.* (2009). After drilling and shipping to Kraków, the core samples, each weighing about 300 grams, were stored in a dark and cold warehouse in order to prevent the development of microorganisms.

Analytical methods

Equal weights of each sample were homogenized and dried at room temperature, then pulverized in a mortar to fraction below 0.2 mm. Pyrolysis was run with the Delsi Model II Rock-Eval instrument, equipped with the organic carbon module (Espitalié *et al.*, 1977, 1985, 1986). The basic parameters measured with the Rock-Eval are: free hydrocarbons content (vaporized at 300°C – S_1), residual hydrocarbons content (pyrolyzed at 300–600°C – S_2), carbon dioxide produced during pyrolysis at 300–390°C (S_3), and residual organic carbon content (oxidation of unpyrolyzed carbon at 600°C – S_4). The above parameters are the basis for calculating indices used for quantitative and qualitative evaluation of organic matter in the analysed rocks, *i.e.*: total organic carbon content (TOC), production index [$PI = S_1/(S_1+S_2)$], hydrogen index ($HI = S_2*100/TOC$), and oxygen index ($OI = S_3*100/TOC$) (Espitalié *et al.*, 1977).

Table 1

Rock-Eval data, mud saturated by bitumen and chloride ion contents for Pleistocene sediments, mine dump and salt-bearing Lower Miocene Vorotyshcha beds

Type of sediment	peat	peat mud	biogenic mud	clayey mud	mud saturated by bitumen	mine dump	Miocene Vorotyshcha beds
Total organic carbon (wt%)	5.06 to 7.25 (4) 5.78 (2)	4.68 and 6.94 (2) 5.81 (2)	2.52 to 11.4 (6) 6.68 (4)	0.52 to 17.8 (41) 3.56 (15)	2.79 and 10.2 (2) 6.49 (2)	1.20 to 5.83 (7) 3.47 (2)	0.99 to 3.25 (5) 1.63 (4)
Total extract (wt%)	0.52 to 5.4 (4) 2.44 (2)	2.86 and 5.78 (2) 4.32 (2)	1.16 to 9.26 (6) 5.02 (4)	0.04 to 9.07 (41) 2.25 (15)	1.79 and 7.00 (2) 4.39 (2)	0.60 to 2.05 (7) 1.64 (2)	0.33 to 2.97 (5) 1.18 (4)
Bitumen carbon/ TOC	0.08 to 0.80 (4) 0.35 (2)	0.51 and 0.69 (2) 0.60 (2)	0.38 to 0.67 (6) 0.59 (4)	0.03 to 0.82 (41) 0.47 (15)	0.53 and 0.57 (2) 0.55 (2)	0.27 to 0.60 (7) 0.43 (2)	0.28 to 0.76 (5) 0.53 (4)
S_1 (mg HC/g rock)	5.75 to 37.3 (4) 19.7 (2)	22.4 and 45.0 (2) 33.7 (2)	7.64 to 66.6 (6) 34.9 (4)	0.25 to 61.1 (41) 15.2 (15)	12.0 and 58.5 (2) 35.2 (2)	3.01 to 15.7 (7) 10.1 (2)	2.11 to 21.0 (5) 8.22 (4)
Saturated hydrocarbons (wt%)	57 to 65 (4) 62 (2)	65 and 65 (2) 65 (2)	63 to 70 (6) 66 (4)	57 to 81 (29) 68 (11)	61 and 63 (2) 62 (2)	64 (1)	66 to 75 (5) 71 (4)
Aromatic hydrocarbons (wt%)	27 to 30 (4) 28 (2)	30 and 32 (2) 31 (2)	26 to 30 (6) 29 (4)	18 to 35 (29) 28 (11)	30 and 32 (2) 31 (2)	28 (1)	22 to 81 (5) 25 (4)
Resins (wt%)	6 to 13 (4) 10 (2)	3 and 5 (2) 4 (2)	3 to 7 (6) 5 (4)	1 to 9 (29) 5 (11)	5 and 9 (2) 7 (2)	8 (1)	3 to 6 (5) 4 (4)
S_2 (mg HC/g rock)	16.0 to 20.9 (4) 17.7 (2)	12.7 and 21.0 (2) 16.8 (2)	7.72 to 34.4 (6) 19.1 (4)	0.56 to 56.9 (41) 10.2 (15)	4.59 and 37.8 (2) 21.2 (2)	3.2 to 18.2 (7) 10.9 (2)	0.89 to 7.83 (5) 3.04 (4)
Production index	0.26 to 0.70 (4) 0.48 (2)	0.64 and 0.68 (2) 0.66 (2)	0.50 to 0.69 (6) 0.62 (4)	0.24 to 0.73 (41) 0.56 (15)	0.61 and 0.72 (2) 0.67 (2)	0.42 to 0.60 (7) 0.50 (2)	0.69 to 0.76 (5) 0.72 (4)
Hydrogen index (mg HC/g TOC)	286 to 334 (4) 309 (2)	272 and 302 (2) 287 (2)	250 to 336 (6) 289 (4)	59 to 408 (41) 254 (15)	165 and 371 (2) 268 (2)	266 to 343 (7) 303 (2)	90 to 241 (5) 162 (4)
Oxygen index (mg CO_2/g TOC)	12 to 88 (4) 58 (2)	12 and 237 (2) 124 (2)	21 to 106 (6) 70 (4)	13 to 631 (41) 138 (15)	13 and 39 (2) 26 (2)	42 to 157 (7) 73 (2)	14 to 125 (5) 69 (4)
Chloride ion (wt%)	0.00 to 4.66 (4) 3.13 (2)	0.18 and 1.24 (2) 0.71 (2)	0.00 to 0.68 (6) 0.23 (4)	0.00 to 3.97 (41) 0.79 (15)	0.00 and 0.59 (2) 0.29 (2)	0.85 to 1.68 (7) 1.18 (2)	0.00 to 7.13 (5) 2.72 (4)

TOC – total organic carbon; bitumen carbon = 0.83 x total extract; S_1 – oil and gas yield (mg HC/g rock); S_2 – residual petroleum potential (mg HC/g rock); production index = $S_1/(S_1+S_2)$; n.a. – not analysed. Geochemical parameters and indices are given as numerators of minimum and maximum values, mean values in denominator and parenthesized (numerator of number of core samples, numer of sampled boreholes in denominator)

Bitumens were extracted ultrasonically with *n*-hexane (15 min., 4 times) at room temperature. The main volume of solvent was recovered in a rotary evaporator at 30°C and 200 mbar, and the rest was evaporated in a fume hood. The elemental sulphur was removed with native copper. The extracts were separated into saturated hydrocarbons, aromatic hydrocarbons and resins with column chromatography. Alumina/silica gel (2:1 v/v) columns (0.8×25 cm) were eluted with *n*-hexane, toluene and toluene/methanol (1:1 v/v), respectively.

For chloride ion analysis weighed samples, 10 g each, were taken from the primary samples and annealed in a porcelain crucible at temperature of 450°C for 4 hours in order to remove organic matter, then weighed again in order to establish any loss of mass. The annealed samples were dissolved in about 400 ml of distilled water and boiled for about 30 min. The solutions were separated from the precipitates by filtration. The residual precipitate was washed with hot distilled water until reaction of Cl^- ion with $AgNO_3$ showed negative results. Obtained filtrates were diluted to 1 litre in a measuring flask filled up with distilled water. Chloride ion was determined by titration with 0.1 N silver nitrate ($AgNO_3$) solution using potassium chromate (K_2CrO_4) as an indicator (Mohr's method). Concentrations obtained in g/litre of chloride ion in the solution were recalculated to weight percents in samples.

