Diet and subsistence practices in the Dnieper area of the North-Pontic region (4^{th} - 3^{rd} millennium BC):

An integrated archaeological, molecular and isotopic approach.

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To my Dad

Abstract

The late Eneolithic and early Bronze Age period (4500 to 2300 BC) of the Dnieper region of Ukraine is considered a key period for the understanding of the prehistoric Pontic steppe (Rassamakin, 1999). For this reason, it has been subject of considerable research over the past decades. Unfortunately, a number of issues, such as the isolation of Eastern Europe and Central Asia during the twentieth century and a lack of evidence with much literature unpublished, means Eurasian prehistory is poorly understood. In particular, problems with the reconstruction of Eurasian prehistory relate to the subsistence economy, the extent of the exploitation of domesticates and, overall, the lifestyle of prehistoric Eurasian people associated with this region.

It is known that domesticated ruminants appeared in the North-Pontic region at around the 6th millennium BC (Bunyatyan, 2003; Kotova, 2003), and other evidence, such as faunal remains and previous isotopic analysis, suggested that animal exploitation was driven by local environmental conditions (e.g. Bunyatyan, 2003; Rassamakin, 1999; Kuzmina, 2003). Furthermore, archaeological and archaeobotanical evidences from sites across the North Black Sea suggested that the gathering and processing of wild and domesticated plants was a significant component of local subsistence strategies (e.g. Bibikova, 1969; Levine, 1999a; Pashkevich, 2003; Velichko et al., 2009; Bendrey, 2011).

This thesis aimed to resolve these difficulties by using an interdisciplinary approach to determine the subsistence economy of the populations living along the Dnieper River. Significantly, it comprises the first study of diet and subsistence practices in the North-Pontic region during the Eneolithic and early Bronze Age, through the application of a combined archaeological, molecular and isotopic approach.

Lipid extracts of >200 potsherds from 5 Ukrainian settlements were analysed by gas chromatography (GC), GC-mass spectrometry (GC/MS) and GC-combustion isotope ratio-MS, revealing excellent preservation of animal fats.

The carbon isotope results confirmed that the North-Pontic communities practised a various economy especially in relation to regional needs, developing a *flexible system* (Bunyatyan, 2003). Interestingly, the exploitation of secondary products, e.g. dairy fats, played a significant role only in the subsistence strategies of the steppe populations, reinforcing the idea of a full pastoral economy, as sheep, goats and cattle were intensively exploited for their secondary products. In contrast, the forest-steppe sites showed a high exploitation of wild animals, horses and aquatic products. These results also revealed that the animals raised in the steppe environment subsisted on a range of different forages composed mainly by a predominant C_3 environment with some C_4 plant input.

In conclusion, this research has clarified some of the aspects related to both the extent of the exploitation of domesticates and the subsistence economic strategies of prehistoric people living in the area of the North-Pontic region. The information obtained from molecular and compound-specific stable carbon analysis, generally reflects both existing botanical and zooarchaeological records confirming (i) the archaeological theory of a subsistence economy mainly driven by environmental regional differences and (ii) the predominance of ruminant husbandry in the steppe sites and hunting and fishing in forest-steppe settlements.

Zusammenfassung

Das späte Äneolithikum und die Frühbronzezeit (4500 bis 2300 v.Chr.) in der Dnepr-Region, heutige Ukraine, werden als Schlüsselperioden zum Verständnis der prähistorischen nordpontischen Steppe angesehen (Rassamakin,1999). Daher waren die zeitlichen Perioden in den letzten Jahrzehnten Gegenstand etlicher Forschungen. Eine Reihe von Problemen, wie die politische Isolation Osteuropas und Zentralasiens während des 20. Jahrhunderts, und fehlenden archäologischen Zeugnissen bzw. das Manko, dass vieles noch unpubliziert ist, führten leider dazu, dass die Vorgeschichte Eurasiens in vielen Aspekten noch wenig bekannt ist. Als problematisch erweist sich bei der Untersuchung der Vorgeschichte Eurasiens insbesondere die Rekonstruktion der Subsistenzwirtschaft, das Ausmaß der Nutzung domestizierter Tiere und insgesamt die Lebensweise der vorgeschichtlichen Gemeinschaften in dieser Region.

Bekanntermaßen sollen domestizierte Wiederkäuer im Nordpontikum erstmals etwa für das 6. Jahrtausend v.Chr. nachgewiesen sein (Bunyatyan,2003; Kotova, 2003). Andere Belege, wie Faunenreste und bisherige Isotopenanalysen, machen wahrscheinlich, dass die Art und Weise, wie Tiere genutzt wurden, durch die lokalen Umweltbedingungen bedingt war (z.B. Bunyatyan, 2003; Rassamakin, 1999; Kuzmina, 2003). Zudem geben archäologische und archäobotanische Hinterlassenschaften aus Fundorten im gesamten nördlichen Schwarzmeergebiet Hinweise darauf, dass das Sammeln und die Zubereitung wilder und domestizierter Pflanzen eine bedeutende Komponente der lokalen Subsistenzstrategien darstellte (z.B. Bibikova, 1969; Levine, 1999a; Pashkevich, 2003; Bendrey, 2011).

In der vorliegenden Dissertation wurde den dargestellten Schwierigkeiten mit Hilfe eines interdisziplinären Ansatzes entgegengetreten, mit dem die Subsistenzwirtschaft der entlang des Flusses Dnjepr ansässigen Gemeinschaften untersucht wurde. Bezeichnenderweise stellt die Arbeit die erste Studie zu Ernährung und Subsistenzpraktiken im Nordpontikum während des Äneolithikums und der frühen Bronzezeit dar, in der eine Kombination aus Archäologie, Molekularbiologie und Isotopie zum Einsatz kam.

Lipidextrakte von mehr als 200 Keramikscherben aus fünf Siedlungen in der heutigen Ukraine wurden mit GC, GC/MS und GC/C/IRMS untersucht. Es ergab sich eine exzellente Erhaltung von Fettrückständen in den Proben.

Die Ergebnisse der Kohlenstoffisotopie bestätigten, dass die nordpontischen Gemeinschaften unterschiedliche Wirtschaftsweisen pflegten, die sich vor allem an den regionalen Bedürfnissen orientiert waren, und daher flexible Systeme entwickelt wurdenen (Bunyatyan, 2003). Interessanterweise spielte die Nutzung von Sekundärprodukten, wie beispielsweise Milchfette, nur in den Subsistenzstrategien der Steppenpopulationen eine bedeutende Rolle. Schafe, Ziegen und Rinder wurden intensiv wegen ihrer Sekundärprodukte genutzt, wodurch die Idee einer ausschließlichen Weidewirtschaftsweise untermauert wird. Im Gegensatz dazu zeigte sich für die in der Waldsteppe gelegenen Fundorte eine hohe Nutzung wilder Tiere, Pferde und aquatischer Ressourcen. Die Ergebnisse zeigten auch, dass sich die Tiere, die in der Steppe gehalten wurden, von verschiedenen Futterquellen ernährten, die sich hauptsächlich aus C_3-Pflanzen zusammensetzten und nur ein geringer Einfluss von C_4-Pflanzen nachweisbar ist.

Zusammenfassend konnte durch diese Studie einige der Aspekte geklärt werden, die zum einen mit dem Ausmaß der Nutzung von Haustieren und zum anderen mit den Subsistenzwirtschaftsstrategien der prähistorischen Menschen im Nordpontikum in Zusammenhang stehen. Die Informationen, die aus der Molekularanalyse und verbindungsspezifischen stabilen Kohlenstoffanalyse gewonnen wurden, entsprechen weitgehend den bereits existierenden archäobotanischen und archäozoologischen Erkenntnissen. Sie bestätigen von Archäologen aufgestellte Theorien, dass die Subsistenzwirtschaft vornehmlich von regional unterschiedlichen Umwelteinflüssen geprägt war. Zudem unterstützen die Ergebnisse, dass in den Fundorten im Steppengebiet überwiegend Wiederkäuer gehalten wurden, während in den Fundorten der Waldsteppe Jagd und Fischfang während des Äneolithikums vorherrschten.

Abbreviations

AMS accelerator mass spectrometry
APAA ω-(o-alkylphenyl) alkanoic acid
BC before Christ
BP before present
BSTFA *N,O*-bis(trimethylsilyl)trifluoroacetamide
$C_{16:0}$ Palmitic fatty acid
$C_{18:0}$ Stearic fatty acid
$C_{14:0}$ Mystiric fatty acid
Cal calibrated
DAG diacylglycerols
DCM dichloromethane
DHYA dihydroxy acid
EBA Early Bronze Age
FA fatty acids
FAME fatty acid methyl ester
GC gas chromatography
GC/*C*/IRMS gas chromatography/combustion/isotope ratio mass spectrometry
GC/MS gas chromatography/mass spectrometry
GC/TC/IRMS gas chromatography-thermal conversion-isotope ratio mass spectrometry
IS internal standard
LE Late Eneolithic
MAG monoacylglycerol
NISP number of identified species
ME Middle Eneolithic
MNI minimum number of individuals
SIM selected ion monitoring
TAG triacylglycerol
TLE total lipid extract
TMS trimethylsilyl
VPDB Vienna Pee Dee Belemnite
VSMOW Vienna Standard Mean Ocean Water

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L&C climatology and the land classification scheme of Matthews (1983). Panel a) shows the areas corresponding to C3 (blue), C4 (red), and mixed C3C4 (yellow) grasslands based on the T>22°C, and pCO_2 = 35 Pa. Panel b) shows the corresponding distributions based on T>18°C, and pCO_2 = 27 Pa.

Figure 8.8 Plot showing the mean $\delta^{13}C$ and $\delta^{15}N$ values of human bones from (i) the forest-steppe sites (red, black and yellow dots) and (ii) the steppe sites (greys and white dots) overlapping on the isotope map (Dunn 2011 *ref*. O'Connell 1996). Dereivka human bones come from the Neolithic cemetery, Molyukhov Bugor dated Eneolithic and Stepnaya, Vinogradnoe, Peshtchanka and Kirovograd dated Late Eneolithic/Early Bronze age (EBA).

Figure 8.9 Scatterplots of $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values for (a) modern reference animal fats collected from Britain (Copley et al., 2003); (b) modern reference fats collected from Kazakhstan (Stear, 2008) and (c) modern reference animal fats collected from Libya and Kenya (Dunne, 2015). In the figure: ruminants dairy fats (black dots), ruminants adipose fats (squares), equine adipose fats (rhombus), equine dairy fats (white dots), porcine fats (triangles).

Figure 8.10 Scatterplots of $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values for (a) archaeological forest-steppe fats (black dots), modern reference animal fats collected from Britain (green dots) modern reference fats collected from Kazakhstan (red dots); and (b) archaeological steppe fats (black dots), modern reference animal fats collected from Britain (green dots) modern reference fats collected from Kazakhstan (red dots).

Figure 8.11 Scatter plots of mean δD values of the $C_{16:0}$ and $C_{18:0}$ fatty acids of animal fats from a) Modern equine adipose fats from Kazakhstan (black square) and United Kingdom (green square); b) Modern equine adipose and dairy fats (black and yellow squares) and Botai equine adipose and dairy fats (black and yellow dots); and c) Botai equine adipose and dairy fats (black and yellow dots) and Ancient North-Pontic region equine fats (grey dots) where i) represents the real results and ii) the expected results.

Figure 9.1 Pie charts showing the proportions of animal products detected within pottery vessels from the Eneolithic settlement of Dereivka (n=27); Molyukhov Bugor (n=11); Mikhailovka I (n=34); Nizhniy Rogachik (n=24) and Mikhailovka II (n = 19); and from the Early Bronze Age settlements of Mikhailovka III (n=16) and Generalka (n=27). Only those lipid residues that have been assigned by compound-specific stable isotope analysis are included (i.e. sherds containing plant lipids are not included, nor are sherds that did not yield any lipid). Total number of lipid extracts are given at the base of the pie charts. Abbreviations: Horses (H); Fresh water fish (F); Ruminant adipose fat (Ra); Ruminant dairy fat (Rd); Porcine/Pigs (P).

