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PRELIMINARY SUGGESTIONS ON THE PLEISTOCENE PALAEOVEGETATION AROUND THE BIŚNIK CAVE (CZĘSTOCHOWA UPLAND, POLAND) BASED ON STUDIES OF MOLECULAR FOSSILS FROM CAVE SEDIMENTS

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Abstract

Biśnik Cave is an important site of Middle Palaeolithic, with the longest sequence of Neanderthal settlement phases in Central Europe. In the previous studies of the Biśnik sediments, different elements of palaeoenvironment in the periods of Neanderthal occupation have been recognised, except of palaeovegetation, which could not be derived because of lack of preserved plant micro- or macrofossils. The current work is an attempt to reconstruct palaeovegetation in vicinity of the Biśnik Cave, using analysis of composition of plant-derived n-alkanes, preserved in sediments.

In our study, we analyzed one sample from each of the sediment's layers 11 – 19c (early Late Pleistocene and late Middle Pleistocene). Abundant n-alkanes (mostly n-C_{27}, n-C_{29} and n-C_{31}) were found in all the sampled layers except for the layers 12, 16 and 19d, showing no alkanes at all.

There is clear diversification of n-alkanes composition and CPI (carbon preference index) values between layers. Analysis of this composition, allows us to claim that the layers 11 and 14 were accumulated when the cave's vicinity was covered by dense coniferous forests, hence upon warm climate. The layers 19, 19a lower, 19b and 19c, presumably originated during cold periods when open woodlands or grasslands dominated. The other analyzed layers could be connected with intermediate vegetation in form of open woodland. However, not all of the achieved results stay in compliance with the actual stratigraphy, established basing on lithological data and palaeoecology of fossil fauna, and we hope that explanation of this discrepancy would be possible after more extensive studies of molecular fossils are done.

Key words: cave sediments, biomarkers, n-alkanes, gas chromatography, palaeoenvironment

INTRODUCTION

Biśnik Cave is an archaeological site of high importance at a scale of Central Europe. The most attractive are Middle Palaeolithic cultural horizons, with traces of two different cultures: Mousterian and Micoquian. Especially interesting are Micoquian horizons from Biśnik Cave, dated to OIS 8, whereas all over Europe this culture is known, except of few controversial sites, from much younger sediments, from OIS 5 to 3. Chronostratigraphy and age determination of sediments from Biśnik Cave are based on several methods *i.e.* palaeoecology of fossil mammals, sedimentological features, and thermoluminescence and U/Th dating (Cyrek *et al.* 2010). The whole sequence of sediments containing the Middle Palaeolithic artifacts is the longest one in the Central Europe.

Necessity of palaeoenvironmental reconstructions for periods of Neanderthal occupancy of Biśnik Cave, was evident from each archaeological publication about the site (Cyrek 2006, Cyrek *et al.* 2009, 2010). Some elements of palaeoenvironment are actually known, mainly the ancient fauna (Cyrek *et al.* 2010, Socha 2009, Stefaniak, Marciszak 2009, Wiszniowska *et al.* 2002) and the climatic conditions (Cyrek *et al.* 2010, Mirosław-Grabowska 2002). Little is known about palaeovegetation, because of lack or bad preservation of spores, and scarce occurrence of plant macrofossils, being preserved as charcoals (Cyrek *et al.* 2009). In addition, no profile of Pleistocene sediments from the vicinity of the cave has been palynologically investigated yet.

It is known from many sites that palaeovegetation may be recorded in sediments not only in form of micro- or