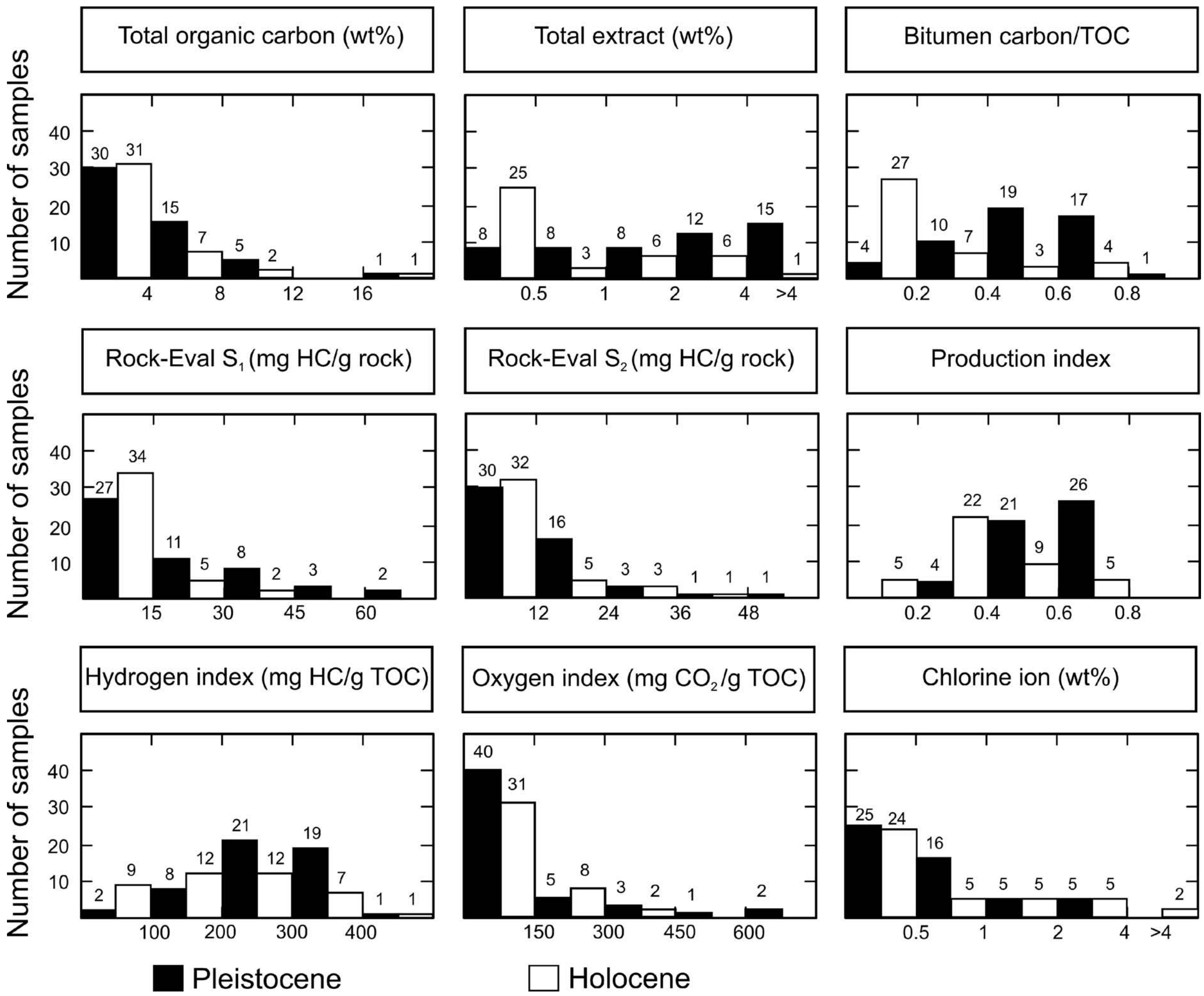


Fig. 2. Histogram of TOC and total extract contents, bitumen carbon/TOC, Rock-Eval S_1 and S_2 parameters, Rock-Eval production, hydrogen and oxygen indices, and chloride ion content for the Pleistocene and Holocene sediments

RESULTS AND DISCUSSION

The study area is unusual and specific because two types of organic substances occur within the Quaternary sediments. The first type is residual organic matter composed of the remains of plants and animals living in the Pleistocene and the Holocene (Stachowicz-Rybka *et al.*, 2009). The second type is oil migrating from deep accumulations (Kotarba *et al.*, 2005a). Migrating oil underwent many secondary processes, the most important being biodegradation accompanied by evaporation, water-washing and weathering (Kotarba *et al.*, 2009a). The emplacement of the brines was secondary to the migrating oil (Mościcki *et al.*, 2009).

Below, the results are presented of geochemical studies of bitumen and chloride ion from the Pleistocene and Holocene sediments, and for comparison, also from the salt-bearing Miocene Vorotyshcha beds and from the mine wastes.

Pleistocene sediments

The ranges and median values of geochemical parameters and indices of bitumen and chloride ion for Pleistocene sediments are listed in Table 1. The total organic carbon (TOC) content usually does not exceed 4 wt% (Fig. 2), but locally, over 8 wt% occurs, and the highest TOC value of 17.8 wt% was found in the sample collected from clayey muds in borehole No. 33, at 8.1 m depth (Fig. 3A). The same sample shows also very high bitumen content (9.07 wt%, Table 1, Fig. 3A). The highest bitumen content, 9.26 wt%, was observed in sample No. 25/2.6 (biogenic mud) (Table 1, Fig. 3B). Correlation of total extract content in clayey muds (Fig. 3A) and in biogenic muds (Fig. 3B) versus the TOC content indicates that the main mass of organic carbon in the Pleistocene muds is connected with bitumen.

Bitumen carbon (defined after Espitalié *et al.*, 1985) constitutes 83 wt% of hydrocarbons weight. The ratio of bitumen carbon to the TOC exceeds 0.5 in large number of samples (Fig. 4A, B), which means the bitumens are the dominant organic matter. This is supported by correlation of Rock-Eval S_1 free hydrocarbons with the TOC content (Fig. 5A, B). According to organic matter categories after Smith (1994), it indicates that most of the analysed samples were saturated with migrating oil (Fig. 5A, B). Correlation of the extracted C_{15+} hydrocarbon contents (saturated and aromatic hydrocarbons) versus the TOC (Fig. 6A, B) reveals the domination of saturated and aromatic hydrocarbons in