Figure 9.2 Pie charts of the percentage of bone finds recognized as being horses, cattle, sheep/goats, pigs, wild animals and fish are illustrated. Total number of bone finds are given at the base of the pie charts. Abbreviations: Horses (H); Fresh water fish (F); Porcine/Pigs (P); Wild animals (W); Cattle (C); Sheep and Goat (SG).

Figure 9.3 Summary of (i) the climate reconstruction made by Kremenetski (1995) based on the pollen analysis, showing the annual precipitation (ap mm) and the temperature (T°C) through the summers of the late Atlantic period (SLA), the winters of late Atlantic period (WLA), the summers of the Subboreal period (SS) and the winters of the Subboreal period (WS); (ii) the bulk carbon isotope analysis of bones from Dereivka (Der), Molyukhov Bugor (Mb) carried out by Lillie et. al, (2011) and from Kirovograd (Kr), Peshtchanka (Ps), Sh Stepnaya (St) and Vinogradnoe (Vn) carried out by Gerling (2013); and (iii) the compound-specific stable carbon analysis of residues from pots from Dereivka (Der), Molyukhov Bugor (Mb), Mikhailovka I (MikI), Mikhailovka II (MikII),

Nizhnyi Rogachik (Nr), Mikhailovka III (MikIII) and Generalka (Gen) carried out over this research project. The fats have been grouped in adipose fats (dots) and ruminants dairy fats (squares) in order to make a more seasonal distinction.

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CHAPTER 1

INTRODUCTION: A GENERAL BACKGROUND

1.1 **Modern Eurasia**

Eurasian steppe is the vast ecosystem stretching from Moldova and Ukraine in the west, to Mongolia in the east (Figure 1.1). The Ural Mountains can be considered as a natural border that divides this vast area into two ecosystems: the western Pontic region and the eastern Kazakh zone, each characterized by diverse soils, climatic zones and vegetation (Kerven et al., 1996).

Figure 1.1. Map of the Eurasian steppe.

The North-Pontic region or Western steppe includes part of Moldova, Ukraine and southern Russia. The environment is temperate-continental and characterized by an annual precipitation in the range 400 to 600 mm, depending on the locality (Kremenetski et al., 1999); summers and winters are generally mild. In contrast, the eastern steppe is a larger drier area characterized by a more continental climate, stretching from the North Kazakhstan to the Caspian Sea in the west, and the Altai Mountains in the east. Summers are typically hot and dry; winters are harsh and snow cover extensive. Annual precipitation is 250 to 300 mm (based on Climate Change Knowledge Portal – CCKP - of the World Bank).

Ukraine region is part of the North-Pontic area, bordering the Black Sea in the south, Poland, Romania, and Moldova in the west and Russia in the east (Kremenetski, 1995). According to the Köppen Climate Classification System, Ukraine is categorized as *D Climate Type*: the "Moist Continental Mid-Latitude Climates" consisting of warm, cool summers and cold winters. As can be seen from looking at Figure 1.2, climate of Ukraine changes according to the longitude. Indeed, three main climates are present in the region: *Dfb* (Humid with severe winters, no dry season, warm summers), in the northwest, *Dfa* (Humid with hot summers) covers the steppe area in the southeast, while the southern Crimea, is characterized by a general *Dfb* climate together with a "Moist Mid-Latitude Climate (*Cs*)" (i.e. Mediterranean climate with mild winters) characteristic of the southern-east coast of the Azon Sea (Pidwirny, 2011). Like the climate, vegetation and soils vary across the region (Kremenetski, 2003) which comprises three main flora habitat: forest in the northwest and southwest, steppe in the south-east of the region and forest-steppe located in between. The main soil is *chernozem* (French and Kousoulakou, 2003; Kremenetski, 2003). However, the latter dominated the forest and the forest-steppe; the steppe environment is characterized also by *humus* soil and *dark chestnut soils*.

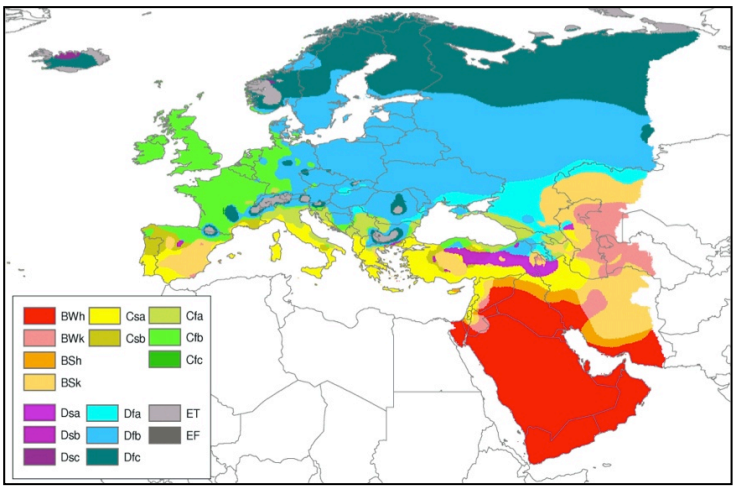


Figure 1.2. Distribution of Köppen climate classification system types in Europe and Middle East (Peel et al., 2007).

During prehistory, the North-Pontic region was characterized by similar climatic and environmental diversity (Kremenetski, 2003) and the boundary between steppe and forest-steppe oscillated over the millennia in relation to climate changes. This produced different environments and consequently different needs of the communities that lived in those areas. Furthermore, the very central geographical location led the North-Pontic region to serve as a "corridor" between Asia and Europe (Kuzmina, 2003; Sherratt, 2003); several and different societies inhabited this area, migration waves led to the spread of cultural knowledge, materials and technologies, making this region particularly interesting and, at the same time very difficult to interpret.

1.2 Archaeological questions and general overview

Over the last twenty years, the vast Eurasia has been studied by many scholars (e.g. Harrison and Heyd, 2007; Kuzmina, 2003; Sherratt, 2003) attracted by the cultural innovations occurred in this area during prehistoric times: for example ox-drawn wooden wagons with four solid disc wheels, horse domestication and cord ornamentation on vessels. The Eurasian steppe zone is often considered as a "zone of contact" between various cultures of Europe and Asia. Innovations were transferred over vast distances from east to west and vice versa. During the last years, new palaeogenetic evidence has been uncovered indicating migrations from the steppe to Central Europe involving a substantial number of people (Allentoft et al., 2015; Haak et al., 2015). This reinvigorated the controversial debate surrounding the homeland of Proto-Indo-European language (PIE). Several scholars (e.g. Kristiansen, 2014) have interpreted the new palaeogenetic data as supporting the hypothesis that the original speakers of PIE lived the western area of the Eurasian steppe (for a critical approach cf. Heyd, 2016; Kaiser, 2017).

As a consequence, this very interesting geographical area has received great attention especially in relation to the Eneolithic and the Bronze age periods that in the Eastern European archaeology correspond to the period between the middle of the 4th and the 1st millennium BC. Interestingly, during the latter period, the very first traceable contact between Eastern Europe and western Eurasia and the appearance of new customs and technologies occurred (Rassamakin, 1999). However, the periods of the Eneolithic and the Bronze Age have mainly been studied in relation to the sedentary Tripolye culture sites located in the northwest Pontic forest-steppe (Figure 1.3). In contrast, over the last decades interest in the semi-mobile/mobile steppe Eneolithic and Early Bronze Age cultures has grown with several studies (Anthony, 2007; Kaiser and Schier, 2013; Kuzmina, 2003; Levine, 1999a; Rassamakin, 1999; Schier, 2015) attempting to clarify many of the questions related to social and economic lifestyles of the populations that lived in the vast Eurasian corridor. However, developing and understanding of cultural processes and their chronologies in this specific area and period of time, is extremely challenging for several reasons. Notably, during the twentieth century European

and American archaeologists experienced difficulties in working with the Soviet Union both because of the barrier of the language and the political difficulties, such that significant developments in Eurasian archaeology only actually began to emerge in the 1950s (Levine et al., 1999). Consequently, there is a lack of published information, which complicates interpretations. In addition, there is a scarcity of evidence commonly regarded as commonplace or routine in western archaeology, such as: (i) spore-pollen records, (ii) archaeozoological evidence, (iii) the lack of dendrochronological dates, and (iv) the small numbers of calibrated radiocarbon dates (Kuzmina, 2003), which factor has hindered progress and limited interpretations. Regarding the latter point, improvements have been achieved as new radiocarbon analysis (discussed in Chapter 4) has being carried out on materials recovered from the North-Pontic region (Rassamakin and Kaiser, 2018 in prep.). Nevertheless, due to the abovementioned matters many questions, doubts and misunderstandings are related to the Eurasian prehistory and the way of living of the people that inhabited these regions during this specific period.

Figure 1.3. Tripolye-Cucuteni culture location. Map of the North-Pontic region (Videiko, 2011).

1.2.1 *Archaeological background and subsistence economy*

The middle, late Eneolithic and the early Bronze Age (4th – 3rd millennium BC) have been studied by several scholars. Many assumptions and conclusions have been offered in relation to social and economic events; however, many questions and doubts exist concerning social and economic habits of the populations lived in these areas during this specific time. According to a group of scholars (e.g. Rassamakin, 1999), important social and economic changes occurred at around the 3rd millennium BC, which represents the transition from the Eneolithic to the Bronze age. These changes are mainly related to burial traditions, material culture and economic system and are associated with a possible climate change occurred at around the 3rd millennium BC (Bostonalieva, 2015; Kremenetski, 2003) and the disappearance/collapse of agricultural systems such the one of the Tripolye Culture.

The new form of burial traditions is associated to the culture of the Yamnaya. The latter is so called because of the characteristic pit-graves (*Yama* is a Russian term that means pit). Indeed, all graves of the Yamnaya culture are situated in or under a burial mound. The deceased were buried in a crouched position and often covered with ochre (Figure 1.4). The graves and most of the inventory objects are very similar over the very large area of the culture's dissemination, which stretches from the Transurals in the east to the Lower Danube in the west. The Yamnaya burial tradition suddenly appeared in the Eurasian steppe and forest-steppe at around the 3rd millennium BC. However, it has been so far too difficult to trace archaeologically therefore the information concerning this culture is still very scarce. In addition, it is characterized by an unusual mismatch between the low frequency of settlement structures and the wide spread and homogeneous nature of the Yamnaya pit-graves in the open steppe so that its reconstructions are based (almost solely) on the interpretation of data from their graves. As a consequence, many different interpretations exist and the matter about the Yamnaya culture is still under debate (Rassamakin, 1999). One of the main hypotheses is that, at the end of the Late Eneolithic, the ancient North Pontic Steppe people replaced a settled way of life in favour of a mobile lifestyle and a nomadic economy influenced by the eastern steppe communities (Anthony 1995; 2007). However, others argued that the Yamnaya culture likely was a common burial tradition shared by distinctive smaller sedentary cultures (Rassamakin, 1999).