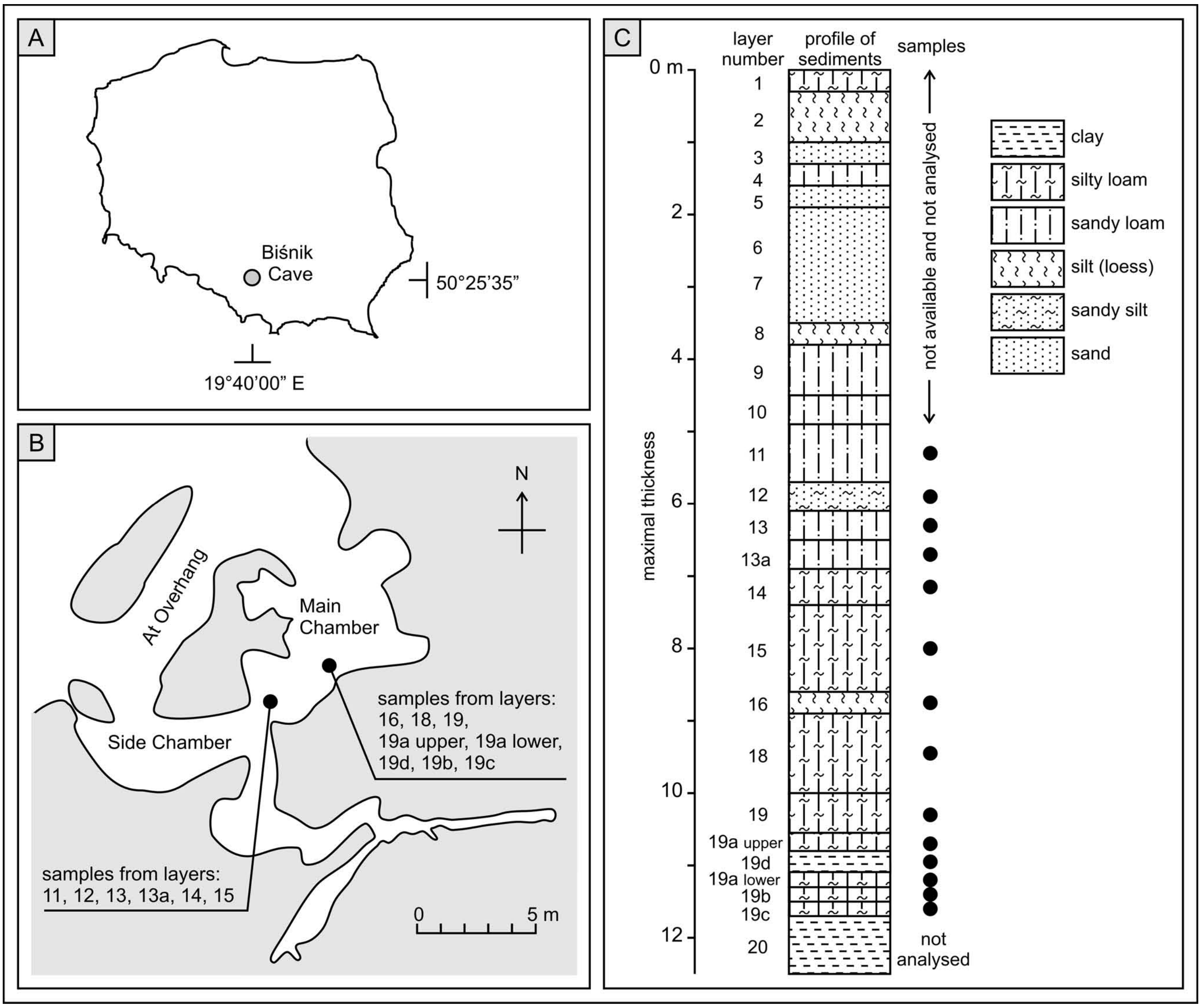

Fig. 1. The site Biśnik Cave. **A** – localization of a site in Poland. **B** – plan of the cave with marked position of sampled profiles. **C** – lithological profile of sediments with marked position of samples. The profile shown is a compilation of numerous partial profiles exposed in several archaeological trenches. Many layers contain a limestone rubble, artifacts and animal bones. Detailed lithostratigraphy of sediments was presented by Mirosław-Grabowska (2002) and Cyrek *et al.* (2010).

macrofossils, but may also leave chemical traces (for example Ishiwatari *et al.* 1993, Marseille *et al.* 1999, Meyers, Ishiwatari 1993, Rao *et al.* 2009, Schwark *et al.* 2002, Wiesenberg *et al.* 2004, Xie *et al.* 2002, Zhang *et al.* 2008). These chemical signs are amino acids, nucleic acids, photosynthetic pigments and many types of lipids. Most important of them are lipids, because they show high resistance to degradation (weathering or diagenesis) and may survive in sediments through a time longer than the Pleistocene (Cranwell 1984, Meyers, Ishiwatari 1993, Schwark *et al.* 2002).