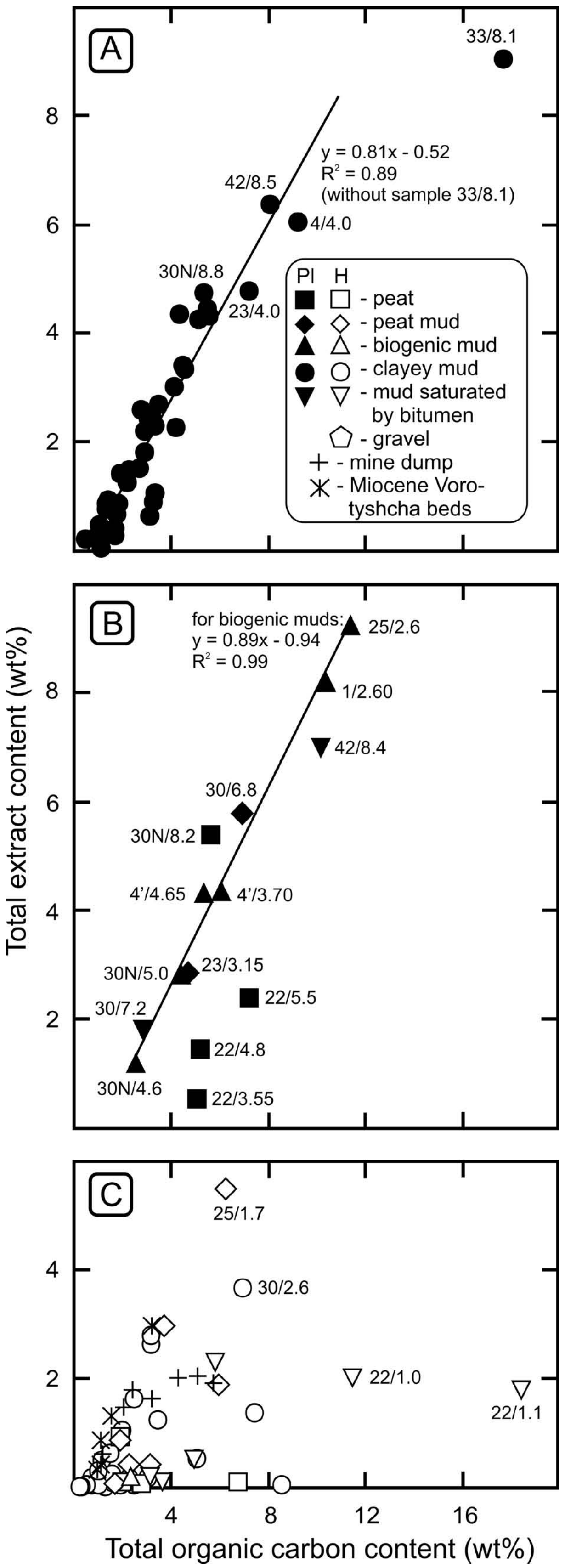


Fig. 3. Total extract versus TOC contents for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, and (**C**) Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Samples descriptions include the number of borehole and sampling depth (in metres). Pl – Pleitocene, H – Holocene

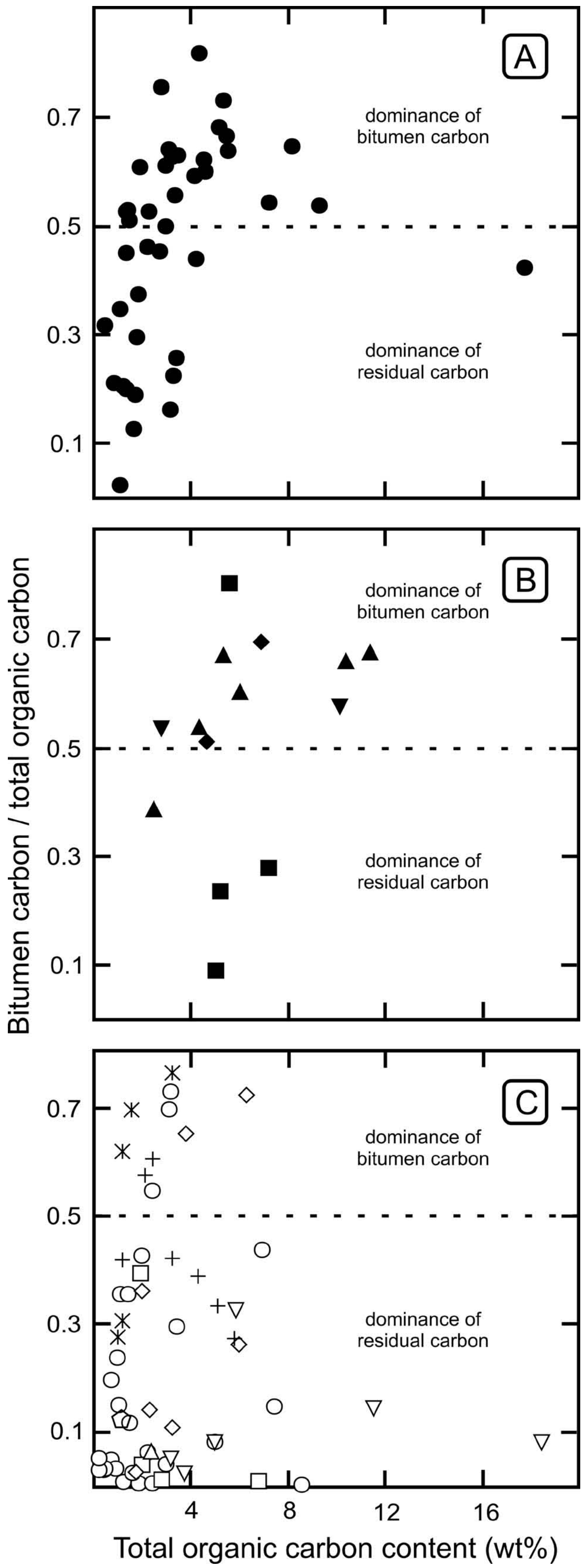


Fig. 4. Bitumen carbon/TOC ratio versus TOC contents for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, and (**C**) Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Explanations of symbols as in Fig. 3

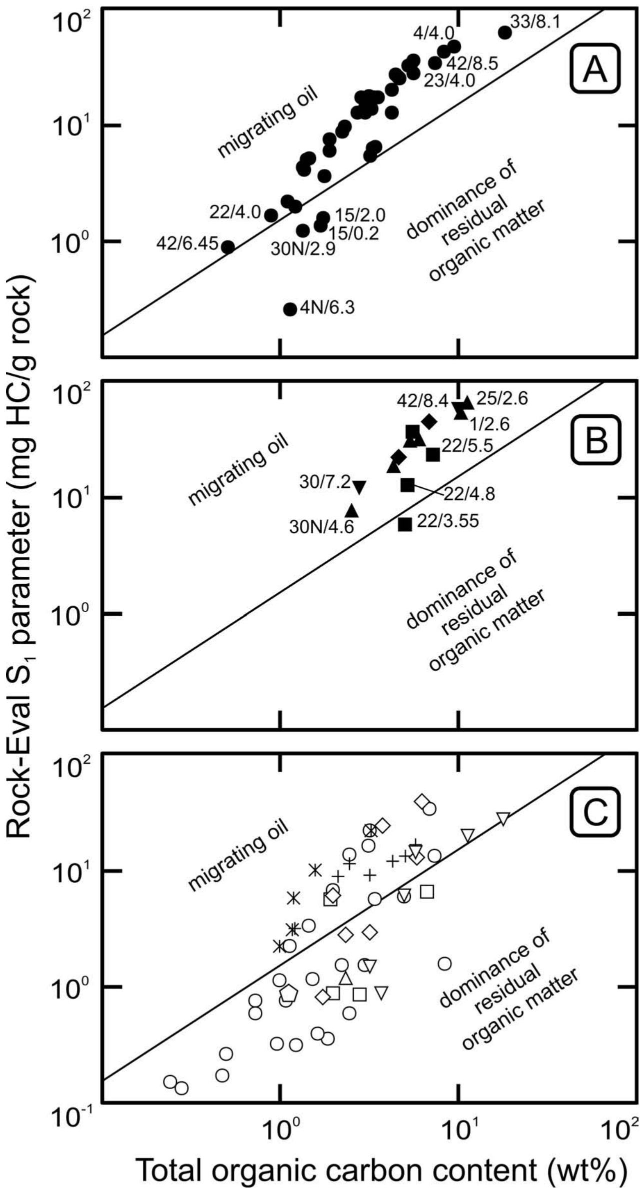


Fig. 5. The Rock-Eval S_1 parameter versus TOC contents for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, and (**C**) Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Samples descriptions include the number of borehole and sampling depth (in metres). Boundary line after Smith (1994). Explanations of symbols as in Fig. 3

