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USE-WEAR AND ORGANIC RESIDUES AS EVIDENCE FOR PERISHABLE TECHNOLOGIES: A CASE STUDY OF LBK SITES IN SW POLAND (GNIECHOWICE 2, STARY ZAMEK 2A)

Abstract: This paper presents new data on perishable raw materials worked by early farmers and recovered through use-wear and gas chromatography coupled with mass spectrometry (GC-MS) analysis. Artefact studies included a potsherd and 53 flint specimens from two LBK sites in SW Poland: No. 2 at Gniechowice and No. 2a at Stary Zamek. Tools were used for working plants, hide, meat and bone. Seeds and nuts as well as roots and tubers were stored and/or prepared in the vessel. Moreover, betulin – a compound characteristic of products obtained from bark of birch trees, mainly birch tar – was detected in the pottery sample.
Keywords: use-wear, GC-MS, Neolithic, perishable technologies

INTRODUCTION

The excavations at the early LBK sites in SW Poland yielded fairly large source database. Unfortunately, these materials constitute a somewhat limited cognitive source. First of all these sites were repeatedly occupied in later times – both in the Neolithic as well as in younger periods. This reduces to some extent the possibility of appropriate separation of artefacts from different phases of the settlement. Another drawback is the fact that archaeological artefacts included only those made from durable raw materials, such as stone or backed clay. That is why methods of pottery production, processing of flint and other rocks as well as species profile of animals are best known areas.

The solution may be, however, use of innovative analytic methods, such as examining residues of organic and inorganic substances permeating vessels' walls during their use and usewear analyses of stone tools. They can be helpful for determining methods of gathering and processing of particular perishable products.

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Remains of the early Neolithic settlements located on sites No. 2 at Gniechowice (gm. Kąty Wrocławskie, woj. dolnośląskie) and No. 2a at Stary Zamek (gm. Sobótka, woj. dolnośląskie) are of great significance amongst the archaeological discoveries from SW Poland. It is due to the fact that during excavations, for the first time, the oldest traces associated with a long-term stay of the earliest farming communities of the Danubian cycle, belonging to the Linear Pottery culture (LBK) were recorded.

The beginnings of systematic excavations on the site No. 2 at Gniechowice date back to the 1930s, when remains of a multiphase settlement were unearthed (Boege 1935). However, remains of buildings associated with the population of the LBK were discovered there, as late as during excavations carried out in 1971–1972 (Fig. 1). In total, the area of 2070 m² was excavated back then, and 25 pits linked with stay of this community were discovered. Apart from 1450 LBK vessel fragments, 21 flint artefacts, five specimens made of other stone raw materials, blocks of daub with plant imprints and 468 animal bones were found there as well (Kulczycka-Leciejewiczowa, Romanow 1985).

The site No. 2a at Stary Zamek was excavated in 1973–1976 (Fig. 2). As a result of the work carried out, the area of 1800 m² was uncovered, where, apart from the LBK›s