Among lipids the n-alkanes, mainly long-chain ones, bear the most useful information on palaeovegetation. N-alkanes form among others the building material of epicuticular waxes of higher plants (Eglinton, Hamilton 1967). Waxes protect plants against dehydration, attacks of microorganisms, mechanical damages and other environmental factors. Composition of n-alkanes is different for different ecological groups of plants. Ratio of some n-alkanes content, especially n-C_{27}/n-C_{31} (n-heptacosane/n-hentriacontane) ratio, allows us to differ the herbaceous-derived organic matter from the tree-derived matter (among others: Blyth *et al.* 2007, Meyers, Ishiwatari 1993, Marseille *et al.* 1999, Rieley *et al.* 1991).

Our aim was to check if there are n-alkanes preserved in the sediments of Biśnik Cave, and if they show any differences between particular layers, which might be connected with particular horizons of Neanderthal occupation.

MATERIAL AND METHODS

Biśnik Cave is formed in a shape of three connected chambers, called the Main Chamber (the deepest one, with sediments >6 m thick), the Side Chamber, located laterally to the former one, and the At-Overhang chamber, actually outside the cave, being contiguous to the rock wall and undoubtedly being the old cave chamber that has collapsed in the past

Table 1

Lithological characterization of the layers sampled in Biśnik Cave

Layer number*	Lithology of sediments (partially after Cyrek *et al.* 2010 and Mirosław-Grabowska 2002)	Humus content (after Cyrek *et al.* 2010, Mirosław-Grabowska 2002)
11	black humic sandy loam with weathered limestone rubble	1.8%
12	laminated yellowish-green sandy silt	max. 0.2%
13	gray silty loam with weathered limestone rubble	0.9%
13a**	orange silty loam with weathered limestone rubble**	0.9%**
14	gray silty loam with slightly weathered limestone rubble	0.9%
15	yellow-brown humic silty loam with slightly weathered limestone rubble, with intercalations of loess	0.4-1.5%
16	laminated yellow loess	max. 0.2%**
18	gray silty loam with non-weathered limestone rubble	0.6-1.6%
19	brown humic silty loam with weathered limestone rubble	0.7-2.9%
19a upper	brown humic silty loam	1.0%**
19d**	laminated orange clay**	max. 0.2%
19a lower	laminated brown humic silty loam	0.9%**
19b	laminated brown humic silty loam	0.9%**
19c	laminated brown humic silty loam	0.9%**

* sample number is the same as the layer number; layer numbers according to Cyrek *et al.* (2009, 2010), with the exception of layer 19a, divided here into 19a upper and 19a lower, and layers 13a and 19d, not described earlier.; ** M. Krajcarz and K. Cyrek, unpublished data.

(Fig. 1). All samples of sediments were collected from the Main Chamber, from two archaeological trenches. In one of them the layers from 11 to 15 were accessible, in the second – the layers from 16 to 20 (Fig. 1B). Only these layers were accessible for us due to the excavation works and the actual shape of archaeological trenches. Among these layers, the lowest one (layer 20, terra rosa) was out of our interest, because of lack of archaeological artifacts and lack of organic matter (Cyrek *et al.* 2010, Mirosław-Grabowska 2002). All the remaining layers were sampled (Table 1). Layer 19a is intercalated by a layer 19d, which is the redeposited terra rosa. Because of that situation, layer 19a was divided into two sublayers: '19a lower' and '19a upper', which we sampled separately. The layers numbers are taken from references (Cyrek *et al.* 2009, 2010, Mirosław-Grabowska 2002) and are the same as used in archaeological field documentation. Originally the numbers were given to layers during the exploration works, so the numeration is not always continuous (*e.g.* there is no layer with a number 17; the layer 19d lies over the layers 19b and 19c, and partly 19a; and the layer 13a is placed between the layers 13 and 14).

One sample of sediment (about 300 g) was taken from middle part of each chosen layer (as far as possible from the bed and the top of layer). Only some of the chosen layers show a humic character and dark coloration, indicating the presence of organic matter. They are sandy loams and silty loams, containing limestone rubble, vertebrate bones and archaeological artifacts. The lithological characterization of layers is presented in Fig. 1 and Table 1.

Fourteen samples were taken for molecular analyses. The samples were dried and sieved and fraction > 2 mm with any fragments of limestone rubble, fossil bones and teeth was removed. The finer fraction of each sample was mixed and a portion of 10 g was taken to further preparation. These portions were powdered with agate mortar and pestle, and then put in cellulose cases and extracted in Soxhlet apparatus with mixture of dichloromethane-methanol (70–30) through about 72 hours. The extracts were condensed in vacuum vaporizer, filtered through the filter paper and transferred into 2 ml vials.