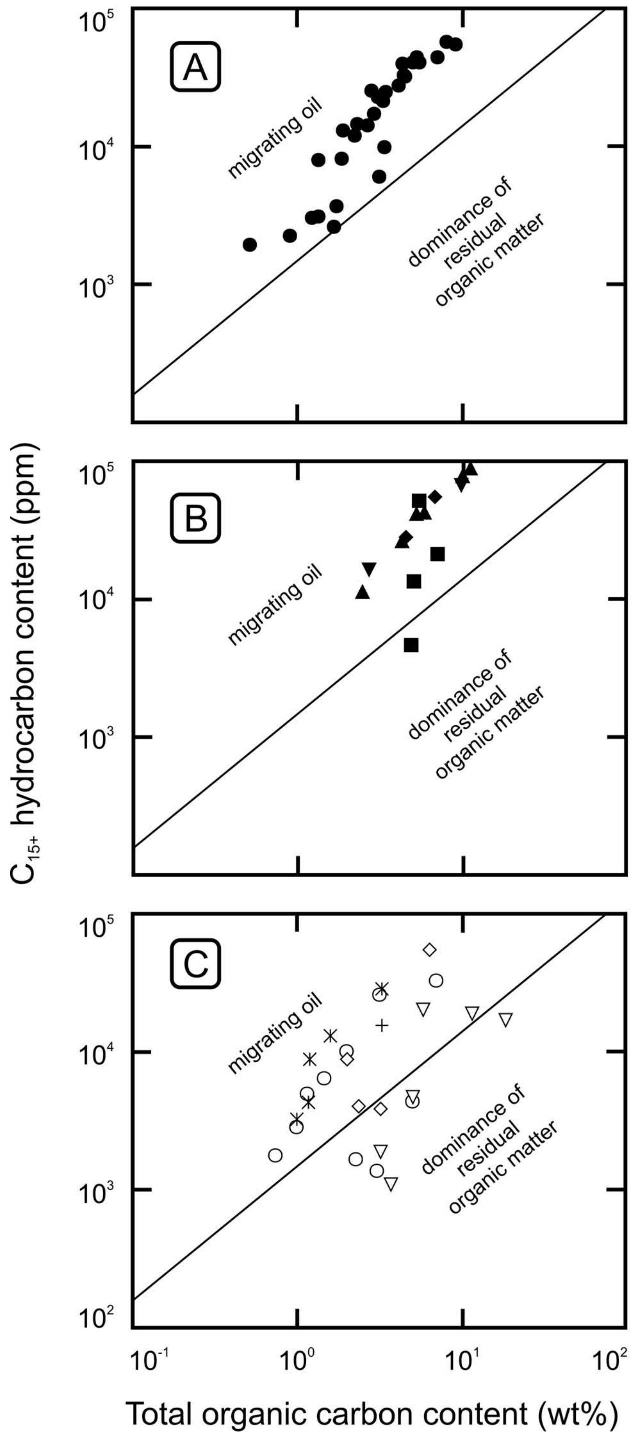


Fig. 6. Identification of epigenetic hydrocarbons in terms of extracted C_{15+} hydrocarbons and TOC contents for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, and (**C**) Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Boundary line after Hunt (1979) and Leenheer (1984). Explanations of symbols as in Fig. 3

fraction composition of bitumen (Table 1). Both the saturated and aromatic hydrocarbon fractions contents usually constitute from 60 to 70 wt% and from 25 to 35 wt%, respectively (Table 1, Fig. 7A, B). The Rock-Eval S_2 residual hydrocarbon content is usually lower than that of free hydrocarbons, so most values of production index (PI) are over 0.6 (Fig. 2). Rocks dominated with migrating hydrocarbons show PI values over 0.4 (Espitalié *et al.*, 1977).

The hydrogen (HI) and oxygen (OI) indices of Rock-Eval analysis were used (Espitalié *et al.*, 1977) to quantify residual hydrocarbons and organic oxygen compounds, respectively. The analysed sediments reveal variable values of HI (Table 1, Fig. 2) and OI (Table 1, Figs 2, 8). The OI index decreases with the increasing TOC content (Fig. 8). This pattern is typical of organic matter at various stages of oxidation. A similar pattern is observed for example in the Kupferschiefer from the Lubin Copper District in Poland (Pieczonka *et al.*, 2008). Sediments rich in organic matter

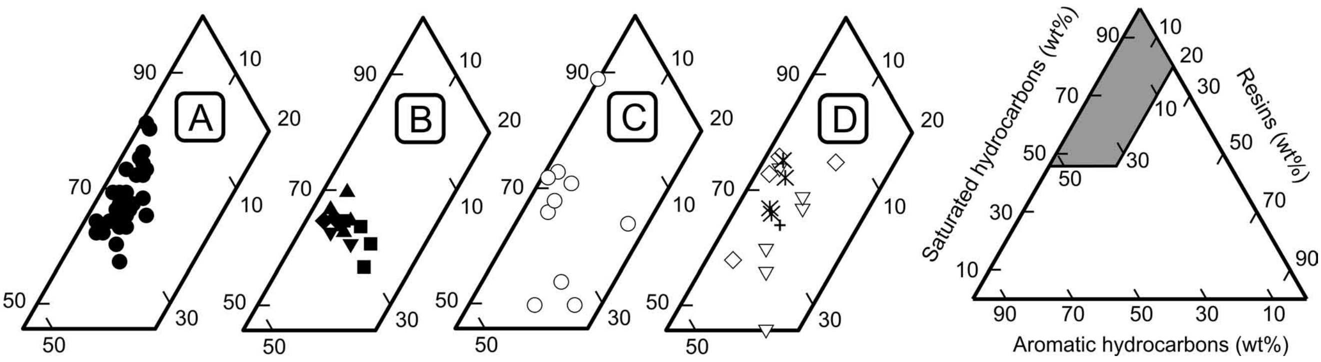
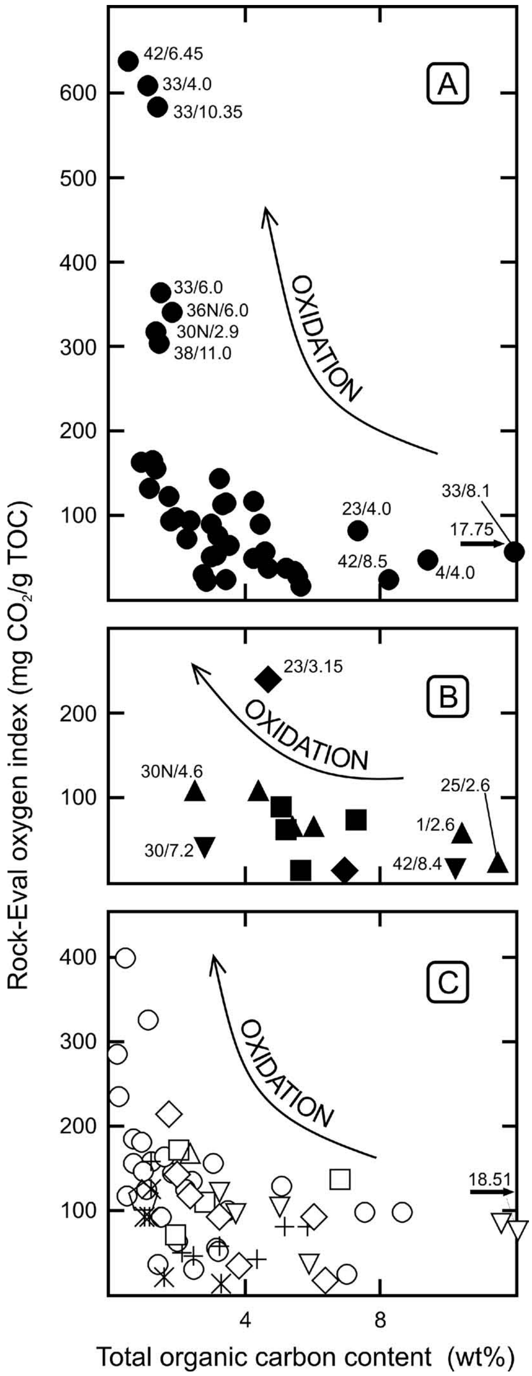


Fig. 7. Ternary diagram of bitumen fractions for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, (**C**) Holocene clayey muds, and (**D**) the rest of Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Explanations of symbols as in Fig. 3



are characterized by high HI and low OI values, whereas these poor in organic matter show low contents of residual hydrocarbons and high contents of organic oxygen compounds. This phenomenon can be explained by easier oxidation of dispersed organic matter. Also, sediments with higher TOC contents (characterized by high HI values, Fig. 9) lose their organic carbon during weathering (oxidation), which is combined with the increasing number of oxygen atoms in the structure. As the Rock-Eval S_2 residual petroleum potential of the studied samples is a mixture of residual Quaternary organic matter and heavy compounds derived from evaporation and oxidation of migrating oil, the identification of kerogen type of dispersed original organics using classic HI - OI correlation (Fig. 9) is impossible.