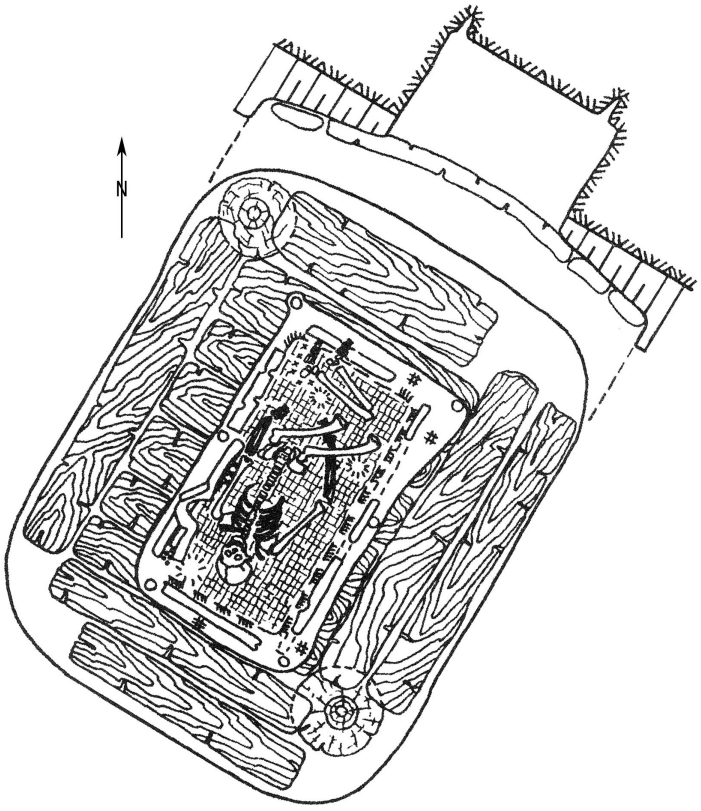


Figure. 1.4. Grave of the Yamnaya culture near the village Nikolskoe in Moldavia, grave mound 7, grave 33 (Agulnikov and Sava, 2004 p. 66, Fig. 32,1).

Concerning the already mentioned new form of economy, the pastoralism, it was based on animal herding and it might have involved seasonal movement (Kuzmina, 2003). However, also this topic is very scarcely known due to the scarce zooarchaeological evidence in this area and during this period, which means that the extent of animal domestication and dietary habits of the North Black Sea communities remain poorly understood. Consequently, there is an ongoing discussion concerning several aspects of the subsistence economy (Rassamakin, 1999, pp. 129–132). It is believed that the transition to food production in North-Pontic region followed a trajectory different to that of the Central European Neolithic and Bronze Age and that "the agricultural revolution took the character of stock-breeding" (Renfrew, 2002). Domesticated cattle, sheep and goat are believed by many scholars to have appeared in the North-Pontic region at around the 6th millennium BC (Bunyatyan, 2003; Kotova, 2003; Kotova and Makhortykh, 2010); the relatively late introduction of animal husbandry has been linked to environmental conditions in the steppe (e.g. Wechler, 2001).

As abovementioned, researches applied on this specific area and period of time are scarce; few isotope studies generally suggest a variability in access to dietary protein sources of the Mesolithic, Neolithic and Eneolithic populations located in the Dnieper region (Lillie, 2003, 1998; Lillie et al., 2011; Lillie and Jacobs, 2006). However, reconstructing the subsistence economy and dietary habits of populations during a period of economic and social changes is generally challenging. The current literature (Kuzmina, 2003; Lillie et al., 2011; Rassamakin, 1999) strongly supports the hypothesis of interchangeable strategies of husbandry-hunting dependent upon the regional ecosystems, which would have been very different in southeast compared to the northwest of the North Pontic (Kremenetski, 2003).

Thus, addressing questions about the extent of domestication, the nature of the economic resources and the balance between different economic activities according to the specific environment is more complicated. There is an ongoing discussion in relation to this subject, and several scholars interested in Eurasian archaeology, have proposed contrasting theories over the last decades (Anthony, 2007; Bendrey, 2011; Bunyatyan, 2003; Kuzmina, 2003; Rassamakin, 1999).

1.2.1.1 Horse domestication

Within the general question regarding the subsistence economy, horse domestication is a crucial Eurasian-archaeological phenomenon. First of all, it is important as a major event that changed the way of living both socially and economically. Prior to domestication, horses were frequently hunted in the Eastern steppe (Benecke and von den Driesch, 2003) as it was an important source of food. The horse also became especially important for secondary products and as a possible transport instrument (Olsen, 2006) for use in the herding of other animals or even a weapon during conflicts (Anthony, 2007). Levine (1999b, pp. 8–9) summarises discussions about horse domestication

highlighting several theories concerning: (i) the reasons why horses were first domesticated, for either meat, riding and traction; (ii) the periods when this important knowledge was firstly attained: Neolithic, Eneolithic or Bronze Age; and (iii) the first centre of domestication, considered by the majority to be the Eurasian steppe, but the precise location or if there was more than one centre of domestication is still unknown (Levine 1999a; 1999b; Sherratt 2003; Olsen 2006; Stear 2008).

In this difficult picture, the North-Pontic region is a candidate for the first centre of horse domestication. The reason for this relates to two sites located in the Ukrainian forest-steppe and characterized by a high abundance of horse bones. Among these sites, Dereivka, which has been considered for a long time as a community based on horse domestication economy. The latter idea emerged in the monograph written by D. Ya. Telegin (1986) that reported an extraordinary percentage of horse bones, roughly 60% of the total assemblage (faunal records are discussed in Chapter 5). Therefore, the conclusions of Telegin reinforced the general belief that Dereivka was indeed an economy centred on horse husbandry. Later research of the Botai site (slightly younger than Dereivka), located in the Kazakh steppe, using a combination of zooarchaeological methods and organic residues recovered from ceramic vessels (Outram et al., 2009), identified equine carcass and, perhaps more significantly, dairy fat in the Eneolithic ceramic potsherds, verifying that in the 4th millennium BC horses were domesticated in eastern Eurasia, thereby further strengthening the idea that horse domestication was likely also extensively practised at Dereivka.

1.2.2 *Climate and Environment*

As above mentioned, the reasons that probably produced the mentioned social and economic changes are related to a possible climate change occurred at around the 3rd millennium BC (Bostonalieva, 2015; Kremenetski, 2003) and/or the disappearance/collapse of agricultural systems such the one of the Tripolye Culture. Regarding the latter matter, in this context it is only necessary to acknowledge that the Tripolye culture fragmentised (Dolukhanov, 2002), possibly producing the interruption of the relationships with the neighbouring populations of the North-Pontic region.

Regarding the climate change, climate and vegetation appear to have considerably changed in the North-Pontic region during the millennia from the 4th to the 3rd (discussed in Chapter 8). Indeed, it is noteworthy that a climatic transition between Atlantic and Subboreal epochs occurred at around the 3rd millennium BC (Bostonalieva, 2015; Cordova and Lehman, 2005; Kleinen et al., 2011; Kotova and Makhortykh, 2010; Kremenetski, 2003; Kremenetski et al., 1999; Tarasov et al., 1999; Wu et al., 2007) involving environmental change that could likely have influenced the activities of ancient Eurasian people. Indeed, it has been widely interpreted that the economic and social changes of the North-Pontic people were driven by a period of aridification. However, despite the fact that Eurasian steppe has been considered as a unique ecosystem for a long time, recent scholars (e.g. Kaiser, 2017)

raised questions about the assumption of homogeneity, supporting instead a variety of ecosystems. Therefore, the abovementioned climate change might have affected differently each specific ecosystem. This topic will be carefully faced in this thesis; Chapter 8 will display the available climate and vegetation evidence recovered in the North-Pontic region.

Thus, the aim of this project is to address the abovementioned questions and to reconstruct the ancient subsistence economy and dietary habits of people lived in the North-Pontic region from the 4th to the 3rd millennium BC. The latter will be achieved by carrying out molecular and isotopic study of organic residues preserved in pots. Indeed, during recent years, the molecular and isotopic examination of organic residues from unglazed pottery vessels has demonstrated extremely valuable in the investigation of prehistoric dietary and economic practices (Copley et al., 2005b, 2003; Craig et al., 2000; Dudd and Evershed, 1998; Dunne et al., 2012; Evershed, 2008a; Evershed et al., 1999; Roffet-Salque et al., 2015). Hence, the examination of organic residues extracted from prehistoric pottery vessels recovered from five settlements located in the North-Pontic region can help to address a number of questions surrounding the subsistence economy, the extent of the animal exploitation and the dietary habits in this area. It is anticipated that integration of evidence from organic residue analysis (both molecular and stable isotope techniques) with existing archaeological evidence will contribute in the reconstruction of past patterns of animal exploitation and economic processes throughout the North-Pontic region during the Eneolithic and the Early Bronze Age.

1.3 **Principles of organic residue analysis**

Organic residue analysis of archaeological pottery involves the recognition of organic materials absorbed in ceramic vessels by comparing the structures of the individual compounds, their distributions ("chemical fingerprints") and stable isotope compositions with those occurring in modern plants and animals (Evershed, 2008a). Sometimes, the identification of a single compound, so called an "archaeological biomarker", is sufficient to define the origin of the residue, although usually several chemical criteria and stable isotope values are necessary, supported further by archaeological information (Evershed, 2008a, 2008b).

Over the last few decades, organic residue analysis has become one of the most powerful techniques in archaeology, able to yield information regarding human activity in the past, inaccessible by other means (Evershed, 1993; Roffet-Salque et al., 2017a). The success of the approach relates to the frequent occurrence of organic residues in different locations and deposits within an archaeological site. Indeed, the survival of organic residues occurs in several classes of archaeological remains (Evershed, 2008a) including: pottery, human and animal remains, plant remains, soils and sediments, resins, dyes and pigments.

Organic residues are a complex mixture of degraded organic materials, which are very often recovered in extremely low concentrations making instruments such as gas chromatography - mass spectrometry (GC/MS) and high temperature-GC/MS particularly important for the separation and characterization of their components at the molecular level. GC/combustion isotope ratio/MS (GC/C/IRMS) and GC/thermal conversion isotope ratio/MS (GC/TC/IRMS) are important techniques in providing stable isotope compositions at the molecular level. Using these approaches, it has been possible to identify a wide range of commodities, such as terrestrial animal fats (e.g. Dudd and Evershed, 1998; Dunne et al., 2012; Evershed et al., 2002; Mukherjee et al., 2007; Salque, 2012), marine animal fats (Craig et al., 2007; Cramp and Evershed, 2014; Evershed et al., 2008a; Hansel et al., 2004; Pääkkönen et al., 2018), beeswax (e.g. Evershed et al., 1997b; Regert et al., 2001; Roffet-Salque et al., 2015), vegetable oils (e.g. Copley *et al.* 2005), plant waxes (e.g. Heron et al., 1991; Reber and Evershed, 2004), plant resins (e.g. Stern et al., 2008, 2003), etc.

1.3.1 *Types of organic residues and their occurrence in ceramic cooking vessels*

Organic residue in vessels can give important information about the use of the vessels. They can survive in three different forms in archaeological pottery: (i) as vessel fills in situ (Charrié-Duhaut et al., 2007); (ii) as visible residues on the interior or exterior of the vessel, for example sooting or carbonized residues (Eerkens, 2002), and (iii) as residues absorbed in the vessel wall and invisible to the naked eye. The latter category is the most common; such residues are relatively protected within the ceramic fabric so are less prone to burial or post-excavation contamination. After mechanical cleaning of potsherd surface, such organic residues appear relatively unaffected by exogenous contamination, e.g. from the surrounding burial soil (Heron et al., 1991). The recovery rate for organic residues from archaeological pottery varies according to (Evershed, 2008a): (i) vessel fabric – lower pore sizes of the ceramic matrix limits the accessibility of microbes and exocellular enzymes produced by degrading microbes, (ii) vessel use, which lead to different rates of organic residue absorption, i.e. storage < transfer (e.g serving and eating) < processing (e.g cooking; Orton 1993), and (iii) burial conditions; arid soils are the most favourable conditions because microbial growth cannot occur without water.

Of all the compound classes that may provide archaeological information, solvent extractable lipids are the most frequently recovered compounds from archaeological contexts (Evershed, 2008a, 1993). This is due to their relative stability to degradation compared to other biomolecules, such as carbohydrates, proteins or nucleotides (Evershed, 2008a) together with their characteristic hydrophobicity, which enables them to persist at the original site of deposition (Evershed, 1993). As a result, lipids are the most widely studied compounds in the field of biomolecular archaeology.