The prepared extracts were analyzed with gas chromatograph coupled with the mass spectrometer (GC-MS) Clarus 500 Perkin Elmer (Warsaw University, Faculty of Geology). The gas chromatograph was equipped with capillary column Elite-5MS (length of the column 30 m, diameter 0.25 mm, thickness of the film 0.25 µm). Temperature of the transfer line between chromatograph and spectrometer was 300°C, temperature of electrons source 200°C, electron ionization at 70 eV. Scope of the scanned mass was 35-600 AMU, with the scanning frequency 1 s^{-1}. Helium was a buoyant gas. Initial temperature of the chromatograph's oven (40°C) was held by 1 minute, next the oven was heated at a rate of 3°C/min until 300°C, and the final temperature was held by 20 minutes. The sample from the (randomly chosen) layer 13 was analyzed twice to check the repeatability of the measurements.

Identification of individual organic compounds was based on comparing the mass spectra with spectra given at the NIST library as well as with data announced in publications (Blyth *et al.* 2007, Vilegas *et al.* 1997, Xie *et al.* 2002). Location of particular n-alkanes' peaks on the axis of retention time is shown on exemplary chromatogram (Fig. 2).

Values of CPI index (carbon preference index) were calculated for each sample according to Rao *et al.* (2009), using the following formula:

$$CPI = 0.5 * ((([C_{23}]+[C_{25}]+[C_{27}]+[C_{29}]+[C_{31}]+[C_{33}])/([C_{24}]+[C_{26}]+[C_{28}]+[C_{30}]+[C_{32}]+[C_{34}])) + (([C_{23}]+[C_{25}]+[C_{27}]+[C_{29}]+[C_{31}]+[C_{33}])/([C_{22}]+[C_{24}]+[C_{26}]+[C_{28}]+[C_{30}]+[C_{32}])))$$

where $[C_x]$ means the relative abundance of n-C_x alkane in a sample.

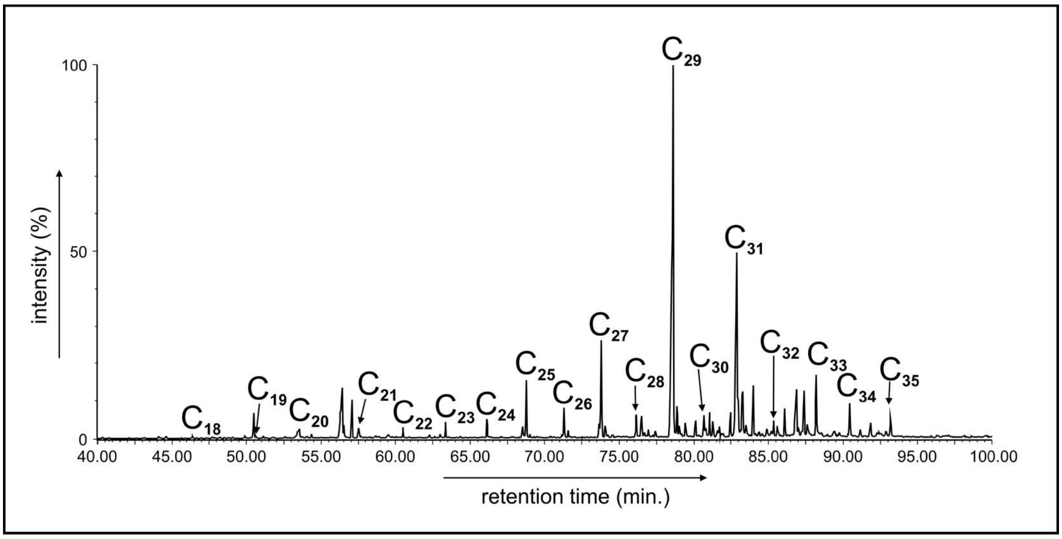

Fig. 2. Partial gas chromatogram of alkane fraction of the sample from layer 11 with marked peaks of particular n-alkanes.

RESULTS

The duplicate analysis of one sample suggests good repeatability of our method. The mean differences of abundances of individual n-alkanes are about 5%, and the difference between the CPI values is close to 10%.

