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MESOLITHIC HUMAN BONES FROM THE UPPER VOLGA BASIN: RADIOCARBON AND TRACE ELEMENTS

A L Alexandrovskiy[1] • E I Alexandrovskaya[1] • M I Zhilin[2] • J van der Plicht[3,4]

ABSTRACT. Human bones from 3 Mesolithic sites in the Upper Volga basin were analyzed for trace elements, and dated by accelerator mass spectrometry (AMS). The radiocarbon dates of the bones correspond to the Mesolithic era. However, some dates differ from those obtained for the enclosing deposits and for the worked wood fragments in the cultural layer. The elemental composition of the bones is interpreted in terms of increased concentrations of some elements and their impact on human health and behavior.

INTRODUCTION

Human bone tissues from archaeological sites are of great importance for both radiocarbon dating and paleoenvironmental reconstructions. Bone collagen is used for ^{14}C dating, while information on ancient diets can be obtained from concentrations of certain trace elements and from the stable isotope ratios of the bones (e.g. Gilbert 1977; Shishlina et al. 2007). In some cases, the stable isotopic composition of the bones can be used to reconstruct paleoclimates (Nikolaev et al. 2002).

Until now, such studies have not been performed for the Mesolithic era in Russia. No ^{14}C dates exist for human bones from the Upper Volga region, and studies of diets of Mesolithic people are very limited.

Here, we present the first ^{14}C dating results of bones of Mesolithic people from this region. The bones were dated by accelerator mass spectrometry (AMS) in Groningen, the Netherlands. In addition, we obtained conventional ^{14}C dates on peat and other large samples from the layers in which the bones were found. Also, the trace elemental composition of the dated bones was measured. From this, we derive information on ancient diets, as well as—more generally—the chemical interaction of prehistoric people with their environment. This is a relatively new field of science that can be referred to as anthropochemistry. In earlier studies, bone tissues of people living in the Paleolithic, Late Neolithic, Bronze Age, Iron Age, and Middle Ages have been analyzed in this way (Alexandrovskaya and Alexandrovskiy 2003; Alexandrovskaya and Panova 2003).

THE STUDIED SITES

A map of the region showing the sites we investigated is shown in Figure 1. The Ozerki peat bog is located 20 km south of the city Tver (#1 in Figure 1). About 20 sites were discovered in its western area; 3 of them contain Mesolithic layers with well-preserved organic materials (Zhilin 2003, 2006). The Ozerki 17 site is located at the ancient outlet of a small river, starting from an ancient lake with an area of about 5 × 3 km^2. An area of 67 m^2 was excavated. Human bones were found in the lower (IV) middle Mesolithic cultural layer of the site, dated to the early Boreal period by pollen analysis. This layer is overlain by a 2.5-m-thick layer of peat with 3 Neolithic cultural layers, dated to the Atlantic period (Zhilin et al. 1998). The Mesolithic site was occupied during a regression of the ancient lake, and flooded during the second part of the Boreal and the beginning of the Atlantic

[1]Institute of Geography, Russian Academy of Sciences, Moscow, Russia.
[2]Institute of Archaeology, Russian Academy of Sciences, Moscow, Russia.
[3]Center for Isotope Research, Groningen University, Groningen, the Netherlands.
[4]Faculty of Archaeology, Leiden University, Leiden, the Netherlands. Corresponding author. Email: J.van.der.Plicht@rug.nl.