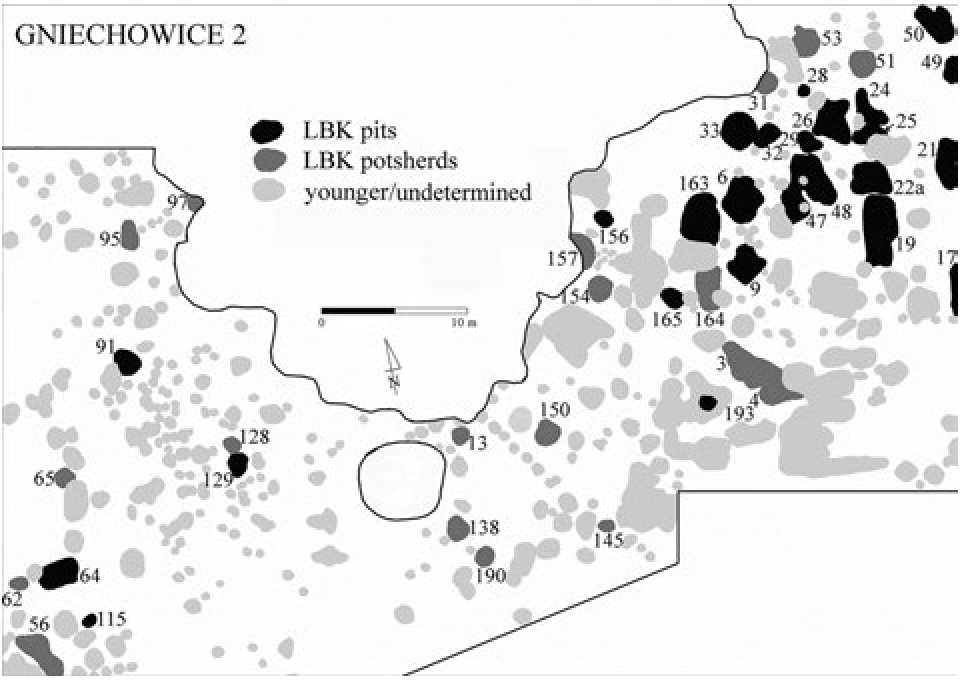

Fig. 1. Plan of the LBK settlement at Gniechowice 2, Wrocław distr. (after Kulczycka-Leciejewiczowa, Romanow 1985, modified by B. Kufel-Diakowska)

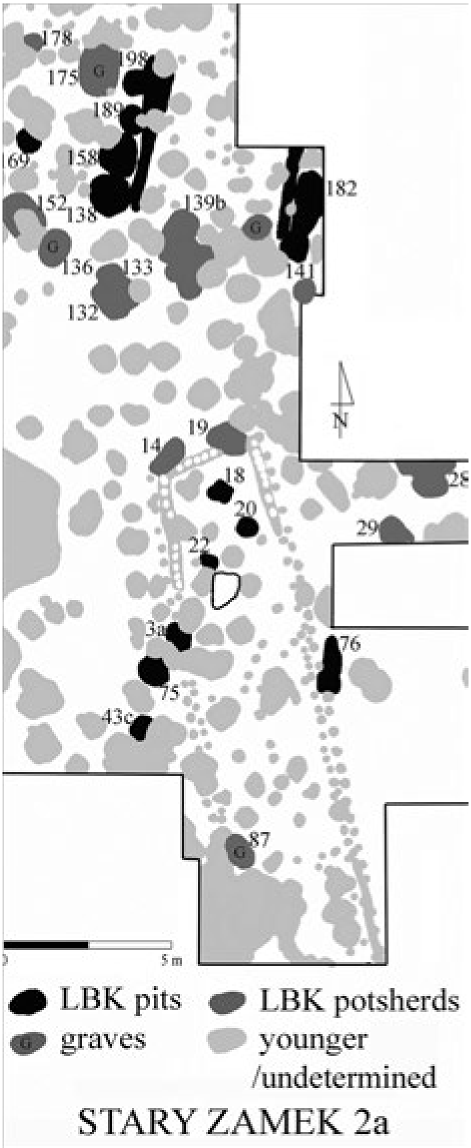

Fig. 2. Plan of the LBK settlement at Stary Zamek 2a, Wrocław distr. (after Kulczycka--Leciejewiczowa, Romanow 1985, modified by B. Kufel-Diakowska)

post building remains, also 13 settlement features from this time were discovered[1]. The result of the field work was also acquiring 818 vessels fragments and 32 flint artefacts, five specimens made of other stone raw materials, blocks of daub with plant imprints and 50 animal bones (Kulczycka-Leciejewiczowa, Romanow 1985).

[1] In this publication four other pits are mentioned – i.e. inhumation graves without grave goods, back then included to the LBK (features: 87, 136, 175, 181). Radiocarbon analysis carried out recently indicated, however, the relationship of individual graves with communities of the younger Neolithic age (Furmanek, personal communication).

Despite the considerable growth of the source materials related to the LBK, sites from the earliest colonization phase between the rivers Bystrzyca and Oława still belong to very rare ones. Therefore, both sites in question, despite the time which has passed, still constitute a solid source basis for understanding the oldest period of the Neolithic settlement in the aforementioned area.

METHODS AND MATERIALS

In our study we applied two analytical methods: use-wear analyses for determining the function of flint tools, based on microtraces of use, and chromatographic analyses with mass spectrometry (GC-MS) for detecting organic residues inside the ceramic vessel.

The use-wear analyses were carried out the Laboratory for Archaeometry and Archaeological Conservation, Institute of Archaeology, Wrocław University, according to the methodological protocol elaborated by Semenov (1964) and Keeley (1980), with the use of stereomicroscope Olympus SZX9 (up to 114×) and metallographic microscope Nikon ECLIPSE LV100 (50–500×). Prior to the microscopic observations artefacts were cleaned in the ultrasonic tank and then with alcohol (C_2H_5OH), if it was necessary. The experimental collection gathered by one of the authors (Kufel-Diakowska) and the results of experiments and use-wear studies of flint artefacts coming from the early Neolithic published to date (van Gijn 1988; 2010; Małecka-Kukawka 2001; Osipowicz 2010; Torchy, Gassin 2011; and others) were used as the reference materials. All flint specimens were selected to the use-wear analyses, because of small size of both assemblages (Stary Zamek – 32; Gniechowice – 21). Flint artefacts were previously classified as the LBK products and described in terms of raw materials and technological characteristics by Lech (1985).