Three of the studied layers have shown a total absence of organic matter (layers: 12, 16 and 19d). The other ones were rich in organic compounds with n-alkanes and other lipids (ketones, sterols, fatty acids, triterpenoids; data not shown). N-alkanes from n-C_{21} to n-C_{35} were noted in each of these layers. In some samples traces of shorter-chain n-alkanes also occur. Relative abundance of n-alkanes, calculated from MS-measured intensities of their peaks (the sum of all n-alkanes intensities in a sample is 100%), is shown in Table 2. Measured intensities are comparable only within one sample, so they are not shown. The dominance of odd chain lengths over even ones, is clearly visible and supported by high values of CPI (Table 2).

The most abundant n-alkanes are: n-C_{27} (n-heptacosane, $C_{27}H_{56}$), n-C_{29} (n-nonacosane, $C_{29}H_{60}$), n-C_{31} (n-hentriacon-

Table 2

N-alkanes relative abundance in samples from Biśnik Cave and CPI values.
Samples from layers 12, 16 and 19d with almost no organic matter are not shown. Trace abundances of n-alkanes n-C_{14} to n-C_{20} are not shown. CPI calculated according to Rao *et al.* (2009)

Alkane	Relative abundance (in %) in samples (by numbers of layers)											
	11	13	13*	13a	14	15	18	19	19a upper	19a lower	19b	19c
n-C_{21}	0.57	1.52	1.64	1.00	0.79	0.37	1.65	0.42	0.37	0.42	0.33	0.19
n-C_{22}	0.71	0.81	1.24	1.29	1.03	0.39	1.82	0.38	0.53	0.40	0.37	0.26
n-C_{23}	1.11	1.36	1.98	1.49	1.51	0.67	2.77	0.88	1.03	0.68	0.54	0.34
n-C_{24}	1.32	1.48	2.21	1.62	1.49	0.72	2.19	0.77	1.34	0.66	0.67	0.36
n-C_{25}	3.78	3.32	3.52	3.28	4.34	2.44	3.51	2.64	2.97	1.93	2.41	1.49
n-C_{26}	2.10	1.61	2.20	2.36	2.54	1.51	2.13	1.27	2.34	1.21	1.37	0.77
n-C_{27}	7.78	6.28	6.87	7.48	11.10	7.01	8.88	5.57	6.31	4.08	5.12	3.30
n-C_{28}	2.85	1.96	2.23	2.99	2.32	2.02	2.07	1.82	2.84	2.08	1.88	1.25
n-C_{29}	51.65	36.58	36.76	29.85	35.75	32.67	32.99	35.49	33.68	28.87	29.45	37.77
n-C_{30}	1.83	2.17	1.49	2.30	2.00	1.99	1.62	1.99	2.41	1.83	2.16	1.53
n-C_{31}	18.21	31.64	28.23	29.79	25.69	35.06	30.77	35.82	33.58	40.79	39.89	39.65
n-C_{32}	1.76	1.48	1.17	6.17	3.67	1.60	0.86	1.26	1.34	1.49	1.13	0.90
n-C_{33}	5.55	8.71	9.05	8.03	6.57	11.29	7.14	11.26	10.68	14.41	14.25	11.65
n-C_{34}	0.27	0.39	0.49	0.54	0.24	0.39	0.73	0.15	0.06	0.26	0.04	0.22
n-C_{35}	0.50	0.70	0.93	1.81	0.95	1.87	0.88	0.29	0.52	0.89	0.38	0.31
CPI	8.50	9.46	8.52	4.89	6.72	10.83	8.50	12.44	8.36	11.93	12.36	18.64