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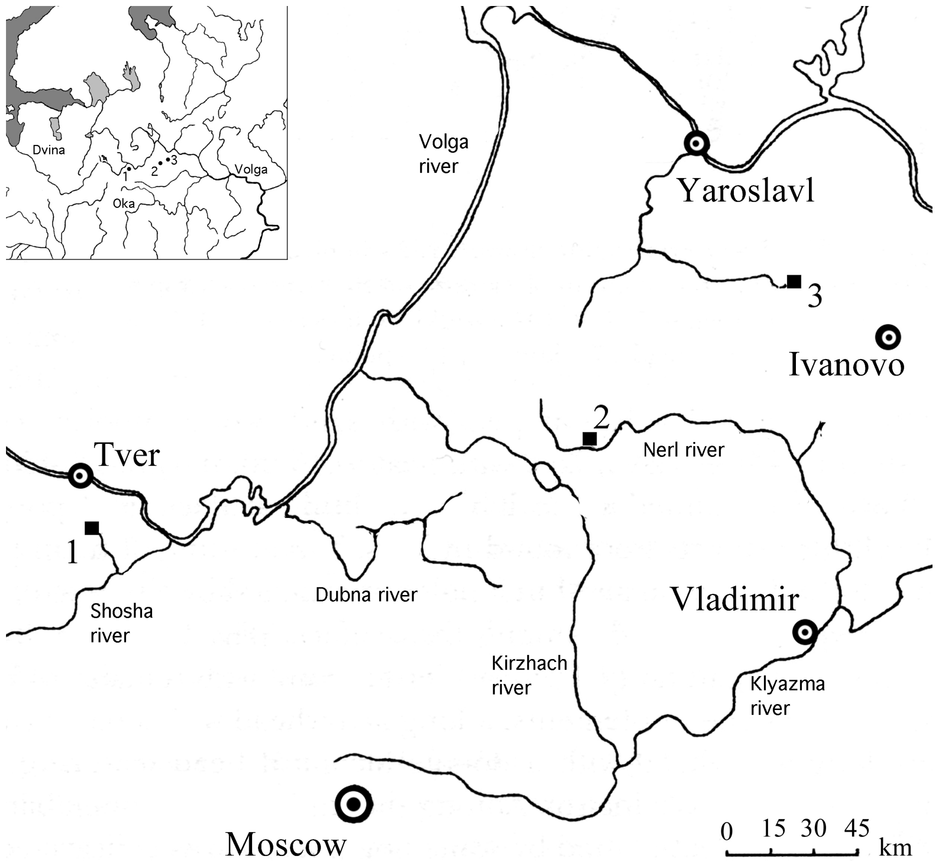

Figure 1 Mesolithic sites in the Upper Volga basin with human remains: 1) Ozerki 17; 2) Ivanovskoye 7; 3) Stanovoye 4.

period. During this flooding stage, occupation of the site and its surroundings was impossible. The northern part of the trench, where the analyzed human bones were found, was partly eroded during this transgression.

The Ivanovskoye peat bog covers an area of 8 × 4 km^2 and is located in the southern part of the Yaroslavl region, about 150 km north-northeast of Moscow (#2 in Figure 1). The archaeological site Ivanovskoye 7 is situated in the central part of the northern half of the peat bog. It is located at a low promontory of the mineral lake shore and the nearby part of the peat bog. The site was excavated during 1974–1975 by D A Krainov and in 1992–1997 by M G Zhilin (Zhilin 2003, 2006; Zhilin et al. 2002). The total excavated area is 1170 m^2. The site is well stratified; the total thickness of peat and gyttja deposits is about 2 m. Three Mesolithic cultural layers, separated by clear layers of peat and gyttja, were studied. Human bones were found in the upper Mesolithic layer (II a) dated to the early Atlantic period by pollen analysis. It was occupied during a lake regression, and later flooded for a short time during a transgression phase. After this period, a layer of peat with 2 Neolithic cultural layers accumulated during the Atlantic period. No traces of disturbance were observed in the upper Mesolithic layer in which the analyzed bone was found.

The archaeological site Stanovoe 4 is located at the Podozerskoye peat bog between the cities Ivanovo and Yaroslavl, 50 km southeast of the latter (#3 in Figure 1). This peat bog emerged as a result of overgrowth of a glacial lake with an area of about 5 × 3 km^2, as indicated by the spread of gyttja deposits under the peat. The site is located at a gentle slope of a promontory, which is a glacial lake terrace at the outlet of the river from the peat bog (ancient lake gulf) and a boggy area just below. The site was discovered in 1992, and about 600 m^2 were excavated during 1992–2002. Three Mesolithic cultural layers, dated by pollen analysis to the end of the Younger Dryas, Preboreal, and Boreal periods were investigated (Zhilin 2003, 2006). Human bones were found in layer III of cut 3, dating to late Preboreal period. It also yielded a variety of stone, bone, antler, and wooden artifacts, shown in Figure 2. This layer is well preserved and overlain by peat and gyttja deposits with a thickness of about 1–1.5 m.