The content of bitumen saturating the Pleistocene sediments is usually independent of sampling depth (Fig. 10), but in some samples, *e.g.* in boreholes Nos 15 and 28 (Fig. 10) it regularly increases with the increasing sampling depth. The highest mean extract contents (over 6.5 wt%) were noticed in boreholes Nos 1 and 25 (Fig. 11A). This area is highly saturated with bitumen and is unfavourable for preservation of large mammals because the thickness of muds is below 2 m (Fig. 11A). The highest saturation in bitumen occurs in the area where thickness of Pleistocene muds exceeds 2 m, *i.e.*, in boreholes Nos 23 and 42 (Fig. 11A).

Another substance having a conserving effect even stronger than bitumen for bodies of Pleistocene mammals is salt (chloride ion). Its content in the studied muds varies from 0 to *ca*. 4 wt% (Table 1, Fig. 12A), but is usually below 1 wt% (Fig. 2). The highest chloride ion contents were detected in peat samples (up to 4.66 wt%, Table 1, Fig. 12B), probably due to filling of unconsolidated sediments with brine. Contents of chloride ion are inversely propor-

Fig. 8. The Rock-Eval oxygen index versus TOC contents for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, and (**C**) Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Samples descriptions include the number of borehole and sampling depth (in metres). Explanations of symbols as in Fig. 3

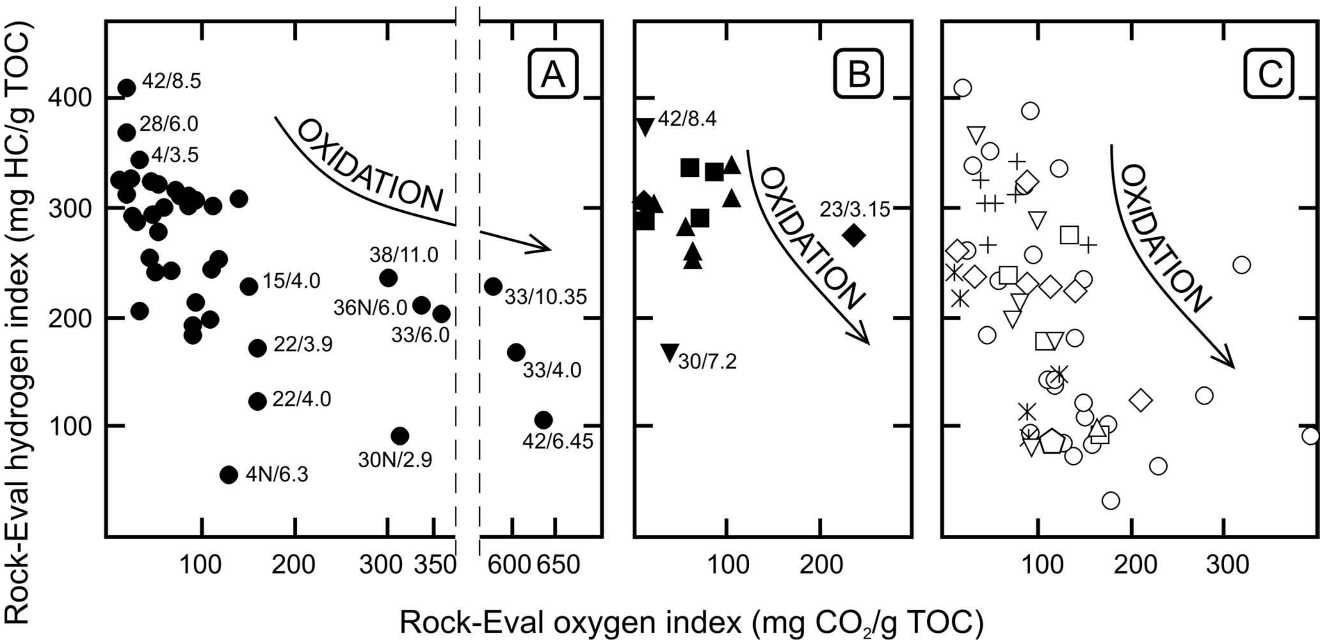


Fig. 9. The Rock-Eval hydrogen index versus oxygen index for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, and (**C**) Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Samples descriptions include the number of borehole and sampling depth (in metres). Explanations of symbols as in Fig. 3

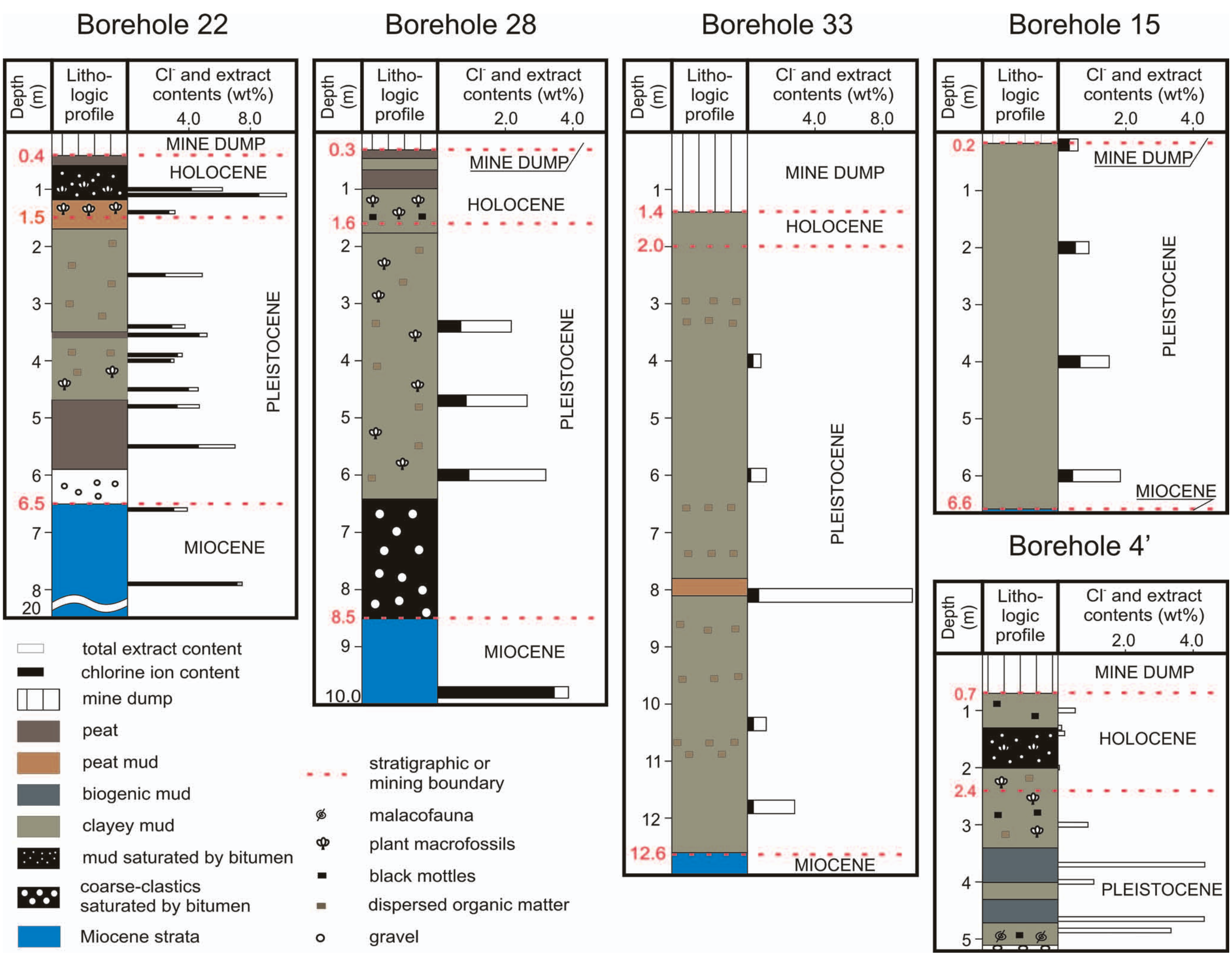


Fig. 10. Depth distribution of chloride ion and bitumen contents in lithological columns of selected boreholes Nos 4', 15, 22, 28 and 33