For study on residues a fragment of footed vessel discovered in pit No. 6 from the settlement at Gniechowice was chosen. During the selection of pottery materials the intention was to avoid 'kitchen' vessels, used repeatedly and extensively in the past. Instead a specific form was selected, which shape could suggest its use for only a specific purpose[2]. The chromatographic analyses of the pottery sample was carried out according to the procedures developed at the Institute of General and Ecological Chemistry, Lodz University of Technology (Rosiak, Kałużna-Czaplińska 2014). The sample taken from fragment of the pottery vessel was initially crushed and then grated in a mortar. A weighed amount of crushed material (5 grams) was transferred to an extraction thimble and subject to extraction in Soxhlet extractor for 4 hours. The extraction solution was a mixture of two solvents: dichloromethane and methanol (200 ml, 2:1 v/v). For the esterification of fatty acids was used 100 ml of derivatization mixture consisting of two reagents: N,O-bis (trimethylsilyl) trifluoroacetamide and trimethylchlorosilane (BSTFA:TMCS; 100:1 v/v). The sample with the mixture was

[2] The presented research is only a part of greater project aimed at identifying residues in specific types of Neolithic vessels, hence it was not possible to take a larger sample from sites described in this article.

heated for 30 minutes at 75° C. For the determination of fatty acids was used gas chromatograph (GC Agilent Technologies 6890) coupled with mass spectrometer (MS, 5973 Network Mass Selective Detector).

The analysed compounds were separated in column HP-5MS (5% diphenyl-95% – dimethylpolysiloxane) at a flow rate of carrier gas (He) – 0.9 ml/min. The gas chromatograph was programmed as follows: initial temperature – 60° C, with temperature accretion 12°C/min until gaining the final temperature of 300° C. The parameters of the mass spectrometer were: temperature of the ion source and the mass analyzer were 230° C and 150° C respectively. Mass spectra were obtained in electron ionisation mode EI (Electron Ionisation) at the potential 70eV and the sweep rate of 50–550 m/z (a.m.u.).

The qualitative analysis of fatty acids was carried out based on Wiley and NIST08 mass spectral library. The quantitative analysis of fatty acids was carried out by the internal standard ($C_{24}H_{50}$; tetracosane) method.

RESULTS

Residues from ceramic vessel and use-wear on flint tools from Gniechowice and Stary Zamek provide the data for identifying activities, such as food processing and craft.

Evidence for food production

Evidence for production and consumption of plant and animal food products emerges from use-wear traces on five flint tools from Stary Zamek (Tab. 1) and residues from the footed vessel found in Gniechowice. One of the best recognized tool is the truncated piece used as a sickle insert (Fig. 3a). The tool was probably made from Jurassic flint. A fragment of blade was retouched with semi-abrupt retouch in its proximal part. Heavy rounding, smooth and highly reflected sickle gloss were produced on the right edge of the truncated piece. Polish is almost flat and intersected by short and shallow striations, what suggests harvesting cereals, not other high-silica content plants (*e.g.* reed). Traces of use exhibit orientation parallel to the working edge. The truncated piece was inserted obliquely in a haft, like most of sickle inserts from the early Neolithic. The artefact is slightly heated and its working edge was damaged – there are secondary chippings on ventral surface, which partly remove traces of use, as well as random postdepositional striations. Sickle insert was found in pit No. 175.

Another flint artefact, the blade with a tip broken off, made from erratic flint, shows ambiguous traces, suggesting contact with soft/medium material (Fig. 3e). The bright polish is not well-developed, but the widespread distribution of use-wear traces on the left corner is similar to these on the truncated piece. Traces are also more abrasive. Probably the flint blade was used as a sickle insert as well, but was used for relatively shorter period of time and had contact with soil particles. The working edge is slightly rounded and partly damaged. The artefact was found in pit No. 158.