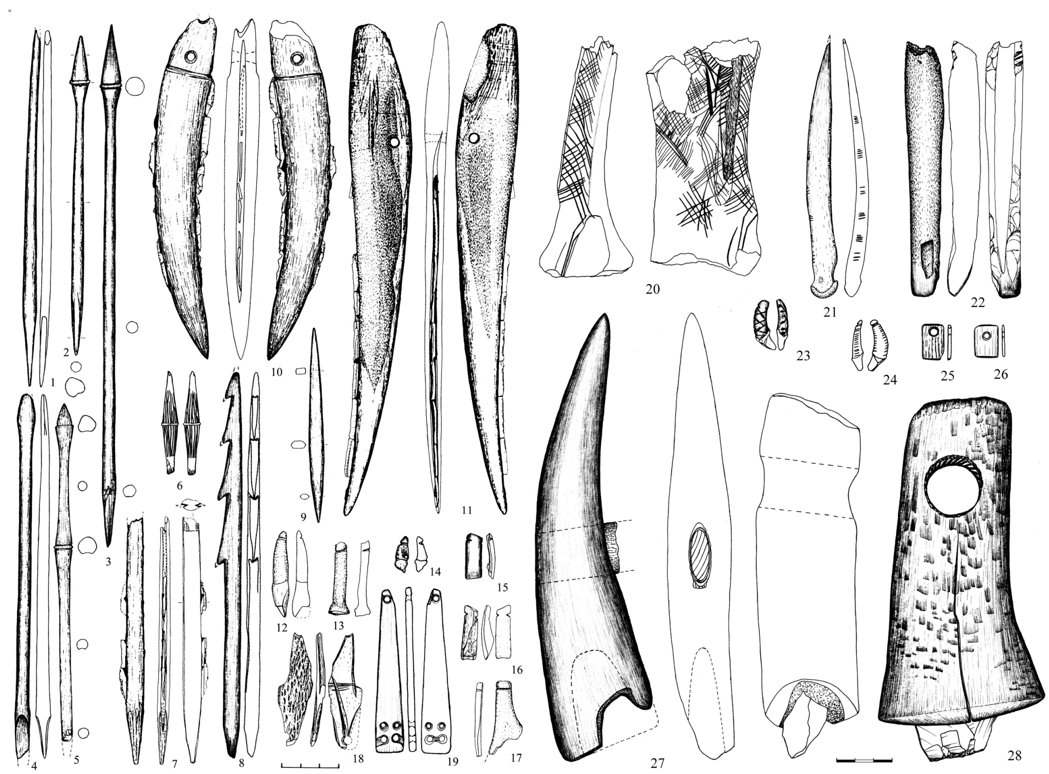

Figure 2 Prehistoric artifacts from Stanovoe 4, cut 3, cultural layer III: (1–9) arrowheads; (10–11) daggers; (12–17), (23–26) pendants; (18) refuse of an intact fishing hook; (19) a plate for dragging cords and ropes; (20) a handle of a broad knife; (21) an awl; (22) a chisel; (27) an ax sleeve with a fragment of a wooden handle; and (28) an adze sleeve with a stone adze blade.

MATERIALS AND METHODS

Radiocarbon Dating

The age of the samples from the Mesolithic sites were obtained by ^{14}C dating. The larger samples of wood, peat, and an animal bone (elk) were dated conventionally by liquid scintillation counting in Moscow (laboratory code GIN) and St. Petersburg (laboratory code LE). The samples were pretreated by the standard AAA (acid-alkali-acid) procedure, using 4% HCl at a temperature of 80 °C, followed by 4% NaOH at 20–80 °C, and again 4% HCl at 80 °C (Mook and Streurman 1983; Zaretskaya et al. 2005).