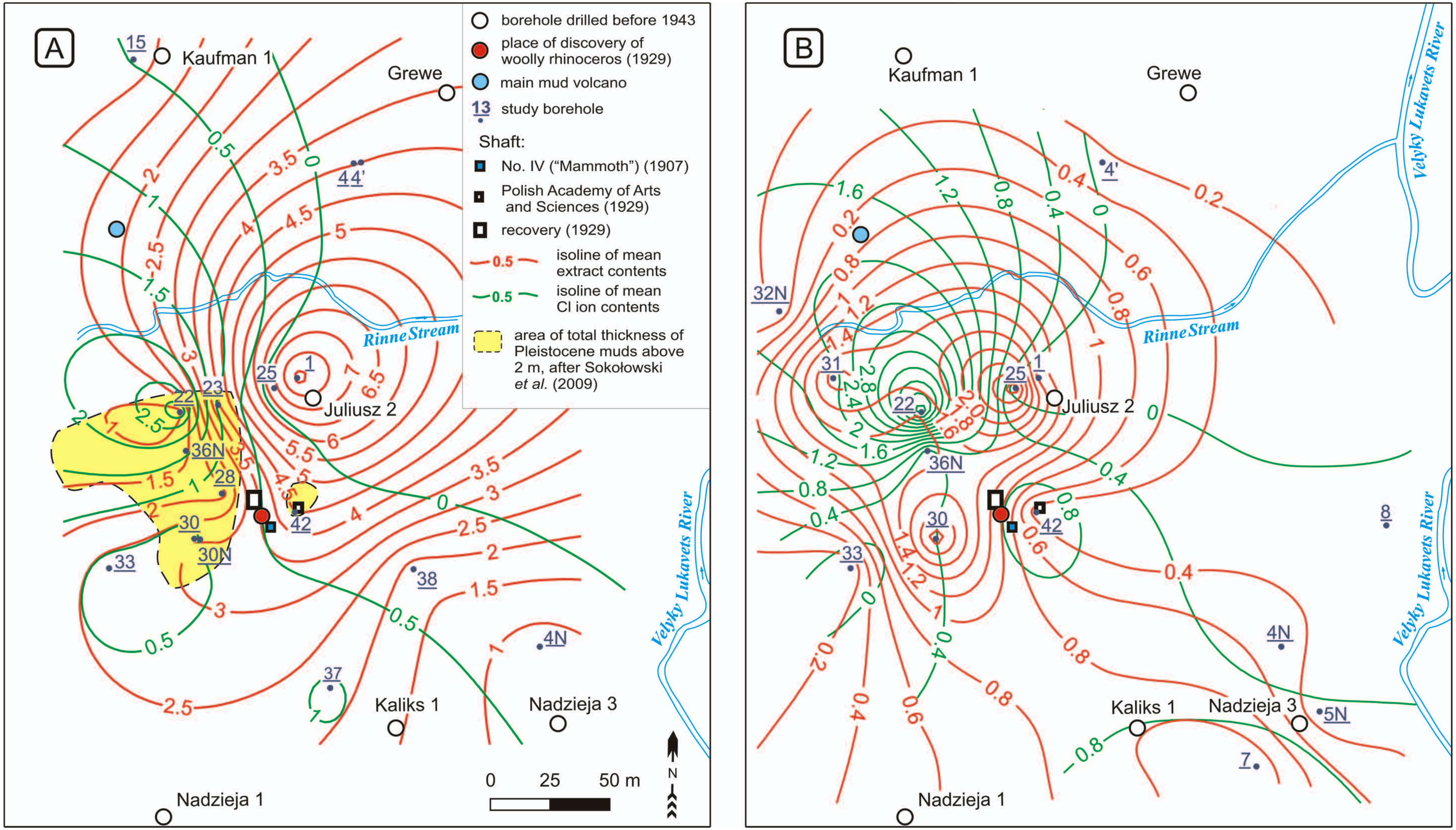


Fig. 11. Maps of mean total extract and chloride ion contents in (**A**) all types of Pleistocene muds and (**B**) Holocene sediments

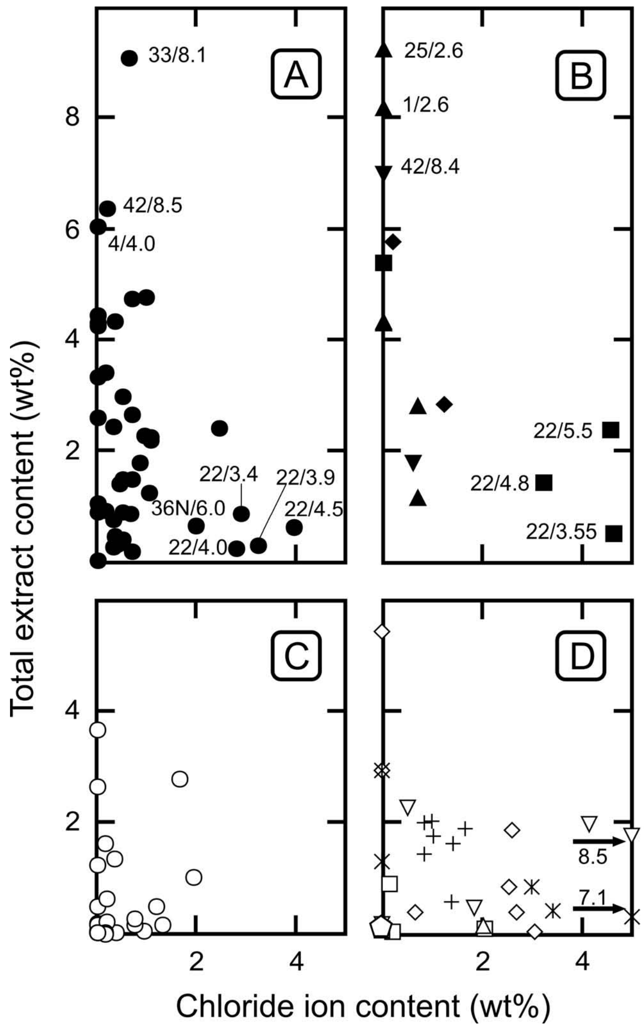


Fig. 12. Total extract versus chloride ion contents for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, (**C**) Holocene clayey muds, and (**D**) the rest of Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Explanations of symbols as in Fig. 3