The most commonly encountered lipid residues within archaeological pottery are degraded animal fats (Mottram et al., 1999). This is due to the widespread exploitation of animal products throughout

prehistory for a wide variety of uses such as food, art materials, rituals, lubricants, illuminants, binders, waterproofing agents, cosmetics, ointments, adhesives, varnishes etc. (Evershed et al., 2001). Additionally, the high number of saturated fatty acids contained in animal fat in comparison with plant or marine fats, increases the probability of their survival during burial. As a result, the study of animal fats within archaeological pottery vessels can provide valuable information regarding the animal exploitation and hence the diets of prehistoric societies.

1.3.2 *Distinguishing lipid sources using biomarkers*

As mentioned in Section 1.3, the identification of an "archaeological biomarker" can sometimes be sufficient to define the origin of an organic residue or at least support the identification of components of an organic residue. However, it is important to be very cautious especially where compounds may derive from a range of sources or be common to exogenous sources of contamination. Some lipid biomarkers are preserved in their original chemical state, surviving over the millennia unchanged; however, archaeological lipids are chemically altered reflecting: thermal alteration, oxidation, hydration or dehydration reactions, during vessel use or burial (Evershed, 2008a, 1993). While identification of the latter products can be challenging, the compounds produced can be of diagnostic value. Some of the compounds commonly used as archaeological biomarkers are discussed in the subsequent Sections.

1.3.2.1 Free fatty acids and acylglycerols

Fatty acids (FAs) are the most common class of lipid residues recovered from archaeological pottery (Evershed, 2008a, 1993; Evershed et al., 2002; Mottram et al., 1999). FAs derive from triacylglycerol (TAGs), which are the major constituents of animal fats and plant oils and can derive from the diet, *de novo* synthesis or other endogenous lipids (Christie, 1981; Evershed, 2008a; Evershed et al., 2002; Heron and Evershed, 2013). Fresh fats can easily be distinguished using the distribution of TAGs so for example adipose fat is characterized by a narrow distribution of TAGs (C_{42}-C_{54}; Dudd & Evershed 1998) while dairy fat is characterised by the presence of a broader distribution (Gresti et al., 1993; MacGibbon and Taylor, 2006).

Over time, the partial or total hydrolysis of TAGs (Figure 1.5 and Figure 1.6) occurs and consequently these compounds degrade into diacylglycerol, monoacylglycerol or free fatty acids (Evershed, 2008b, 1993; Evershed et al., 2002). Among the absorbed lipid residues recovered in ceramic vessels, saturated FAs are the most common because of their higher resistance to degradation compared to unsaturated fatty acids, that are generally the dominant FAs, especially in fish and plant seeds, hence are often not detected (Evershed, 2008b).

The most abundant FAs in nature are palmitic ($C_{16:0}$), stearic ($C_{18:0}$) and myristic ($C_{14:0}$) acids (Christie, 1981; Evershed, 2008b, 1993, Evershed et al., 2002, 1999). The latter is most abundant in milk fats, fish oils and some plant seeds (e.g. kernel and coconut). In contrast, $C_{16:0}$ and $C_{18:0}$ fatty

acids are found in appreciable abundances in animal fats and plant tissues; however, $C_{18:0}$ fatty acid is usually more abundant in animal fats. Odd-chain ($C_{13:0}$-$C_{19:0}$) and branched-chain fatty acids ($C_{15:0br}$, $C_{17:0br}$) are produced by bacteria and are most commonly seen in ruminant animal fats (Christie, 2014). Finally, long-chain fatty acids ($C_{23:0}$-$C_{32:0}$) occur most commonly as constituents of plant waxes. However, the identification of plant processing based on the detection of waxes can be reinforced by the identification of other classes of compounds such as *n*-alkanes and *n*-alcohols; a more detailed description of plant biomarkers is given below in Section 1.3.2.3. Hence, examination of the distributions of saturated FAs can provide the first indication of the origin of lipids residues.

1.3.2.2 Long-chain ketones

Long-chain ketones (odd chain-number, C_{29}-C_{35}) are commonly seen in lipid extracts of potsherds (Evershed et al., 1995). Long-chain ketones are usually ascribed to epicuticular waxes; however, laboratory pyrolysis experiments (Evershed et al., 1995; Raven et al., 1997) demonstrated that these ketones can derive from the condensation of mono-unsaturated FA ($C_{18:1}$) and saturated FA ($C_{16:0}$ and $C_{18:0}$) and, therefore, can be produced during cooking of animal products. They are formed via a ketonic decarboxylation reaction between two fatty acids in presence of an inorganic catalyst at temperatures in excess of 300°C (Figure 1.7). The ketone distribution (*ca*. 1:2:1 ratio) observed in archaeological ceramics is not seen in modern plants. Further, the absence of other plant wax biomarkers (e.g. *n*-alcohols and *n*-alkanes) and $\delta^{13}C$ values consistent with those of the fatty acids present in the same extracts, confirms that these compounds derive from the heating of fats during cooking.

1.3.2.3 *n*-alkanes and *n*-alcohols

n-alcohols and *n*-alkanes are considered together here because their presence together with long-chain fatty acids (C_{22}-C_{32}) can be used as indicators of the presence of plant wax derived from plant processing in pots.

n-alkanes are important constituents of the epicuticular waxes that cover the external surface of higher plants, with distributions varying between taxa. Long-chain *n*-alkanes distributions range from C_{25} to C_{35} (Chibnall et al., 1934; Dunne, 2015), with an odd-over-even predominance and C_{27}, C_{29}, C_{31} and C_{33} as the major components (Eglinton and Hamilton, 1967). Despite their importance in the recognition of plant wax, *n*-alkanes can mislead. Indeed, consequent to burial conditions or more likely to post-excavation during processing, transport and storage, *n*-alkanes can be absorbed by the archaeological ceramic potsherds from fossil fuels (e.g. petroleum, bitumen, oil, etc.). However, it is possible to distinguish between the two different categories. In contrast to leaf waxes, the alkane fractions of crude oils have a different distribution characterized by an increased abundance of both even and odd carbon number (Figure 1.8; Eglinton and Hamilton, 1963; Hofmann et al., 1992).

Aliphatic long-chain *n*-alkanols are major components of plant leaf waxes occurring in the range C_{20} to C_{34}, with even carbon number homologues predominating (Christie, 2012; Eglinton and

Hamilton, 1963). In many plants a single carbon number homologue predominates, e.g. C_{28} is dominant in several *Triticum* species, C_{32} in maize and C_{26} in barley, rye and oats (Bianchi et al., 1995; Tulloch, 1976).

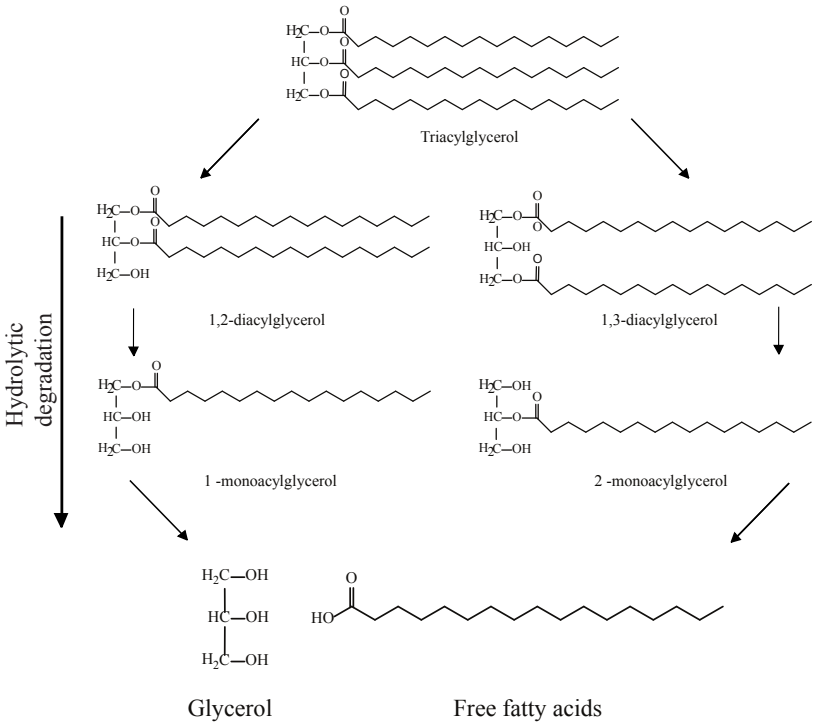


Figure 1.5. Hydrolytic pathway for the transformation of triacylglycerols to free fatty acids.

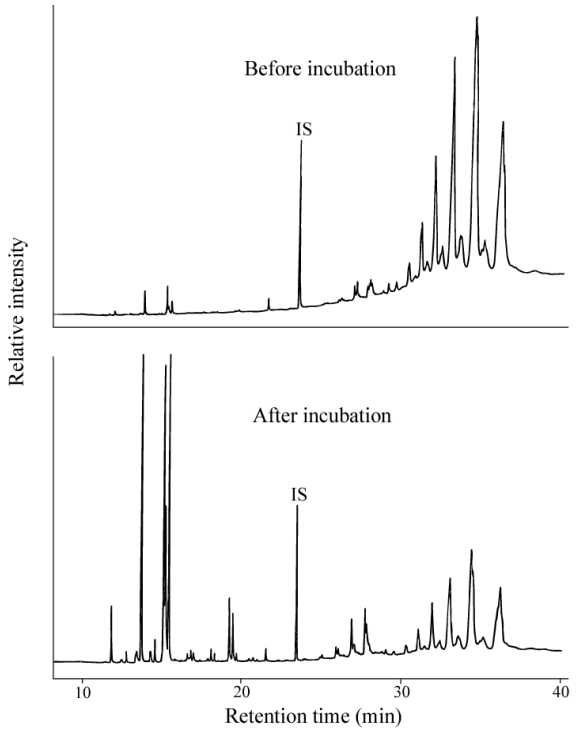


Figure 1.6. Gas-chromatograms showing a fresh animal fat analysed before and after laboratory incubation (Evershed et al., 2002).

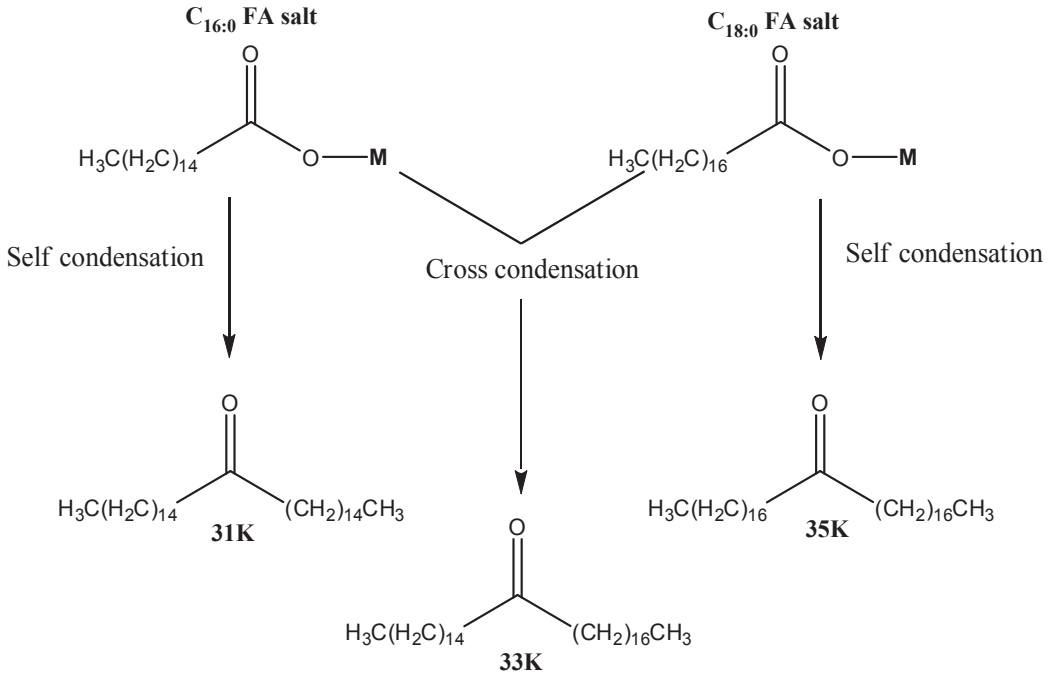


Figure 1.7. Mechanism of formation of primary ketones found within archaeological lipid residues from the fatty acid precursors $C_{16:0}$ and $C_{18:0}$. M is a metal, which is derived from the inorganic matrix of the clay. Adapted from Raven et. al. (Raven et al., 1997).