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The small samples of bone were dated by AMS in Groningen (laboratory code GrA). From the bone samples, collagen was extracted as a datable fraction in Groningen using a modernized version of the Longin method (Longin 1970). The collagen was combusted, purified and transferred into graphite (Aerts-Bijma et al. 2001). The graphite is pressed into target holders for the ion source of the AMS. The AMS measures the isotope ratios $^{14}C/^{12}C$ and $^{13}C/^{12}C$ of the graphite, from which the conventional ^{14}C age is determined (van der Plicht et al. 2000).

The stable isotope ratios $^{13}C/^{12}C$ and $^{15}N/^{14}N$ are measured for the same collagen dated by AMS. These stable isotope ratios were measured by an elemental analyzer, combined with a mass spectrometer (Aerts-Bijma et al. 2001).

Trace Element Analysis

Bones show a network of blood vessels, which can gradually exchange chemical elements with the environment. Fossil bone material preserves its elemental composition even after the long period of being buried in the soil, which makes it possible to use data on element concentrations in the bones for reconstructing ancient food diets (Gilbert 1977).

Trace elemental analysis was done by means of X-ray fluorescence (XRF). It is a nondestructive method, suitable to study unique objects, such as the bones of Mesolithic people. A wide range of elements can be investigated by XRF. We used an energy-dispersive XRF machine, ORTEC type TEFA-III, applying the multichannel pulse-processing system SBS-50 “Greenstar.”

The bone samples were first cleaned mechanically. The bone fragments were not smaller than 1 cm; their weight was 200 mg or more. The method was developed using large series of samples (Alexandrovskaya and Alexandrovskiy 2003). Fore more technical details, we refer to Revenko (1994).

RESULTS AND DISCUSSION

Radiocarbon Dating

The AMS ^{14}C dates obtained for the human bones correspond to the Mesolithic epoch. These dates are shown in Table 1. The ^{14}C dates of the deposits at the excavated archaeological sites are shown in Table 2.

Table 1 ^{14}C dates and stable isotopic data (^{13}C,^{15}N) for human bones. For sample St4-4, there was not enough collagen left for ^{15}N analysis.

Sample	Lab code	^{14}C age (BP)	cal BC (1 σ)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Oz17-1	GrA-34078	7760 ± 50	6643–6563 6547–6528 6518–6511	–19.29	11.87
Oz17-2	GrA-34082	7680 ± 45	6586–6585 6568–6543 6532–6467	–22.37	12.27
Oz17-3	GrA-34083	7755 ± 50	6641–6562 6548–6527 6519–6510	–20.27	11.99
St4-4	GrA-34084	9310 ± 60	8692–8687 8638–8464	–21.08	n/a
Iv7-6	GrA-34112	8410 ± 50	7544–7455 7391–7382	–24.48	12.63

Table 2 ^{14}C dates of the deposits at the excavated archaeological sites.

Sample	Dated material	Lab code	^{14}C age (BP)	cal BC (1 σ)
St 4	Gyttja	GIN-10122	9280 ± 120	8636–8330
St 4	Worked wood	GIN-8375	9220 ± 60	8538–8511 8484–8334
St 4	Elk bone	GIN-11093	8850 ± 90	8204–8036 8015–7933 7930–7909 7903–7828
Oz 17	Worked wood	GIN-6635	8830 ± 40	8170–8115 8054–8046 7983–7816 7798–7796
Oz 17	Worked wood	GIN-7474	8840 ± 50	8181–8112 8090–8076 8061–8042 7993–7825
Iv 7	Peat	GIN-9361 II	7520 ± 60	6451–6357 6291–6269
Iv 7	Peat	GIN-9361 I	7530 ± 150	6559–6550 6522–6521 6508–6228
Iv 7	Peat	GIN-9369 I	7320 ± 190	6379–6026
Iv 7	Peat	LE-1260	7490 ± 120	6450–6236
Iv 7	Peat	LE-1261	7375 ± 170	6395–6080