Three other blades made from erratic flint: the blade with a butt broken off found in pit No. 136 (Fig. 3g), the blade with a tip broken off from pit No. 158 and a slightly

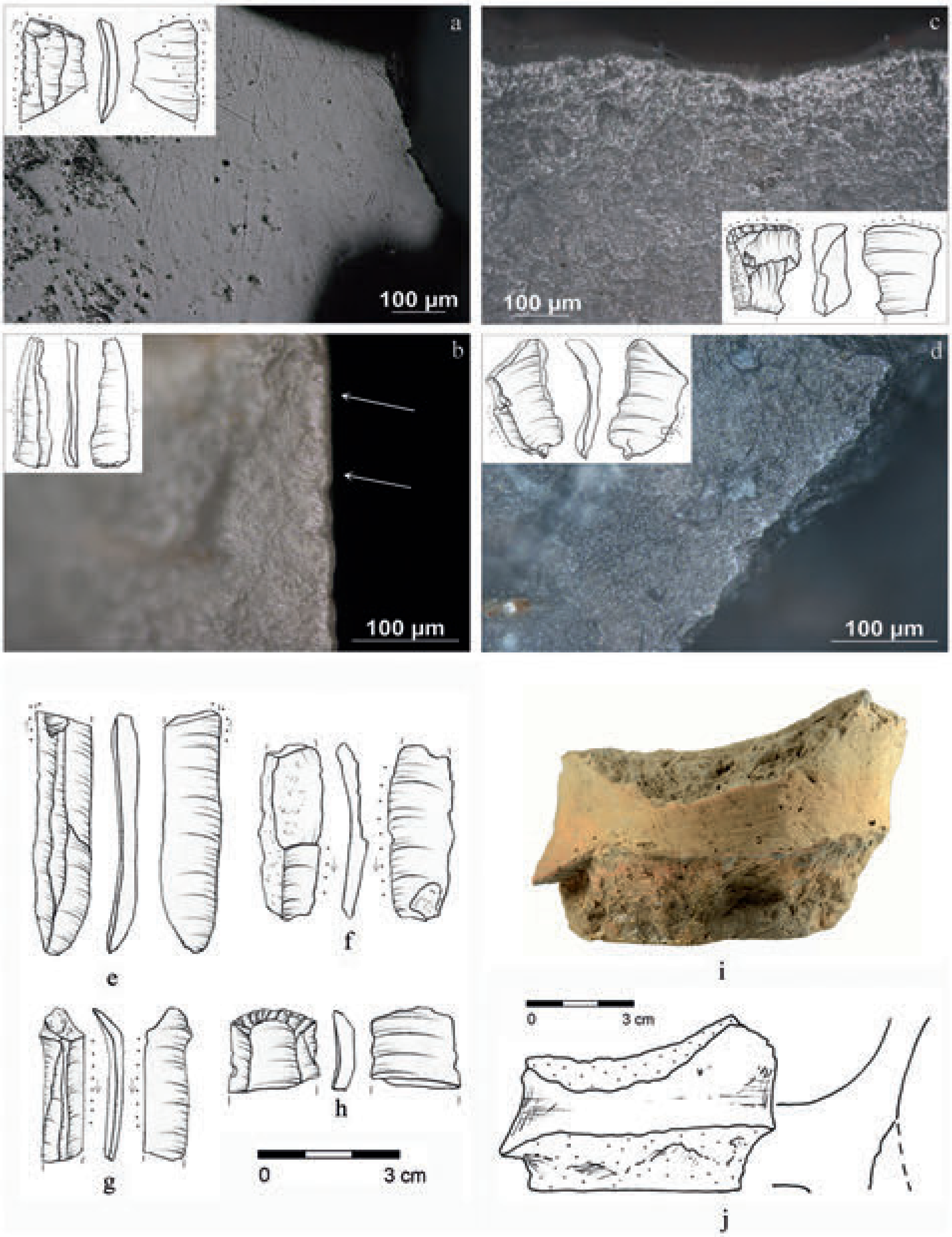

Fig. 3. Artefacts with usewear traces and residues:
a – truncated piece with sickle gloss, b – blade with traces of scraping plants, c – scraper with traces of scraping fresh hide, d – blade with traces of whittling bone/antler, e–g – blades, h – endscraper (photo and drawings B. Kufel-Diakowska), i–j – fragment of footed vessel (photo J. Sawicki, drawing K. Czarniak)