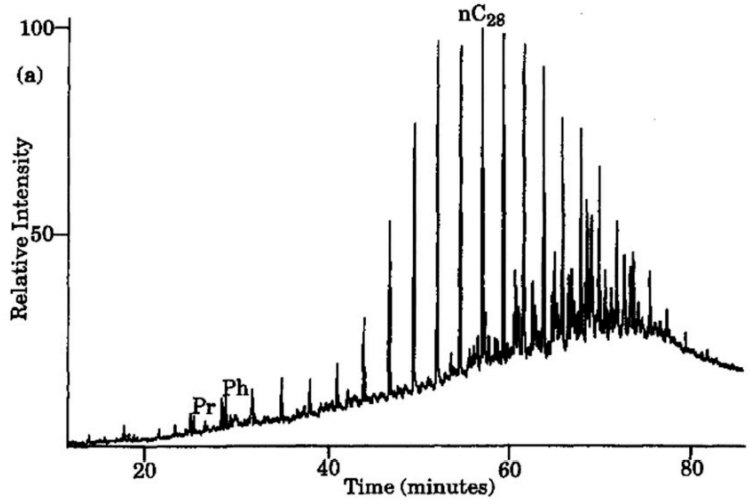
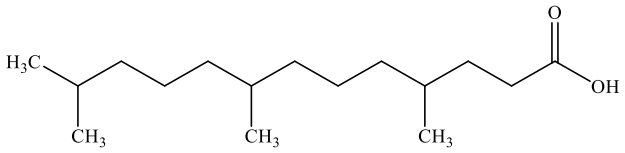


Figure 1.8. Chromatogram showing a distribution of alkanes derived from fossil oils (Hofmann et al., 1992).

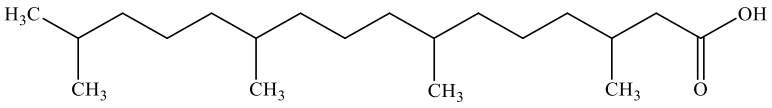
1.3.2.4 Isoprenoid acids

Among the most common isoprenoid compounds detectable in archaeological ceramic vessels are 4,8,12-trimethyltridecanoic (or 4,8,12-TMTD; Figure 1.9a) and 3,7,11,15-tetramethylhexadecanoic (or phytanic acid; Figure 1.9b). These biomarkers are found in particularly high concentrations in marine animal fats and oils (Craig et al., 2007; Cramp and Evershed, 2014; Evershed et al., 2008a;

Hansel et al., 2004), but are absent, or present in only very low concentrations, in terrestrial animals (e.g. Ackman and Hooper, 1968; Christie, 2012).



a)



b)

Figure 1.9. Isoprenoid acid biomarkers detected in lipid extracts of archaeological pottery: 4,8,12-trimethyltridecanoic (a) and 3,7,11,15-tetramethylhexadecanoic (phytanic acid; b).

1.3.2.5 Degradation products of unsaturated fatty acids

Degradation of lipid residues containing unsaturated FAs is inevitable due to the effects of aging or through thermal alteration during cooking. This makes the detection of commodities characterized by a predominance of unsaturated fatty acids, such as plant or fish oils, difficult to detect. However, several degradation products of unsaturated FAs have been recognised as characteristic of these sources, notably: (i) short-chain-dicarboxylic acids; (ii) ω-(*o*-alkylphenyl) alkanoic acids (APAAs); (iii) dihydroxy fatty acids (DHFA).

The short-chain-dicarboxylic acids derive from a series of radical reactions of mono-saturated fatty acids (Copley et al., 2005b; Dudd and Evershed, 1998). The carbon chain length of the dicarboxylic acids ranges from C_5-C_{14}. Commonly, azelaic acid (C_9) is the most abundant diacid found in archaeological pottery as it derives from the major unsaturated FA occurring in nature, oleic acid ($C_{18:1}$, Figure 1.10).

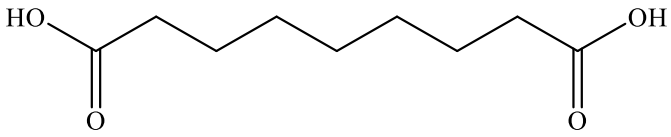


Figure 1.10. Azelaic acid.

The ω-(*o*-alkylphenyl) alkanoic acids have been recently identified as a valuable indicator of the processing of aquatic animal products in antiquity (Copley et al., 2005b; Cramp and Evershed, 2014; Evershed et al., 2008a; Hansel et al., 2004). ω-(*o*-alkylphenyl) alkanoic acids or APAAs (Figure 1.11) are cyclic compounds with even carbon numbers ranging from C_{16} to C_{22}. Laboratory experiments (Evershed et al., 2008a; Hansel et al., 2004) have demonstrated that these compounds derive from heating, most likely cooking of lipid rich marine foodstuff at temperatures >260-270°C,

with the ceramic providing a catalytic phase for the reactions involved in their formation. APAA carbon number distributions will vary depending on fat source and have the potential to be used as biomarkers of any commodity containing high concentrations of unsaturated fatty acids, such as plants oils or horse fat where the C_{18} APAAs will predominate.

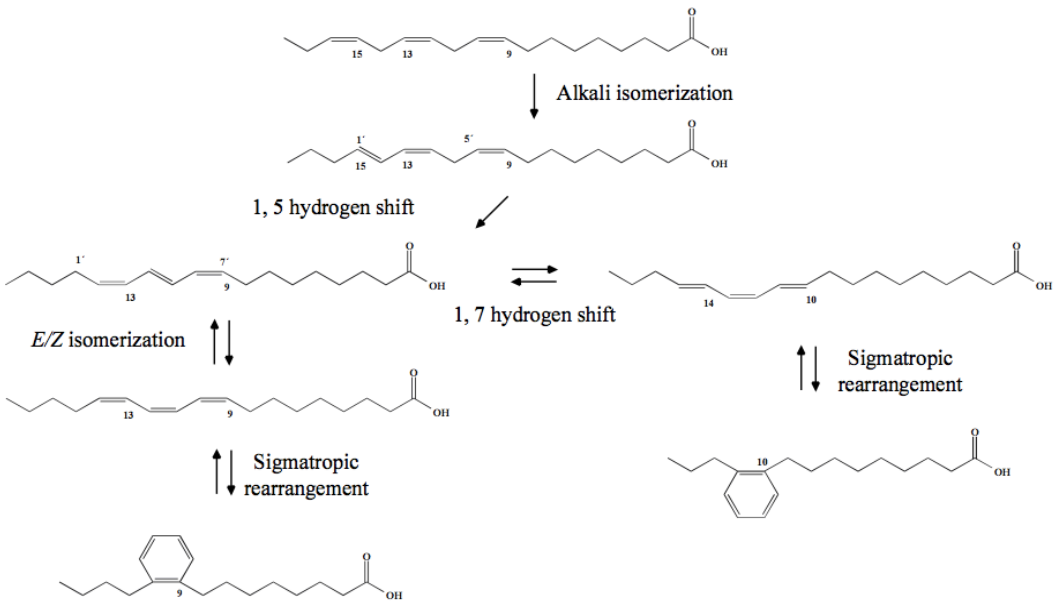


Figure 1.11. Formation of ω-(o-alkylphenyl)alkanoic acids. Adapted from Hansel et al. (2004).

Finally, Evershed and co-workers have demonstrated that vicinal dihydroxy fatty acids (DHFA) (Figure 1.12) can be formed by oxidative degradation reactions. Co-occurring with other biomarkers, vicinal dihydroxy acids (C_{16}-C_{22}) have served as indicators of marine animal product processing in archaeological pottery (Cramp et al., 2014; Cramp and Evershed, 2014; Hansel and Evershed, 2009).

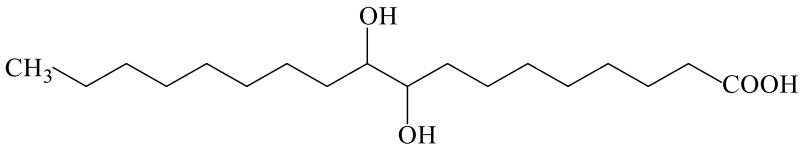


Figure 1.12. $C_{18:0}$ Dihydroxy fatty acid: the original fatty acid was $C_{18:0}$ fatty acid which double bond has undertaken oxidation.

1.4 Stable isotope analysis

The stable isotopic analysis of archaeological organic residues is a very powerful tool that allows the reconstruction of the ancient economies, specifically animal and plant exploitation by hunter-fishers and agricultural populations. The main principles are that: (i) the ratio of the two stable isotopes in natural materials varies slightly as a result of isotopic fractionation during physical, chemical and biological processes; (ii) the isotopic composition of an organism tissue depends on the

relative contributions of isotopically distinct components of the individual diet (Art et al., 1997; Evershed et al., 1999), and (iii) despite the degradation of the organic residues, the isotopic ratio remains constant over millennia (Evershed, 2008a).

The determination of stable isotopic composition is achieved by using an isotope ratio mass spectrometer (GC/C/IRMS) which separates the individual components of a mixture allowing determination of the abundances of the heavy and light isotopes of a given element relative to a standard, which has an assigned δR value of 0 ‰ (Art et al., 1997; O'Leary, 1988). The stable isotopic composition of a sample is expressed as a δR value with units of per mil (‰) according to the following convention:

$$\delta R = \frac{R_{sample} - R_{std}}{R_{std}} x1000$$

δR is measured in ‰
$R_{sample}={}^{x}R/{}^{y}R$ in the sample
$R_{std}={}^{x}R/{}^{y}R$ in the standard

The isotopes most commonly used in archaeological studies are carbon ($^{13}C/^{12}C$), hydrogen ($^{2}H/^{1}H$), nitrogen ($^{15}N/^{14}N$) or oxygen ($^{18}O/^{16}O$). The subsequent Section provides a detailed description of compound-specific stable carbon and hydrogen isotope analyses as these have been extensively used in organic residue research. However, it is important to mention the powerful combination of carbon and nitrogen bulk isotopic analyses applied to ancient bones because of their potential to provide complementary information about the main protein source of whole diet (Reitsema et al., 2010). The latter isotope analyses have been applied on animal and human bones recovered from the Dnieper region, and dated Neolithic, Eneolithic and Early Bronze Age (Gerling, 2015, 2014; Lillie, 2003; Lillie et al., 2011, 2009) and will be discussed further in Chapter 5, Section 5.9, as additional evidence for the palaeodiet reconstruction of ancient people lived in the North-Pontic region.

1.5 Compound-specific stable carbon isotope analysis ($\delta^{13}C$)

The compound-specific stable carbon isotope analysis allows determination of $\delta^{13}C$ values of the major FAs, $C_{16:0}$ and $C_{18:0}$ fatty acids, which occur widely in archaeological lipid residues and have been shown to be stable to extensive degradation (Evershed, 2008a). The latter characteristic makes this the most reliable proxy available for identifying the nature of animal fat source. Assignments rely on comparing the isotopic values of modern reference materials with those derived from organic residues extracted from archaeological vessels. The $\delta^{13}C$ values of the fatty acids differ according to

the different physiologies of the major domesticates, e.g. pigs versus horses versus ruminants, and fat source, i.e. ruminant carcass versus dairy.