The date (GrA-34084) for Stanovoe 4 (cut 3, layer III) is consistent with the ^{14}C dates obtained from gyttja deposits and worked wood from this layer (Table 2; Zhilin 2003, 2006; Zaretskaya et al. 2005). The latter is the end of a birch wood stake, sharpened by a stone adze. Pollen analysis dates this layer to the late Preboreal period. Two human bones (probably from different individuals) were found among kitchen refuse, consisting mainly of elk and beaver bones.

Dates from the site Ozerki 17 (Table 1: GrA-34078, -34082, and -34083) are the same within error. The average date for these 3 measurements is 7710 ± 30 BP, which is about 1000 yr younger than the ^{14}C dates and pollen data for the layer IV in which these bones were found (see Table 2). According to the pollen analysis (Zhilin et al. 1998), this layer was deposited during the first quarter of the Boreal period; the ^{14}C age (average value for GIN-6635 and -7474) is 8835 ± 30 BP (Table 2; Zhilin 2003, 2006). Pollen analysis showed that this layer was deposited during the first part of the Boreal (Zhilin et al. 1998). The site was inhabited during regression phases of the lake. Faunal finds (bones of fish and waterbirds) indicate that it was occupied during the warm season. The dated bones were found in the northern end of the excavation trench, where interruption of normal sedimentation is observed, indicating that the Mesolithic layer probably eroded during a later transgression that flooded the site during the second half of the Boreal period (Zhilin et al. 1998). The site was flooded about 8500 BP and habitation here and in the surrounding area was impossible until about 7400 BP. The dates of these 3 human bones correspond to the period of this flood. Therefore, we conclude that these bones are not connected with the habitation of this site. The nearest sites that could be occupied during this transgression phase are located at a distance of about 300–500 m from Ozerki 17. The dated bones, most probably belonging to 1 person, could not emerge at the site Ozerki 17 as a result of natural processes. They must have been brought here by humans. Probably it is a sacrifice, and the bones of this person were intentionally thrown into the water at the outlet of the river. All human bones from this site were excavated from a small area of 1 m^2, which supports our hypothesis that they were placed here intentionally.

The ^{14}C dates are calibrated using the calibration curve IntCal04 (Reimer et al. 2004). The calibrated age ranges for all dated materials are shown in Figure 3, and are also listed in Table 1.