* repeated analysis

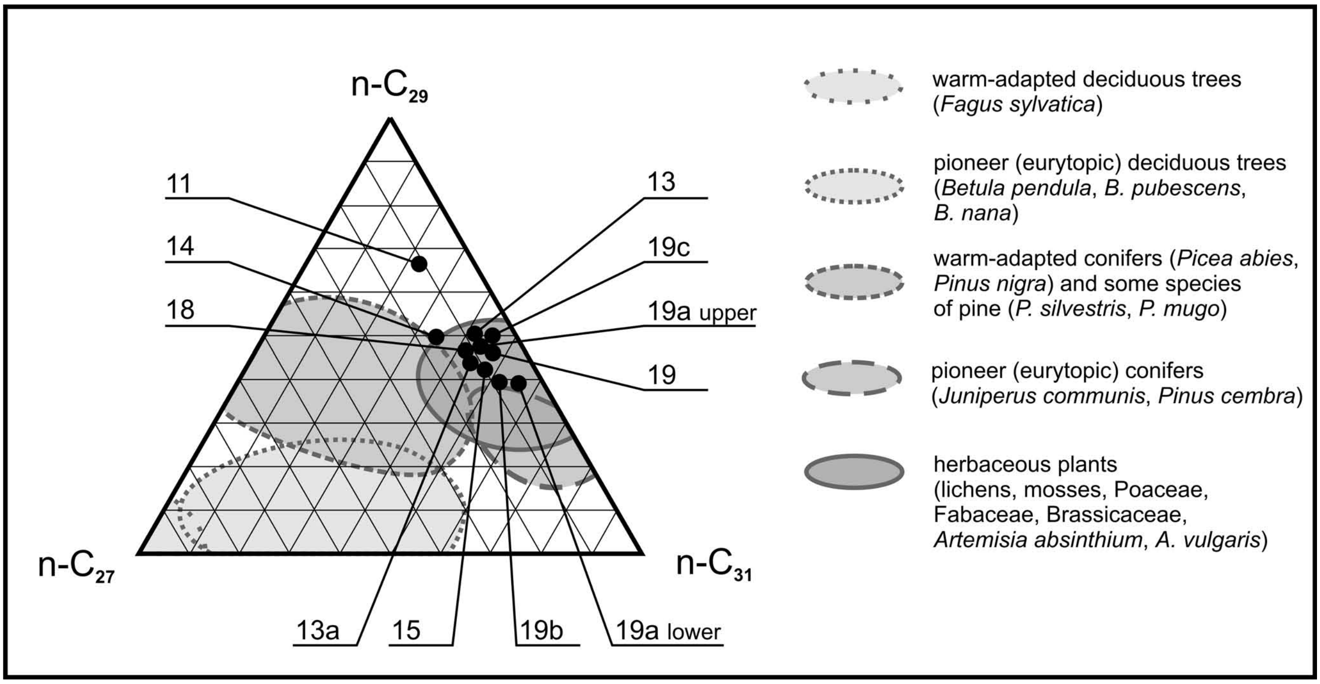

Fig. 3. Triangular diagram of n-C_{27}, n-C_{29} and n-C_{31} concentration with position of studied samples (black dots). The areas of n-alkane composition of waxes of different plant groups are shown as a background (according to the authors' compilation based of n-alkanes composition of cuticular waxes in modern plants, presented by: Maffei 1996, Marseille *et al.* 1999, Nott *et al.* 2000, Schwark *et al.* 2002, Uchiyama, Ogasawara 1981).

tane, $C_{31}H_{64}$) and in some samples n-C_{33} (n-tritriacontane, $C_{33}H_{68}$). Triangular diagram based on the concentrations of the three alkanes the most important for palaeovegetational interpretation (n-C_{27}, n-C_{29} and n-C_{31}) shows depletion of tree-descending alkanes (n-C_{27} and n-C_{29}) in most layers (Fig. 3). The exceptions are layers 11 and 14.

DISCUSSION

The presence of n-alkanes and other phytogenic organic compounds (triterpenoids, phytogenic sterols) in almost all the studied layers indicates the impact of surrounding vegetation on cave sediments' accumulation. The origin of organic matter in a cave may be quite diverse. It may be generated *in situ*, as a result of growth of plants in the area near entrance, growth of bacteria or fungi, accumulation of animal carcasses, excrements or as a result of human activity. Alternatively, the organic matter may be transported to the cave by geological media *i.e.* wind or groundwater. N-alkanes with overrepresentation of odd chain lengths are generated by leaves of higher plants (Baker 1982, Eglinton, Hamilton 1967, Nott *et al.* 2000). The bacterial, fungal or algal origin of n-alkanes from Biśnik Cave may not be excluded, however the participation of such alkanes here is insignificant. For us the most possible explanation is that the leaves' remains entered the cave via geological transport, or sometimes via biological transport, brought by animals or humans. The human impact on the presence and composition of organic matter was probably low, as the archaeological data indicate only rare, episodic residence of Palaeolithic people in the Biśnik Cave (Cyrek *et al.* 2009, 2010). The geological transport was probably mainly by wind, as in the sand fraction of most layers, grains with aeolian character of surface are the most abundant ones (indication from micromorphological studies, not shown here). Whatever was the way of transport, the organic matter of plant origin indeed represents palaeovegetation of the cave's surrounding.