Table 1. Function of flint tools

	Site	Pit No	Type of tool	Function
1	Stary Zamek 2a	175	truncated piece	harvesting cereals
2	Stary Zamek 2a	158	blade	harvesting cereals? (contact with soil)
3	Stary Zamek 2a	136	blade	cutting soft/medium organic material
4	Stary Zamek 2a	158	blade	cutting soft/medium organic material
5	Stary Zamek 2a	153a-house 2	blade	cutting soft/medium organic material
6	Stary Zamek 2a	138	blade	scraping plants
7	Stary Zamek 2a	3a	scraper	scraping fresh hide
8	Stary Zamek 2a	189	scraper	scraping hide
9	Gniechowice 2	50	blade	whittling bone/antler

Table 2. Fatty acids in the pottery sample

	Systematic nomenclature	Trivial nomenclature	Shortcut	Provenance	Percentage
1	hexanoic acid	caproic acid	C6:0	ruminant milk fat	0.15
2	octanoic acid	caprilic acid	C8:0	milk fat	0.27
3	nonanoic acid	pelargonic acid	C9:0	ethereal oil obtained from pelargonium	0.51
4	decanoic acid	capric acid	C10:0	milk fat, animal fat	0.16
5	undecanic acid	–	C11:0	plant fat	0.07
6	dodecanoic acid	lauric acid	C12:0	laurel oil	0.44
7	tetradecanoic acid	myristic acid	C14:0	milk products, oleic plant product	1.93
8	pentadecanoic acid	–	C15:0	milk fat	0.72
9	cis-9-hexadecenoic acid	palmitoleic acid	C16:1	animal fat, fish fat	2.17
10	hexadecanoic acid	palmitic acid	C16:0	ubiquitous, animal fat, milk fat	4.84
11	cis-9-octadecenoic acid	oleic acid	C18:1	ubiquitous, milk fat	1.55
12	octadecanoic acid	stearic acid	C18:0	ubiquitous, animal fat (beef tallow), milk fat	2.58

heated medial fragment of the blade from pit No. 153a-house 2 (Fig. 3f), bear traces of cutting soft and medium organic material, most probably animal tissue. Traces, such as use retouch, slight edge rounding or greasy polish were produced exclusively on right edges of three blades. In one case there are also traces on opposite edge, probably from prehension.

In the tested sample of pottery (Figs. 3i, j) twelve fatty acids were detected (Tab. 2). Amongst them dominate saturated fatty acids: stearic acid (octadecanoic acid, C18:0) and palmitic (hexadecanoic acid, C16:0). We also managed to detect significant quantities of only two unsaturated fatty acids: oleic acid (cis-9-octadecenoic acid, C18:1) and palmitoleic acid (cis-9-hexadecenoic acid, C16:1). The research proves that these fatty acids more readily undergo degradation processes (decomposition, oxidation) and therefore are rarely detected in archaeological samples (Eerkens 2005).

The contents of individual fatty acids are not basis for direct assumption about the origins of organic residues. American researchers (Copley et al. 2005; Gregg, Slater 2010) propose to assess the source of residue based on ratio of acids C16:0/C18:0. If calculated ratio is from 1 to 2, the residues are probably of animal origin, while the result over 3 suggests decomposed plant remains as the source of residues. In the case of the sample in question the ratio is 1.88.

More reliable seems Eerkens' study (2005), in which assumptions about the origins of residues are based on four ratios: C12:0/C14:0; C16:0/C18:0; (C15:0 + C17:0)/C18:0 and C16:1/C18:1. After calculating acids ratios proposed by this researcher and based on adopted by him criteria for evaluation of the results, it could be speculated that the examined residues are mainly of plant origins. Three calculated ratios indicate seeds and nuts as well as roots and tubers as food stored and/or prepared in the vessel from which comes the sample.

Evidence for craft production

Evidence for craft production, including production of objects and substances from vegetal and animal materials, emerge from use-wear traces on three flint tools from Stary Zamek, one flint tool from Gniechowice (Tab. 1) and residues from the footed vessel found at Gniechowice. One complete blade from erratic flint, found in pit No. 138 at Stary Zamek, was used for scraping high-silica content plants. The tool bears traces of use on its left lateral edge (Fig. 3b). The working edge is highly rounded, especially on its ventral aspect. There is bright polish on the very edge and no use retouch, only tiny chips were detached from the edge on its dorsal aspect.

Two flint endscrapers made from erratic flint, found in pit Nos. 3a and 189 at Stary Zamek, were used for scraping hide. One of them is preserved as a complete artefact (Fig. 3c). Distal edge of a partly cortex flake was abruptly retouched. Retouch was also made on a fragment of the right edge. Working edge is highly rounded and polished. Polish produced as a result of scraping fresh hide is bright and greasy. Both lateral edges are chipped. The second endscraper was made from a distal fragment of a blade (Fig. 3h). There are no use-wear traces on retouched edge, but right and left sides of the tool are rounded. The working edge was probably resharpened during work.