The carbon atom has three isotopes: ^{12}C and ^{13}C (stable) and ^{14}C, which is radioactive. They account for 98.89%, 1.11% and $1.12x10^{-12}$ % of the global carbon pool, respectively. The internationally accepted standard for carbon against which relative carbon isotopic abundance is measured, is the VPDB or Vienna Pee Dee Belemnite. Carbon isotope compositions are defined as $\delta^{13}C$ values, where:

$$\delta^{13}C = \frac{(^{13}C / ^{12}C)_{Sample} - (^{13}C / ^{12}C)_{Std}}{(^{13}C / ^{12}C)_{Std}} 1000$$

1.5.1 *Stable carbon isotope ratios in plants*

The stable carbon isotope ratio ($\delta^{13}C$) in plants is mainly controlled by the different pathways of photosynthesis (Art et al., 1997; O'Leary, 1988; Smith and Epstein, 1971). There are three different types of photosynthesis. The most common photosynthetic pathways occur in dicotyledons (C3 plants), such as flowering plants, wheat, rice, rye, tubers, legumes and cotton; plants mainly found in temperate zones. C3plants employ the Calvin–Benson photosynthetic cycle, fixing the atmospheric CO_2 using ribulose bisphosphate oxygenase (RuBisCO), resulting in $\delta^{13}C$ values of approximately -28‰. The monocotyledonous plants (C4 plants), such as sugar cane, corn, tropical grasses, desert plants and marine plants, employ the Hatch–Slack photosynthetic cycle, using the enzyme phosphenol pyruvate carboxylase to reduce HCO_3^- to malic acid (Hatch and Slack, 1966). In this pathway, the ^{13}C isotope is less discriminated leading to $\delta^{13}C$ values of approximately -14 ‰. Finally, the crassulacean acid metabolism (CAM) plants, such as pineapple, cactus and orchids, can utilize either the C3 or C4 photosynthetic systems, depending on sunlight exposure, and therefore have $\delta^{13}C$ values ranging between -10 and -34‰ (O'Leary, 1988).

1.5.2 *Stable isotope ratio in terrestrial animals*

Animal fats have $\delta^{13}C$ value that varies according to the diet of the animal from which they derive, that will be fundamentally controlled by the environment in which they live. However, subtle differences in the physiology and metabolism of different animals means that the assimilation of these fatty acids from dietary sources and *de novo* biosynthesis, differs between species, causing distinct differences in the compound-specific $\delta^{13}C$ values, which allows differentiation between the fats of major domesticates (Mottram et al., 1999). The first demonstration of the potential of compound-specific stable carbon isotope analysis was by Evershed et al. (1997a) in demonstrating that the stable carbon isotope composition of the two major fatty acids in degraded animal fats, $C_{16:0}$ and $C_{18:0}$ fatty acids, could be used to distinguish between the fats of ruminant and non-ruminant

animals (Figure 1.13). The study analysed lipid residues from medieval 'lamps' and 'dripping' dishes from Causeway Lane, Leicester, UK. GC and GC/MS analysis of residues revealed that both contained significant concentrations of lipid with characteristic distributions of degraded animal fats. Comparison of the $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ FA with those of modern reference animals revealed that the values of the dripping dishes correlated with those obtained from reference pig fats, whereas in the case of the lamps, the $\delta^{13}C$ values were similar to those obtained from modern ruminant animal fats (Evershed et al., 1997b; Mottram et al., 1999).

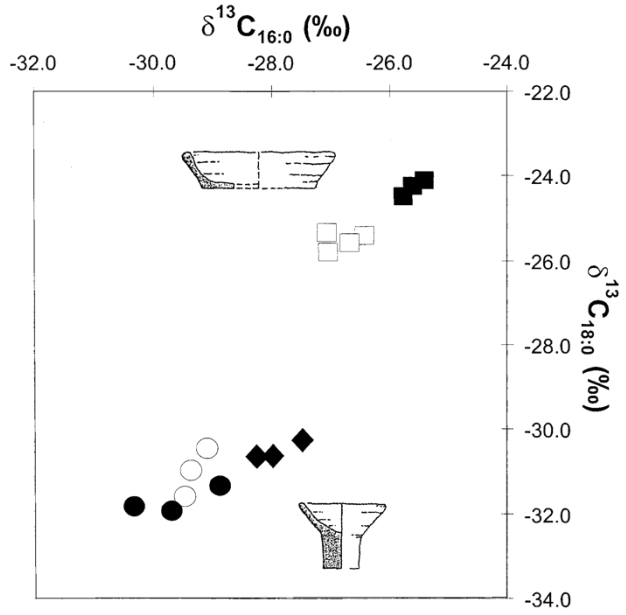


Figure 1.13. Plot of the $\delta^{13}C$ values obtained from the $C_{16:0}$ and $C_{18:0}$ fatty acids extracted from archaeological lamps and dripping dishes compared with modern reference animal fats. The empty squares and circles correspond to fatty acids from dripping dishes and lamps, respectively, while the filled squares, circles and diamonds correspond to pig, sheep and cattle reference fats (Evershed et al., 1997a).

Further work showed that ruminant adipose and ruminant milk fats could be distinguished (Dudd and Evershed, 1998). This is possible because of the different source of the $C_{18:0}$ fatty acid in the mammary gland, which is unable to biosynthesize essential fatty acid component of milk fat (Moore and Christie, 1979). Indeed, the mammary gland derives *ca*. 50% of the $C_{18:0}$ required for milk fat production, directly from the diet and specifically from the unsaturated fatty acids present in the forage material following biohydrogenation in the rumen; the other 50% of $C_{18:0}$ is derived from the mobilisation of adipose fat (Christie, 1981). In contrast, the synthesis of $C_{18:0}$ in the adipose fat derives to a significant extent from *de novo* biosynthesis from acetate (as acetyl CoA), which is predominantly derived from dietary carbohydrates in the rumen (Figure 1.14). As a result of the two different physiological processes, $\delta^{13}C$ values of the ruminant milk fats are ~ 2-3 ‰ depleted in the $\delta^{13}C_{18:0}$ relative to ruminant adipose (Copley et al., 2003; Dudd et al., 1999; Dudd and Evershed, 1998).

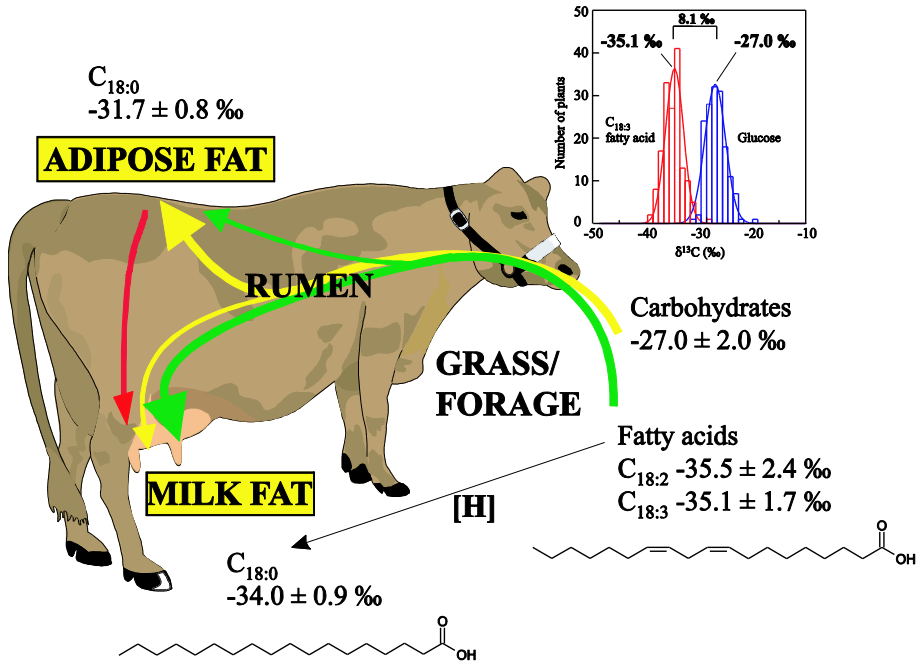


Figure 1.14. Diagram showing the routing of dietary fatty acids and carbohydrates in the rumen, adipose tissue, and mammary gland of the ruminant animal and histogram of the $\delta^{13}C$ values of $C_{18:3}$ fatty acid and glucose extracted from plants demonstrating the difference between them.

1.6 Compound-specific stable hydrogen isotope analysis (δD)

Determination of the stable-isotope ratio of hydrogen (δD) in animal tissues can be a powerful tool in food web delineation (Smith and Epstein, 1971), paleoclimatic reconstruction (Cormie et al., 1994) and animal migration (Hobson, 1999). Hydrogen has three naturally occurring isotopes, denoted ^{1}H, ^{2}H and ^{3}H. Protium (^{1}H) consists of a single proton and electron; deuterium (^{2}H or D) and tritium (^{3}H or T) have one and two neutrons, respectively. Tritium is radioactive, whereas hydrogen and deuterium are stable. Deuterium natural abundance is around 0.015% of all hydrogen (Rosman and Taylor, 1998). The internationally accepted standard for deuterium against which hydrogen isotope abundances are measured, is Vienna Standard Mean Ocean Water, (Coplen et al., 1996). The expression for δD is:

$$\delta D = \frac{D/H_{Sample} - D/H_{Std}}{D/H_{Std}} 1000$$

1.6.1 *Hydrogen isotopes in precipitation*

Numerous investigations beginning in the early 1930s attempted to clarify the factors that govern the fractionation processes of hydrogen and oxygen in the water cycle (Dansgaard, 1964, 1954, 1953; Epstein and Mayeda, 1953; Friedman, 1953; Gilfillan Jr, 1934). Building on this, in 1961, the International Atomic Energy Association (IAEA) and World Meteorological Organization (WMO)

started a program (Global Network of Isotopes in Precipitation) to collect data from monthly precipitation in over four hundred stations located worldwide. This worldwide network persists and continues to evolve today. The overall aim of the project was to better understand the fractionation and the kinetic isotopic effects of hydrogen and oxygen isotopes in precipitation (Dansgaard, 1964). The researches applied (Coplen et al., 1996; Dansgaard, 1964; Smith et al., 2013) led to define a number of fractionation principles that give rise to five 'effects', summarised in Table 1.1 (Dansgaard, 1964; Rozanski et al., 1993), which cause variation in the δD values of precipitation from different locations worldwide (Figure 1.15).

Table 1.1
Summary of the δD effects occurring globally according the different temperatures and precipitations (Dansgaard, 1964; Rozanski et al., 1993).

Effect	Description	Explanation
Seasonal effect	Precipitation is more depleted in deuterium (D) in rainier seasons.	During summer, rainfall is usually lower, so the D will accumulate in the vapour. Consequently, the summer rainouts will be more enriched in D. Additionally evaporation of the hydrogen (H) from the raindrop is higher during summer as temperatures rise; this leads to further enrichment of D within the raindrop.
Latitude effect	Precipitation becomes more depleted in D at higher latitudes.	Water evaporates from ocean in tropics. The D is distilled first so the remaining vapour, that proceed from the equator towards the poles, is progressively depleted in D. So, subsequent rains will be depleted in D with respect to earlier rains from the same vapour mass.
Continentally effect	Precipitation becomes more depleted in D with increasing distance from the coast.	As vapour moves away from the ocean, the gradual rainout of the D occurs, so that the precipitation inlands will be characterized by lower concentrations of D.
Altitude effect	Precipitation becomes more depleted in D with increasing altitude.	Cooler temperatures at higher altitudes cause progressive depletion in the heavier isotope (D).
Amount effect	The greater amount of precipitation the more depleted the δD value.	When large amount of precipitation occurs, the D will rapidly condense in rainout. The remaining vapour will be very depleted in D. Additionally, in heavy rain, increased humidity beneath the cloud reduces the evaporation of lighter isotopes, causing D to become "diluted" by H.