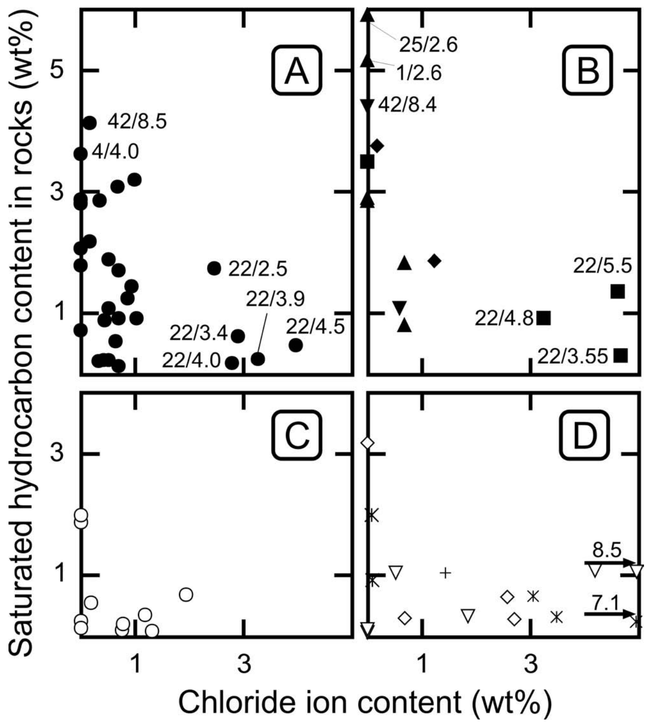


Fig. 13. Saturated hydrocarbon contents in rocks versus chloride ions contents for (**A**) Pleistocene clayey muds, (**B**) the rest of Pleistocene sediments, (**C**) Holocene clayey muds, and (**D**) the rest of Holocene sediments, salt-bearing Miocene Vorotyshcha beds and mine wastes. Explanations of symbols as in Fig. 3

tional to contents of total extract (Fig. 12A & B), which suggests that both cannot coexist in the sediment. In sediments of high chloride content low extract efficiency was noted but the reverse relationships were also observed (Fig. 12A, B). This is probably caused by filling of Pleistocene sediments with brines originating from leaching of salts by meteoric waters within the Miocene Vorotyshcha beds. Then, both the oil and natural gases migrated from deep structures through fracture systems and filled the open spaces. It is possible that oil, as a low-density liquid, had migrated earlier, filling the pore structure of Quaternary sediments and was subsequently partly displaced by brines. This process was particularly strong between the last three decades of the 19th century and 1960, when the intensive mining operations took place. The content of saturated hydrocarbons (*i.e.*, the main components of bitumen) versus content of chloride changes in the studied sediments (Fig. 13A, B) and is comparable to that from the extract (Fig. 12A, B).

The highest mean chloride contents, over 1 wt%, were detected in boreholes Nos 22, 36N and 37. The first two boreholes are localized in the area where the thickness of Pleistocene muds exceeds 2 m (Fig. 11A). In the Pleistocene successions from boreholes Nos 23 and 28, and from their vicinity, the detected considerable amounts of Cl^- (about 1 wt%) provide good preservation conditions for large, extinct mammals.

The most saline waters in the Starunia area result from dehydratation of clay minerals during burial diagenesis followed by leaching of salt layers within the Miocene Vorotyshcha beds (Duliński *et al.*, 2005). Despite the observed low salinity of the investigated samples, attention should be paid to the fact that salinity is caused mainly by the presence of interstitial waters. Their relatively small mass, compared to that of minerals, indicates that these waters originate from highly concentrated brines, as confirmed by geoelectric studies (Mościcki *et al.*, 2009).

In the north-eastern part of the study area, the thickness of Pleistocene muds is less than 2 m and in some boreholes (Nos 1, 4, 4' and 25) no chloride ion was detected within these sediments (Fig. 11A). Therefore, there is minimum chance to discover well-preserved remains of large mammals in this zone.

Taking into consideration the contents of preservatives: chloride ion and bitumen, the most favourable zone for preservation of fossils is in the vicinity of boreholes Nos 22, 23, 28 and 36N (Fig. 11A). This zone also accumulates the least-degraded hydrocarbons (Kotarba *et al.*, 2009a).

Holocene sediments

The Holocene sediments are too young for preservation of remains of the extinct large mammals but they may trap the migrating oil and brine. The ranges and median values of geochemical parameters, indices provided by the Rock-Eval pyrolysis, and chloride ion contents in Holocene sediments are listed in Table 2, whereas the histograms of the main parameters and indices for Holocene muds are presented in Fig. 2. The total organic carbon (TOC) content, comparable to that from the Pleistocene muds, usually does not exceed 4 wt% (Fig. 2), but locally reaches over 8 wt%. The highest value, 18.5 wt%, was determined in a sample collected from mud saturated with bitumen in borehole No. 22 at 1.1 m depth (Fig. 3C). The highest extract yield, 5.49 wt%, was obtained from peat mud sample taken from borehole No. 25 at 1.7 m depth. In the same borehole the highest bitumen content in Pleistocene sediments was observed (Table 1, Fig. 3C). No correlation of the total extract yield versus TOC contents was observed in Holocene sediments (Fig. 3C). The bitumen carbon/TOC ratio is mainly below 0.5 (Fig. 4C). This relationship as well as correlation of free hydrocarbons (S_1) versus TOC content (Fig. 5C) indicate partial saturation of the analysed samples (Fig. 5C), but the share of migrating hydrocarbons is not as high as that in the Pleistocene sediments (Fig. 5A, B). The same effect is visible in the diagram of extracted C_{15+} hydrocarbon content (saturated and aromatic hydrocarbons) versus TOC contents (Fig. 6C). The fraction composition of bitumen is dominated by saturated and aromatic hydrocarbons (Table 2, Fig. 7C, D), comparable to the Pleistocene sediments described previously (Table 2, Fig. 7A, B). The residual hydrocarbons (S_2) content is usually higher than that of free hydrocarbons, hence, the production index (PI) values are mainly below 0.4 (Fig. 2) indicating the dominance of heavy substances pyrolyzed at temperatures over 300°C. These substances are of both migrational (heavy oil compounds resulting from evaporation and/or oxidation of oil) and residual (from Quaternary plants and animals) origins.

Both the hydrogen (HI) and oxygen (OI) indices (Espitalié *et al.*, 1977), which describe quantitatively residual hydrocarbons and organic oxygen compounds in the analysed sediments show variable values (Table 1, Figs 2, 8C, 9C). The oxygen index decreases with the increasing TOC contents (Fig. 8C). Such a pattern is typical for organic matter at various stages of oxidation, *i.e*., comparable to that hosted in the Pleistocene sediments. The oxidation process of organic matter is also visible in HI/OI correlations (Fig. 9C).

The contents of bitumen in Holocene sediments are usually independent on sampling depth (*e.g*., boreholes Nos 22 and 4'; Fig. 10). The highest mean content of extract (over 2.5 wt%), was noticed in borehole No. 25 (Fig. 11B).

Chloride contents in the analysed muds are usually below 0.5 wt% (Fig. 2). The highest values of this parameter were found in muds saturated with bitumen (up to 8.54 wt%; Table 2, Fig. 13D), which is probably the result of filling the granular structure of Holocene sediments with brine. Chloride ion contents are inversely proportional to total extract contents (Fig. 12C, D), but this phenomenon is not as well-marked as in the Pleistocene sediments. The same relationship can be observed for saturated hydrocarbon versus chloride ion contents (Fig. 13C, D). The highest mean chloride contents (over 0.8 wt%) were detected in boreholes Nos 7, 22, 31 and 42, while in boreholes Nos 1, 4', 25 and 33 no chlorides were detected (Fig. 11B).

Miocene strata and mine wastes

The Miocene sediments and mine wastes were sampled only for comparative purposes. The ranges of values and the medians of geochemical parameters and indices determined by the Rock-Eval pyrolysis and chloride ion contents for the Miocene Vorotyshcha beds as well as for mine wastes are presented in Table 1. The TOC contents usually do not exceed 4 wt% (Table 1), corresponding to values found in Quaternary sediments. Maximum TOC values (5.8 wt%) were found in mine wastes. The highest TOC content in the Miocene Vorotyshcha beds reached 3.25 wt% (Table 1). The highest extract yields in the mine wastes and in the Miocene strata amounted 2.05 and 2.97 wt%, respectively (Table 1, Fig. 3C). A positive correlation of the total extract and TOC contents was observed only in the Miocene strata (Fig. 3C). The bitumen carbon/TOC ratio values vary from 0.27 to 0.76 and mean value is around 0.5 (Table 1, Fig. 4C). The relationships of free hydrocarbons (S_1) and extracted C_{15+} hydrocarbon contents (saturated and aromatic hydrocarbons) versus TOC contents (Figs 5C, 6C) indicate that the analysed rocks were saturated with the migrating hydrocarbons, which corresponds to the relationships in Pleistocene sediments. Fraction composition of bitumen is dominated by saturated and aromatic hydrocarbons, similarly to Quaternary sediments discussed previously (Table 1, Fig. 7D). The residual hydrocarbons content (S_2) is usually lower than that of free hydrocarbons, so the production index (PI) values are mainly over 0.5 (Table 1), indicating the dominance of light epigenetic compounds vaporized at temperature 300°C.