One complete, partly cortex blade, made from erratic flint, found in pit No 50 at Gniechowice was used for whittling bone or antler (Fig. 3d). Use retouch perpendicular to the working edge, together with bright 'antler' polish were produced on the left side of the tool.

Amongst the chemical compounds detected in the pottery sample from Gniechowice, also betulin was found. It is a compound characteristic of products obtained from bark of birch trees, mainly birch tar.

PERISHABLE TECHNOLOGIES

Plant cultivation was to date evidenced only by imprints of cereals (*Triticum monococcum*, *Triticum dicoccum*, *Hordeum sp.*) preserved in pottery and daub from two sites. Plants remains were added to clay paste as tempering admixture (Kulczycka-Leciejewiczowa, Romanow 1985). Inside the footed vessel plant microresidues, such as seeds, were recognized with the use of the GC-MS. Two sickle inserts were found in pits at Stary Zamek. The polish on one truncated piece is very intense, what suggests a long-term use of the sickle. We do not know how large were fields under cultivation back then, but the tool could have been used for more than one season. Amongst plant imprints, Kulczycka-Leciejewiczowa and Romanow (1985) did not found weeds typical of agriculture. However, due to the discrepancies in the results of experimental works (see Korobkowa 1981; Unger-Hamilton 1985; Juel Jensen 1988), it is difficult to prove – from the topography of sickle polish – their thesis that fields were regularly weeded.

Some potsherds bear imprints of woody and herbaceous plants, such as grasses (*Gramineae*), as the evidence of the use of other plants. However they only prove that tree branches and twigs were used as wall construction materials. GC-MS analysis identified the components of birch-bark tar, extracted from the bark of *Betula sp.* Wood tar was used from the Palaeolithic as adhesive for hafting, in later periods as glue or for waterproofing ceramic vessels. The discovery of organic residue from Gniechowice is important because there are no lumps or macroresidues of birch-bark tar from the early Neolithic in SW Poland. Such kinds of finds from the Neolithic in Central Europe are scarce (Groom et al. 2015). Betulin was also detected by GC-MS in one more fragment of pottery from Gniechowice, which is dated back to the younger phase of the settlement – the Stroked Pottery culture (Kałużna-Czaplińska 2014). Moreover, on the working edge of one of the flint blades, traces of scraping rigid, probably siliceous plant were recorded. The tool could have been used e.g. to smooth stems or leaves for wickerwork or mats production, or similar activity that engaged plant material and a flint tool.

Besides plant food, people's diet included meat. Both sites provided bones of domesticated (cattle, pig, sheep/goat) and wild animals (aurochs, roe deer, red deer, wild boar). Three flint blades were used amongst others for preparing meat. They show traces of cutting soft and medium organic material. Animal products also satisfied other needs. Two flint endscrapers show traces of cleaning hides, an initial stage of processing hide for clothes, containers, etc. People also used hard animal tissue as raw material for making durable, long-lasting tools. No bone or antler tool was found at the sites, but traces of whittling bone or antler are preserved on one of the flint blades.

The distribution of tools does not tell much about the location of particular activities. Most of the flint tools with traces of use were discarded as worn out specimens and come from extraction pits (Nos. 138, 158, 189 and probably No. 3a at Stary Zamek), where household waste and refuse were usually disposed, or from settlement pits of undetermined function (No. 50 at Gniechowice). Three lithic tools were retrieved from other contexts: foundation trench of a house and fills of two younger graves.

FINAL REMARKS

The archaeometric research revealed different, than it was possible to demonstrate before, types of activity related to food production and consumption as well as craft production. Basing on so far available primary sources, i.e. fragments of pottery vessels, flint and stone tools and animal bones, as well as the secondary ones such as imprints of seeds and plant fragments in clay paste, it was possible to reconstruct methods of pottery production, processing flint and other rocks as well as species profile of animals. The data on technologies from materials unpreserved in the archaeological layers, were hidden in microtraces and residues, and were detected with the use of microscopic and GC-MS analyses. Perishable materials, commonly used by the early farming communities, were important components of their diet (cereals, meat) and offered wide range of sources (woody and herbaceous plants, hide, bone and antler) for every type of Neolithic craft, such as production of clothes and containers, tools and tar-like products.

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