On the triangular diagram (Fig. 3) most of the analyzed layers lie in the areas of herbaceous plants or pioneer conifers. These areas represent composition of alkanes in living leaves, not in sediments. Marseille *et al.* (1999) shown, that in soils, composition of alkanes may be slightly changed with respect to leaves, due to microbial alteration of organic matter. However the n-alkane distributions among soils originated under different vegetation has not been studied in detail yet, so its interpretation in terms of palaeovegetation may only be very rough, although it is being practiced (for example Schwark *et al.* 2002). In addition, high CPI values – observed in the material from Biśnik Cave – indicate, that microbial alteration was not too strong (Dinel *et al.* 1990).

From triangular diagram it is evident that most layers from Biśnik Cave were accumulated in vicinity of grass, pioneer plants (lichens, mosses) or pioneer conifers. Also the CPI index gives information about palaeovegetation. Its value depends on microbial activity, which is higher in warm climate and upon forest environment, and lower in soils developed under grassland or in cooler climatic zone (Meyers, Ishiwatari 1993). Although Rao *et al.* (2009) claimed that CPI values reflect soley climatic conditions, other studies had shown some relations between CPI and the vegetation type (see Blyth *et al.* 2007, Marseille *et al.* 1999). For Biśnik Cave the CPI values are different between layers and indicate many layers connected with grassland or vegetation of cold climatic zones, especially those from the lower part of the