1.6.2 *Hydrogen isotopes in animal tissues*

Upon reaching the ground, precipitation is incorporated into the soil. The δD value of the soil strongly reflects that of the precipitation, except for few subtle further fractionations due to different soil porosity and temperature (Darling et al., 2003). The water is subsequently absorbed by the plants *via* the roots, which preferentially absorb the lighter isotope, such that the δD value in plants is roughly 30‰ lower than the related precipitation (Schiegl & Vogel 1970; Smith & Ziegler 1990).

In contrast to plants, establishing the hydrogen isotope fractionation in animal tissues is complicated by a number of factors (Sharp et al., 2003). Whereas plants are characterized by a δD

value that essentially derives from water, the bulk stable hydrogen isotope content of animal tissue depends upon the δD signal of both diet and drinking water (Alexander et al., 2006; Hobson, 1999; Sehoenheimer and Rittenberg, 1936). Moreover, different digestive systems or trophic levels also influence the tissue δD values, as confirmed by Reynard & Hedges (2008).

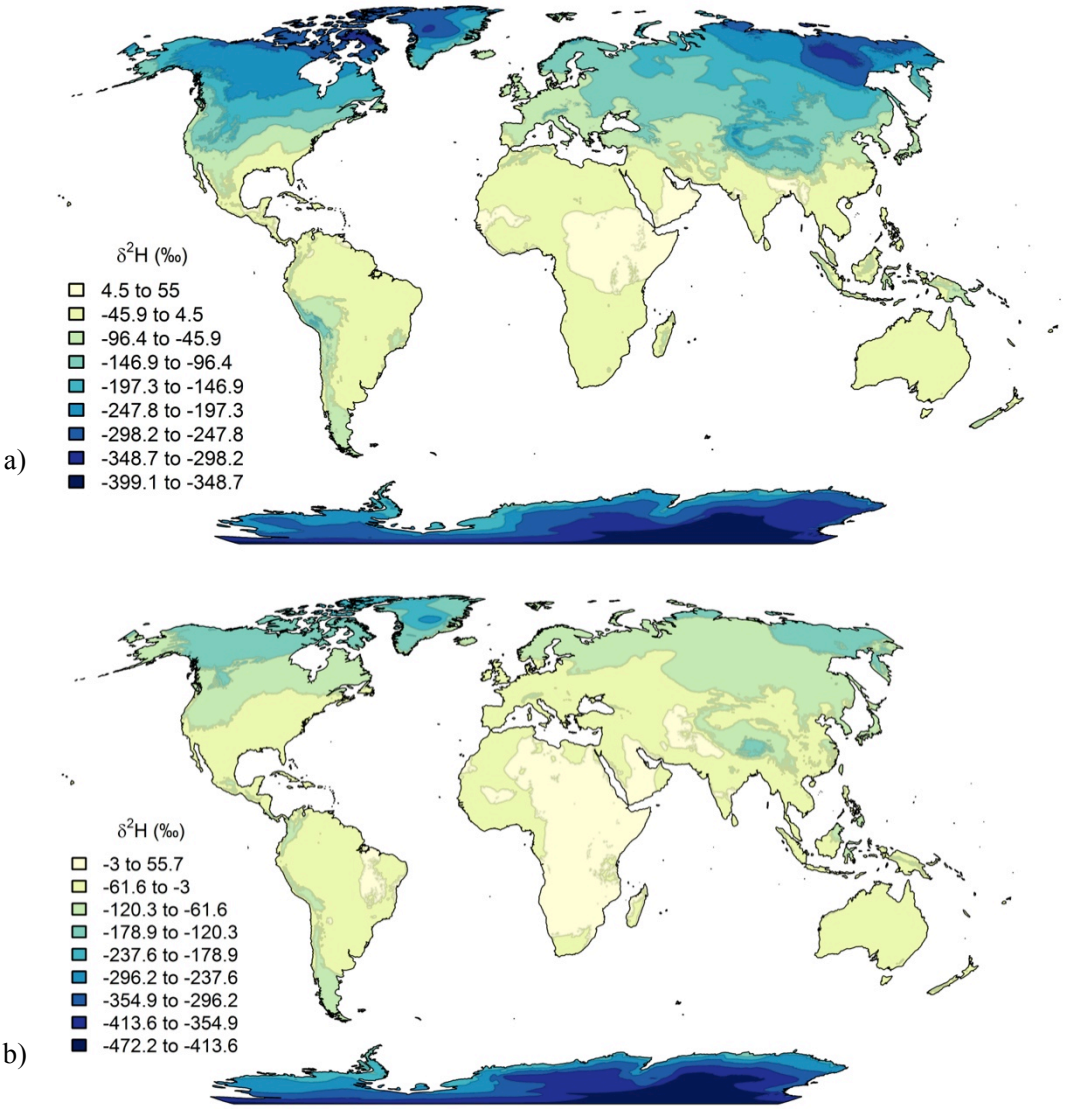


Figure 1.15. Map of isotope ratios in precipitation during January a), and June b) (extracted from Bowen, 2007).

Several studies have focused on the effect of drinking water and diet on the δD value of animal tissues (Hobson, 1999; Hobson et al., 2004; Zhang et al., 2006). The research carried out by Hobson (1999) was based on the study of four experimental groups of quails fed with two different diets and watered with two different isotopically labelled waters (-130‰ and +196‰). The research was able to establish that, during the biosynthesis of internal animal tissue, the relative contribution of drinking water against food of the nonexchangeable hydrogen was approximately 18-24%; and the

conclusion was that, in paleoclimatic reconstruction, the risk of misinterpreting the δD values is high because it could easily reflect a change in feeding and drinking behaviour rather than climate. However, few successful applications (Chivall, 2008; Cormie et al., 1994; Sharp et al., 2003) demonstrated that hydrogen isotope analysis of organic materials could actually give important information about the climate.

For instance, research carried out by a previous PhD student who worked at the University of Bristol (Chivall, 2008) attempted to explain the variations in the δD values of modern animal palmitic and stearic fatty acids from different ecosystems and environments. For this purpose, modern animal fats from UK and Kazakhstan were chosen. The annual mean δD value of meteoric water in Kazakhstan is approximately -115 ‰, calculated using global data (Bowen & Revenaugh 2003; Bowen 2007), whilst in the UK it is ca. -55 % (Darling et al., 2003). Therefore, a strong distinction in δD values resulted from Kazakh and British animal fats was expected. The compound-specific stable hydrogen isotope results produced in Chivall's research are displayed in Figure 1.16. The Kazakh terrestrial animals were characterized by the most depleted $C_{16:0}$ and $C_{18:0}$ fatty acids (Chivall, 2008). The UK terrestrial animals were the next most depleted, while the least depleted fatty acids were those from marine animals. Therefore, the expectation was confirmed; the Kazakh samples were more depleted relative to their UK analogues, due to the relative depletion of meteoric water in Kazakhstan compared to that in UK, confirming that hydrogen isotope analysis of organic materials can give important information about the climate.

1.6.2.1 Adipose and dairy fats

Supported by the previous researches (Chivall, 2008; Hobson, 1999; Hobson et al., 2004; Sharp et al., 2003) and by an increasing awareness of the potential of the hydrogen isotope applications, the compound-specific stable hydrogen isotope analysis was applied on Kazakh equine fats with the attempt to distinguish between adipose and dairy fats and to shed light on the horse domestication in ancient Eurasia (Outram et al., 2009). In order to investigate the domestication of horses in Kazakhstan, fresh samples of adipose and dairy equine fats were collected and compound-specific stable carbon analysis were applied in order to determine the $\delta^{13}C$ values of equine fats. However, the $\delta^{13}C$ values overlapped in a common area of the plot (Figure 1.17a) characterized by similar mean values. Therefore, based on the hypothesis that equine dairy fat hydrogen is derived from environmental summer water while the adipose fats exhibit an annually averaged δD signal (see the seasonal effect in Table 1.1), the same reference samples were analysed by GC/TC/IRMS with the purpose to obtain δD values. Significantly, the δD values of the $C_{16:0}$ fatty acid of the milk equine fat were enriched of roughly 100‰ compared to the δD values of the adipose equine fat (Figure 1.17b), confirming the hypothesis and leading to the discovery of one of the first Eurasian horse domestication centre.

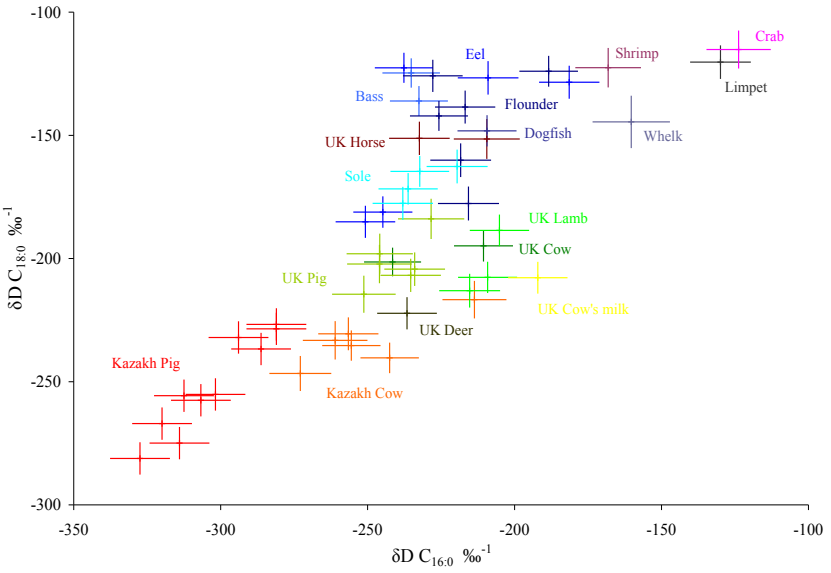


Figure 1.16. δD values of $C_{16:0}$ and $C_{18:0}$ fatty acids from modern UK and Kazakh animals. Adapted from Chivall (2008).

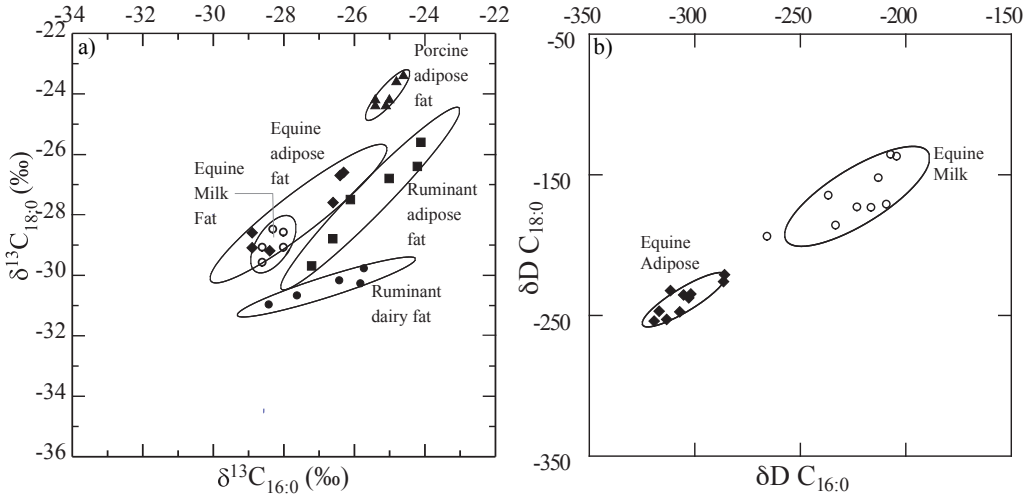


Figure 1.17. Scatter plots of a) $\delta^{13}C$ and b) δD values of the $C_{16:0}$ and $C_{18:0}$ fatty acids of animal fats of modern reference fats from Kazakhstan. Adapted from Outram et al. (2009).