Values of hydrogen (HI) and oxygen (OI) indices (Espitalié *et al.*, 1977) in the analysed sediments are variable (Table 1, Figs 8C, 9C). Like in Quaternary sediments, oxidation of organic matter increases with the decreasing TOC content (Fig. 8C). Oxidation process of organic matter is also visible in the HI versus OI correlation (Fig. 9C).

Insufficient number of analyses precluded correlations of bitumen and chloride ions contents in the Miocene strata and mine wastes with depth (Fig. 10). The chloride contents in the Miocene strata and mine wastes vary from 0 to 7.1 wt% and from 0.85 to 1.68 wt%, respectively (Table 1, Figs 12D, 13D). Most of results exceed 1 wt% and the highest values of this parameter were noted in the Miocene strata (Table 1, Fig. 12D). The Lower Miocene Vorotyshcha beds are rich in halite and sylvite (Mitura, 1944; Korin, 2005) and these minerals are the source of chlorides detected in Quaternary sediments (Mościcki *et al.*, 2009). The mine wastes consist mainly of Miocene rocks, which were removed during ozokerite exploitation, so they probably retain their "residual" salt, not migrated one, as the Quaternary sediments. However, like in Quaternary sediments, in the Miocene strata chloride ion contents decrease with the

Table 2

Rock-Eval data, mud saturated by bitumen and chloride ion contents for Holocene sediments

Type of sediment	peat	peat mud	biogenic mud	clayey mud	mud saturated by bitumen	gravel
Total organic carbon (wt%)	1.93 to 6.79 (4) 3.38 (3)	1.75 to 6.34 (7) 3.63 (6)	2.36 (1)	0.24 to 8.56 (27) 2.40 (13)	3.20 to 18.5 (6) 7.97 (4)	1.11 (1)
Total extract (wt%)	0.05 to 0.91 (4) 0.29 (3)	0.06 to 5.49 (7) 1.73 (6)	0.18 (1)	0.01 to 3.68 (27) 0.65 (13)	0.11 to 2.29 (6) 1.15 (4)	0.16 (1)
Bitumen carbon/ TOC	0.01 to 0.39 (4) 0.11 (3)	0.03 to 0.72 (7) 0.32 (6)	0.06 (1)	0.00 to 0.73 (27) 0.19 (13)	0.02 to 0.32 (6) 0.12 (4)	0.12 (1)
S_1 (mg HC/g rock)	0.80 to 6.29 (4) 3.33 (3)	0.77 to 37.5 (7) 12.2 (6)	1.11 (1)	0.13 to 33.8 (27) 4.97 (13)	0.82 to 26.2 (6) 11.1 (4)	0.82 (1)
Saturated hydrocarbons (wt%)	n.a.	58 to 76 (4) 71 (6)	n.a.	50 to 89 (10) 66 (9)	46 to 74 (6) 62 (4)	n.a.
Aromatic hydrocarbons (wt%)	n.a.	14 to 38 (4) 25 (4)	n.a.	11 to 40 (10) 27 (9)	22 to 39 (6) 29 (4)	n.a.
Resins (wt%)	n.a.	2 to 11 (4) 5 (4)	n.a.	0 to 17 (10) 7 (9)	3 to 15 (6) 9 (4)	n.a.
S_2 (mg HC/g rock)	1.85 to 18.8 (4) 7.55 (3)	2.16 to 16.5 (7) 8.83 (6)	2.33 (1)	0.18 to 29.1 (27) 5.78 (13)	2.97 to 36.7 (6) 17.7 (4)	0.95 (1)
Production index	0.14 to 0.54 (4) 0.31 (3)	0.21 to 0.72 (7) 0.46 (6)	0.32 (1)	0.16 to 0.79 (27) 0.37 (13)	0.20 to 0.43 (6) 0.32 (4)	0.46 (1)
Hydrogen index (mg HC/g TOC)	93 to 276 (4) 196 (3)	123 to 324 (7) 233 (6)	99 (1)	33 to 410 (27) 191 (13)	80 to 366 (6) 221 (4)	86 (1)
Oxygen index (mg CO_2/g TOC)	71 to 170 (4) 122 (3)	17 to 214 (7) 101 (6)	167 (1)	18 to 394 (27) 135 (13)	37 to 121 (6) 86 (4)	119 (1)
Chloride ion (wt%)	0.00 to 2.09 (4) 0.61 (3)	0.00 to 3.09 (7) 1.67 (6)	2.04 (1)	0.00 to 1.94 (27) 0.38 (13)	0.00 to 8.54 (6) 2.51 (4)	0.00 (1)

TOC – total organic carbon; bitumen carbon = 0.83 x total extract; S_1 – oil and gas yield (mg HC/g rock); S_2 – residual petroleum potential (mg HC/g rock); production index = $S_1/(S_1+S_2)$; n.a. - not analysed. Geochemical parameters and indices are given as numerators of minimum and maximum values, mean values in denominator and parenthesized (numerator of number of core samples, numer of sampled boreholes in denominator)

increasing contents of total extract (Fig. 12D), except for mine wastes. The same dependence can be observed for contents of saturated hydrocarbons versus chlorides (Fig. 13D).

CONCLUSIONS

Geochemical studies allowed us to identify the favourable zones for preservation and conservation of large mammal fossils within Pleistocene muds in Starunia. Both the bitumen (oil) and brine (chloride ion) were conserving agents for the large, extinct Pleistocene mammals; therefore, muds of this age were paid a special attention. The study area is unusual and specific since two types of organic matter occur in Quaternary sediments. The first type is residual organic matter constitued from the remains of the Pleistocene and Holocene plants and animals, whereas the second type is oil migrating from deep accumulations in the Boryslav-Pokuttya Nappe.

The total organic carbon (TOC) contents in the Pleistocene muds usually do not exceed 4 wt% and reach maximum 17.8 wt% at various stages of oxidation. The main mass of organic carbon hosted in the Pleistocene muds consists of bitumen. The highest bitumen content (9.26 wt%) was detected in biogenic muds. Another conserving agent, even more effective than bitumen, is salt. Chloride ion contents in studied muds vary from 0 to 4.66 wt% but are usually below 1 wt%. Despite the observed low salinity of the Pleistocene muds, attention should be paid to the fact that it is related to the presence of interstitial water. Its relatively small mass in comparison to that of minerals indicates that it originated from highly concentrated brines ascending from the salt-bearing Lower Miocene Vorotyshcha beds.

The natural pathways of underground fluids (oil, gas and water) migration within Quaternary sediments were disturbed by intensive mining operations run between the last three decades of the 19th century and 1960. Infiltration of meteoric waters, intensive drainage from shallow shafts and also opening of new migration routes for deep fluids from the salt-bearing Miocene Vorotyshcha beds changed the quantities of oil and salt impregnating the Quaternary sediments. These routes are still open. Therefore, the present preservation and conservation conditions of large, extinct mammal bodies can be different from those of Pleistocene age, when the animals were buried, and from before the time of mining operations.

The most favourable area for conservation and preservation of fossils was found close to boreholes Nos 22, 23, 28 and 36N, where the thickness of Pleistocene muds exceeds 2 m and where appropriate quantities of preservatives: salts and bitumen occur.

Generally, the spatial distributions of bitumen and chloride ion contents within the Holocene sediments and the salt-bearing Miocene Vorotyshcha beds are very similar to those found in Pleistocene strata.

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