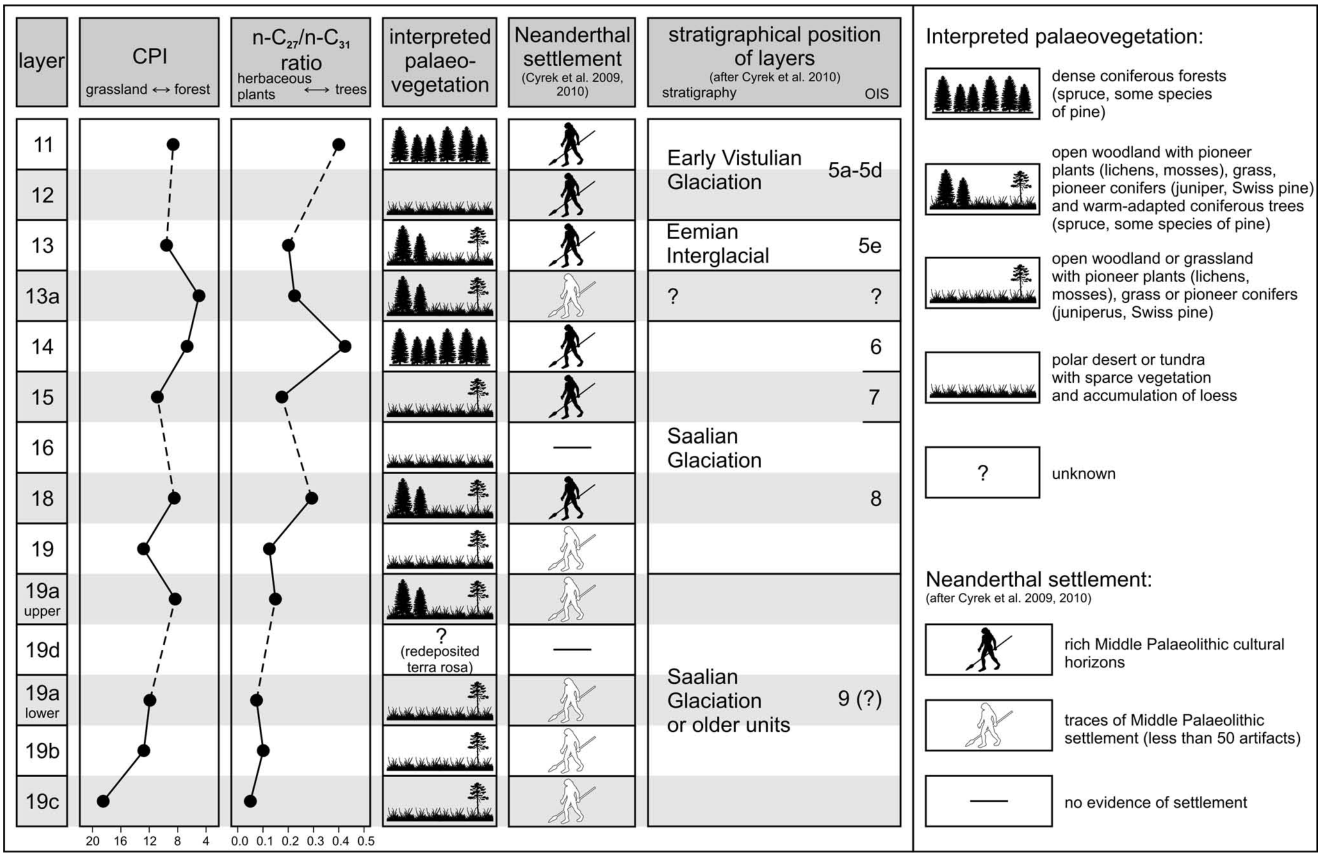

Fig. 4. CPI of n-alkanes and n-C_{27}/n-C_{31} ratio's diagrams followed by an interpretation of palaeovegetation in vicinity of the Biśnik Cave for periods of accumulation of layers 11-19c. Layers numbers after Cyrek *et al.* (2009, 2010). The layers 12 and 16 gave no evidence of n-alkane composition, so their interpretation is hypothetical

profile (Fig. 4, first diagram). If only a n-C_{27}/n-C_{31} ratio is considered (a good tool to distinguish organic matter descending from trees and from herbaceous plants (Marseille *et al.* 1999)), it will become clear that many layers should be connected with vegetation of open landscape (Fig. 4, second diagram). It is especially true for the lowest layers: 19, 19a lower, 19b and 19c. The typical Pleistocene ecosystem of Central Europe fitting well to the description above was steppe-tundra, steppe or pioneer pine-birch forests (Van Andel, Tzedakis 1996). The layers higher up (15, 19, 19a upper) present higher values of n-C_{27}/n-C_{31} ratio. It indicates more dense forest-like vegetation around the cave. However the position of these layers on the triangular diagram (Fig. 3) suggests, that the warm-adapted trees were still absent during that period. Influence of such trees is visible in the upper part of the studied profile, especially in layers 11 and 14, where the n-C_{27}/n-C_{31} ratio suggests the most dense, canopy vegetation (Fig. 4). These facts my be interpreted as a presence of dense coniferous forests around the cave during the period of accumulation of layers 11 and 14. Some less distinct influence of warm-adapted trees is also readable for layers 13a and 19a upper (Fig. 3).

Layers 12 and 16 are almost free of organic matter and show no n-alkanes preserved. These layers are built of loess or loess-like silt, which allows us to believe that the lack of n-alkanes resulted from severe climatic condition during accumulation of sediments, when the vegetation was absent or sparse. The lack of n-alkanes in layer 19d (terra rossa) is probably an effect of long-time diagenesis.

The two analysed sequences were located at different distances from the cave entrance (Fig. 1B). It was an effect of different depth of archaeological trenches and inaccessibility of every layer in the same vertical profile. Although the difference in location was only 3 m, it may not be excluded that the different location has some impact on the n-alkane composition of sediments. Addressing this question surely needs more research.

The interpretations of Pleistocene palaeovegetation proposed in Fig. 4 should be treated with caution. The number of the examined samples was small, and the solely composition of n-alkanes, when not supported by other indicators, is a weak base to reconstruct ancient vegetation. The supporting information could be derived *e.g.* from composition of other organic compounds of plant origin (ketones, fatty acids, sterols and triterpenoids). Such a study is in progress now, and its results will be presented in future papers.

CONCLUSIONS

The study presented above demonstrated the presence of organic matter with lipid fraction and abundant n-alkanes in many layers of Biśnik Cave, and indicated diversification of n-alkanes composition between layers, especially visible in different relative abundance of n-C_{27}, n-C_{29} and n-C_{31}. Having measured the content and relative abundances of n-alkanes, we tried to transpose them to parent group of plants, to derive density of vegetation and in result, reconstruct palaeovegetation.

The presented results have only preliminary character. Our reconstruction of palaeovegetation stays in conflict with actually known stratigraphical position of some layers of Biśnik Cave (Fig. 4, see also: Cyrek *et al.* 2009, 2010, Mirosław-Grabowska 2002). It might be due to small number of samples, which have given a very local information, inadequate in case of strong heterogeneity of sediments. However it is possible, that the stratigraphical scheme of the Biśnik Cave needs some revision. More extensive studies of molecular fossils are necessary to explain this situation.

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