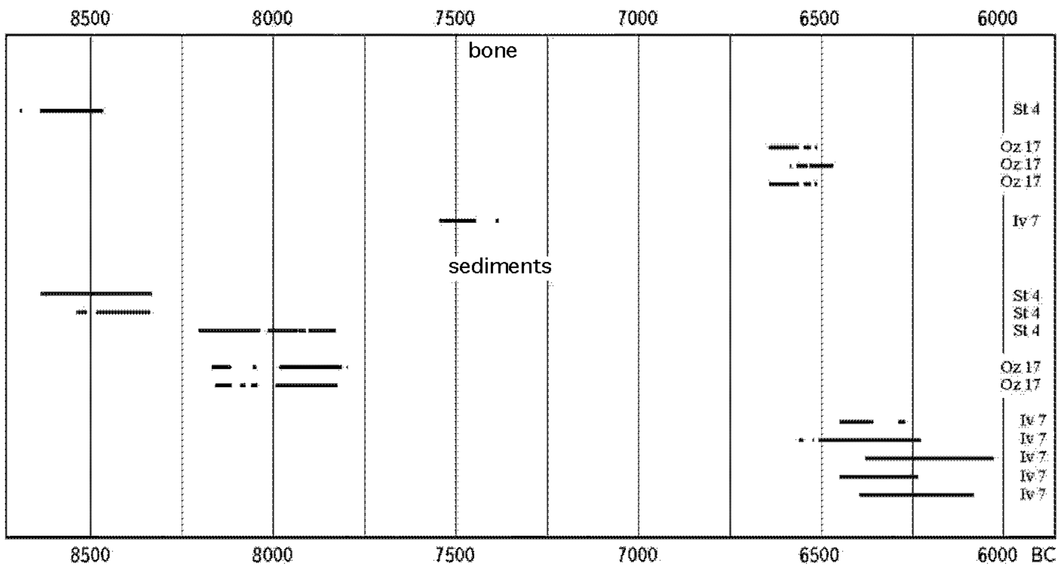

Figure 3 Calibrated age ranges from the measured ^{14}C dates (1 σ)

For Ivanovskoye 7, the date 8410 ± 50 BP (GrA-34112) is about 1000 yr older than the layer, where this bone sample was found. Between 8500–8000 BP, the site was flooded. Later, around 7600 BP, the place became a swamp. Only around 7500 BP did the area become drier and suitable for settlement. The cultural layer IIa of the site Ivanovskoye 7 is embedded in peat dating to about 7400 BP (Table 2). Pollen analysis shows that this layer was deposited during the early phase of the Atlantic period (Zhilin et al. 2002). It is separated by peat and gyttja from a layer, dated to 8700–8500 BP (Middle Mesolithic, layer III); pollen analysis indicates the first half of the Boreal period. Remains of a hearth and a pit with well-preserved vertical walls were excavated in layer IIa.

There are no traces of any disturbance of the cultural layer IIa, which is overlain by a thin deposit of gyttja and a layer of peat containing 2 Neolithic cultural layers. Therefore, we conclude that the bone was most probably brought to the site by its occupants from some other place.

A large component of fish in the diet may cause offsets in the ^{14}C age of human bones (e.g. Shishlina et al. 2007). The stable isotope ratios, however, do not show this (Table 1). Also, the bone remains indicate that flesh of terrestrial mammals was the main food source (Zhilin 2004:58). Therefore, we exclude reservoir effects here, which might cause the ^{14}C dates of human bones to be too old.

Anthropochemical Analysis

We investigated the concentrations of trace elements in human bone remains for dietary information, and to make possibly inferences concerning the environment (Alexandrovskaya and Alexandrovskiy 2003, 2005). The results of trace element analysis of the human bones are shown in

Table 3. The 3 bones from the Ozerki site are characterized by a large increase in the concentrations of iron and arsenic, and by normal or low concentrations of other elements. It is likely that all these bones belonged to the same individual. An extremely high iron content is an indication for poisoning or for a disease, causing exsiccosis of the organism and a high concentration of hemoglobin.

Table 3 Concentrations of iron (%) and trace elements (mg/100 g) in human bone tissues. The so-called Clarke values are given for bone in a relative scale according to Emsley (1991). The element concentrations above these Clarke values are shown in bold. The symbol (-) means none detected.

Sample	Fe (%)	As	Zn	Mn	Cu	Br	Pb	Se	Hg	Sn	Ba
Bone Clarke value	*1.5*	*0.1*	*14*	*10*	*1.8*	*0.7*	*1.9*	*0.5*	*0.04*	*0.14*	*3.0*
Oz-17-IV-93-56, humeral bone	**8.6**	**1.3**	9	10	0.8	0.5	1.0	0.3	–	–	–
Oz-17-IV-93-56, ulna bone	**7.4**	**2.3**	9	10	0.8	0.5	1.0	0.4	–	–	–
Oz-17-IV-93-56, spoke bone	**5.5**	**0.8**	12	10	0.8	0.5	1.0	0.3	–	–	–
Stanovoe 4, 98b, pit 3, layer III, sq. 157, joint	1.1	0.2	**31**	6	0.7	0.3	0.5	0.2	–	–	–
Stanovoe 4-95; pit 3, layer III, vertebra	1.5	0.3	**25**	9	1.2	0.2	0.5	0.2	–	–	–
Ivanovskoe 7, layer IIa, final Mesolithic	1.3	0.3	4	8	1.0	0.3	0.5	0.2	–	–	–

The stratigraphical situation obviously plays an important role. Bones lying at the surface are subject to changes in elemental composition (Trueman et al. 2003). However, for buried bones, as is the case here, the elemental composition is generally conserved (Alexandrovskaya and Alexandrovskiy 2003).

The water and bog sediments in the Upper Volga basin are characterized by a very low content of all trace elements. This is caused by the low content of trace elements in the glacial deposits of the region, which undergo many cycles of redeposition and weathering. The peat sediments show even a lower concentration of trace elements than water-glacial and alluvial sediments (Perelman and Kasimov 1999). This also explains the very low content of these elements in water of the Upper Volga basin (Gordeev 1983). Thus, the river water here contains less zinc than in regions with rocks older than the Quaternary—like Siberia, the Caucasus region, and the Far East. The contents of these trace elements in studied peat deposits may be subject to variations, but are in any case much lower than the bones studied from the Stanovoe and Ozerki sites.

The high content of arsenic in the bone tissues can be an indication of poisoning. Arsenic is known to be present in high concentrations in both poisonous and edible mushrooms. A slightly higher concentration of arsenic is found in the bones from the Stanovoe and Ivanovskoe sites, which is probably caused by a high portion of mushrooms in the diet of the population. However, because the arsenic concentration is still relatively low, it could have a positive effect on the health of these people by means of strengthening of their bones.

The zinc concentrations in the studied bones are low in the 3 bones from the Ozerki site and in the bone from the Ivanovskoe 7 site; in the 2 bones from the Stanovoe site, they are higher.

The input of zinc to human organisms is mainly through the food consumed. It is generally assumed that fish is the main source of zinc; however, we note that the largest content of zinc is present in fish scales and gills. During the Mesolithic era, small fish were cooked and eaten as a whole. Mollusks and some mushroom species are also rich in zinc. Fish played an insignificant role in the nutrition of people from the Stanovoe 4 site; their diets were based on the flesh of mammals (Zhilin 2004:58). There are no data indicating a significant role of mollusks in the diet of these people. Thus, the increased concentrations of zinc, as well as of arsenic, could be related in this case to the consumption of mushrooms. This then would be the first observation of mushrooms in the diet of Mesolithic people in eastern Europe. Zinc is a necessary element for a healthy development of humans. Human teeth, the pancreatic gland, the pituitary gland, and genitals are especially rich in zinc. Zinc deficiency affects the growth and functioning of human bones and can be clearly seen at the interface of calcification zones. To a certain extent, bone tissues are a reservoir of zinc. The toxicity of this element is due to its catalytic activity and competitiveness with several other metals. People suffering from regular excessive zinc uptake are easily subjected to quinsy, gastrointestinal diseases, sleep disturbance, fatigue, and hearing impairment (Filov 1988). Such malfunctions were obviously life-threatening for Mesolithic people.

CONCLUSION

Our multidisciplinary study of 3 Mesolithic archaeological sites in the Upper Volga basin yields new and valuable information on the age and living conditions of Mesolithic people. ^{14}C dates obtained for the human bones found at the site Stanovoe 4 are in agreement with the associated dates obtained for gyttja deposits in the enclosing strata and for the worked wood fragments found in the cultural layer. For the other 2 sites, Ivanovskoye 7 and Ozerki 17, such a correspondence was not found. This raises the question why these bones are present in the cultural layer. We assume that they were brought in by humans from elsewhere, because habitation of both sites was impossible during the time, and because they could not be transported to this location by natural processes. The trace element analysis of the bones showed considerable differences in elemental compositions, in particular for iron, arsenic, and zinc. The zinc deficiency, found in samples from Ivanovskoye 7 and Ozerki 17, could affect the reproductive function of Mesolithic people and partly limit the growth of their population in the region. The excessive amounts of arsenic and zinc in human bones at these sites may indicate a significant role of mushrooms in the diet of these Mesolithic people.

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