1.7 Aims and Objectives

The central goal of the project is to deepen our knowledge of the subsistence economy and lifestyle of the ancient societies that populated the Eastern Europe during the Middle and Late Eneolithic and Early Bronze Age, a period of transitions and changes. The specific aim is to reconstruct the paleodiet and subsistence economic strategies of the ancient people that occupied the steppe and forest-steppe along the Dnieper River of Ukraine, during two specific archaeological stages: Middle/Late Eneolithic and Early Bronze Age (ca. 4500 to 2300 BC) and across two climatic phases, Late Atlantic and Early Subboreal.

This project use an integrated approach based on several sources of evidence: existing archaeological, faunal and botanical evidence are considered and interpreted together with existing paleoclimatic records, employed in order to establish the interconnection between humans and their environment, then molecular and stable isotope techniques are applied to absorbed organic residues recovered from over 200 archaeological ceramic potsherds excavated from the forest-steppe and the steppe region of the modern Ukraine (see map in Figure 1.18), to investigate the subsistence practices, elucidate the extent of pastoralism and explore the importance of secondary products to these ancient communities. In addition, attention is specifically directed at the horse domestication matter.

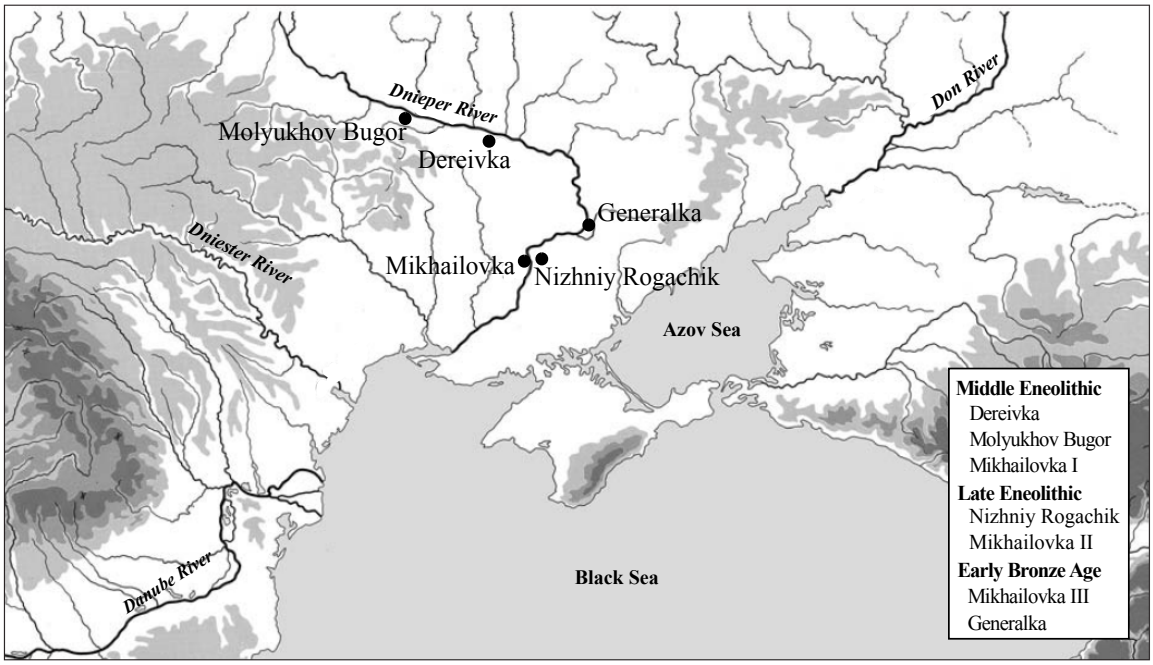


Figure 1.18. Location of the five sites analysed in the current study.

CHAPTER 2

EXPERIMENTAL

2.1 Glassware, solvents and reagents

All solvents used were HPLC grade (Rathburn) and the reagents were analytical grade (typically >98% of purity). Reusable glassware was washed with Deacon 90 (Deacon Laboratories), rinsed with acetone, oven dried and, when possible, furnaced at 450°C from a minimum of 4 h. To prevent contamination, aluminium foil and solvent-washed tweezers were used to manipulate the samples. Analytical blanks were prepared with each batch of samples (usually 11 samples) to monitor for possible sources of contamination in solvents and reagents.

2.2 Archaeological pottery

A total of 210 potsherds from sites of the Eneolithic and Early Bronze Age of the North-Pontic region were subjected to organic residue analysis. The samples were mainly extracted with chloroform-methanol (Section 2.3.1); however, 40 samples (of which 30 were repetitions) were analysed with acid extraction (Section 2.3.2) in order to investigate recoveries using this alternative approach (Correa-Ascencio, 2014; Correa-Ascencio and Evershed, 2014).

The sample selection was carried out at the Institute of Archaeology, National Academy of Science of Ukraine (Kiev), supervised by the senior researcher Yuri Rassamakin. Sherds likely to have been used in cooking processes were chosen; the great majority of the sherds were previously cleaned by archaeologists, therefore no evidence of burning/sooting that could have indicated use in

cooking were seen. However, rim and body of the sherds were mainly selected as these have been proven to contain higher concentrations of solvent extractable lipid (Charters et al., 1993).

2.3 **Analytical protocol**

A flow diagram summarising the analytical protocols employed for the analysis of absorbed and visible lipid residues from archaeological pottery is shown in Figure 2.1.

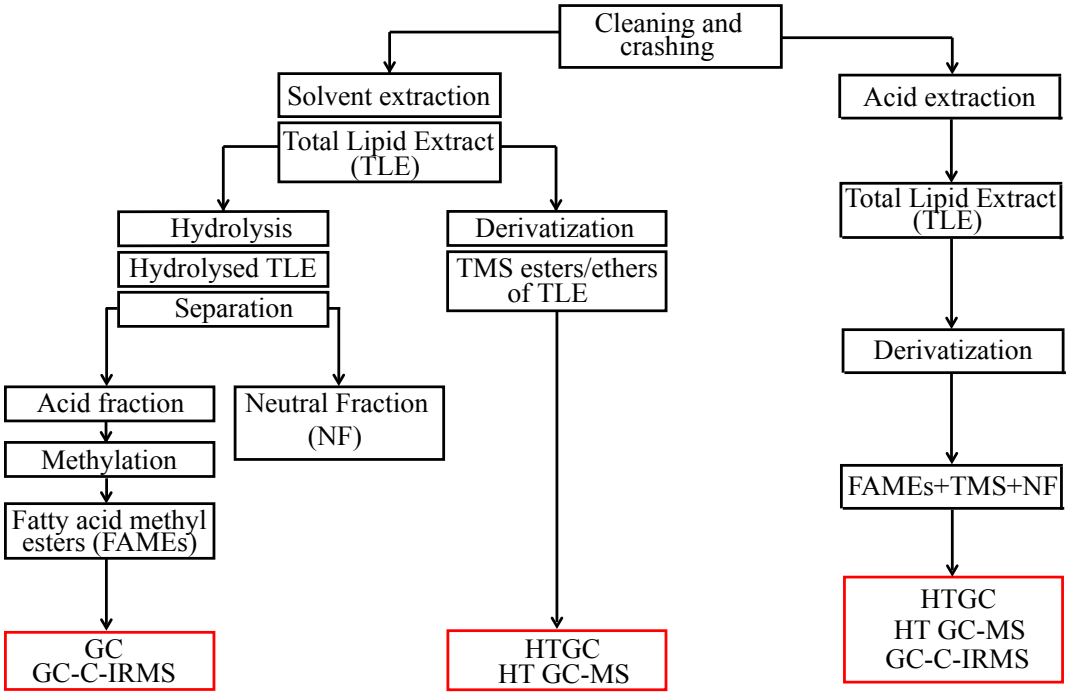


Figure 2.1. Flow diagram summarizing the analytical protocols.

2.3.1 *Solvent extraction of lipid residues from archaeological pottery*

A sub-sample (1-2 g) from the archaeological sherd was cleaned using a modelling drill to remove any exogenous residues, such as those coming from the soil or handling by excavators and/or curators. The cleaned sherd was ground in a glass pestle and mortar; the fine powder was weighed and placed in a glass vial. An internal standard (20 µg of *n*-tetratriacontane) was added to the powdered sherd to enable the quantification of lipid extract. Lipid were extracted using chloroform:methanol (2:1 *v/v*) and sonicated (2 x 20 min). After centrifugation in a test tube (2,500 rpm, 10 min), the total lipid extract (TLE) was transferred to a 3.5 mL vial and the solvent evaporated under a gentle stream of nitrogen to 3 mL. The concentrated TLE was then stored in the fridge until required for analysis.

An aliquot of the TLE was trimethylsilylated (Section 2.3.1.1) for analysis by HTGC (Charters et al., 1993; Evershed et al., 1990). Extracts containing high molecular weight components, such as acylglycerols, were hydrolysed and methylated (Section 2.3.1.2) to form fatty acid methyl esters (FAMEs) before analysis by GC, GC/MS and GC/C/IRMS.

2.3.1.1 Preparation of trimethylsilyl derivates (TMS)

An aliquot of the TLE (1/4) was filtered through silica gel to remove particulate matter and highly charged components, then dried under a gentle stream of nitrogen. The dried aliquot of the TLE was then treated with 40 µL of *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (Sigma Aldrich) for 1 h at 70°C. Excess BSTFA was removed under a gentle stream of nitrogen and the trimethylsilylated TLE dissolved in hexane for HTGC analysis (Charters et al., 1993; Evershed et al., 1990).

2.3.1.2 Hydrolysis of TLE and preparation of FAMEs

A further aliquot of TLE was treated with NaOH/H_2O (9:1 *w/v*) in methanol (5% *v/v*; 70°C, 1 h). After allowing cooling to room temperature, the neutral fraction was extracted with hexane (3 x 3 mL) in a clean glass vial and stored in the refrigerator until required for analysis.

The methanol fraction was acidified to pH 3 with 1 M HCl and the fatty acids extracted with chloroform (3 x 3 mL) for the archaeological fats. The extracted fatty acids in solvent were evaporated under gentle stream of nitrogen and treated with 100µL of BF_3/MeOH (Sigma Aldrich; 14% *w/v*, 70°C, 1 h). After allowing to cool, dichloromethane extracted distilled water was then added (1 mL) and FAMEs extracted (3 x 2 mL) with chloroform. The solvent was evaporated to dryness under a gentle stream of nitrogen and the FAMEs stored in freezer until required for analysis. The FAMEs were dissolved in hexane for analyses by GC, GC/MS and GC/C/IRMS and GC/TC/IRMS.

2.3.2 *Acid extraction of lipid residues from archaeological pottery*

The powdered sherd was placed in culture tube-I (Correa-Ascencio and Evershed, 2014). Lipids were extracted by adding 5 mL H_2SO_4/MeOH (2% v/v, 70°C, 1 h). The H_2SO_4/MeOH solution containing the extract was then transferred to a test tube and centrifuged (2,500 rpm, 10 min). The clear supernatant was transferred to clean culture tube-II and 2 mL of DCM extracted double-distilled water added. For a total lipid extraction, 3 mL of hexane was added (x 2 times) to the extracted potsherd in the culture tube-I to recover any lipids not fully solubilised by the methanol solution. The hexane supernatant was then transferred to the H_2SO_4/MeOH solution in culture tube-II and vortex mixed to extract the lipids. Following this, 2 mL hexane was added directly to the H_2SO_4/MeOH solution in the culture tube-II and vortex mixed to extract the remaining lipid residues (x2). The hexane extracts were combined and solvent removed under a gentle nitrogen stream and re-dissolved in 1 mL of hexane to give the transmethylated total lipid extract (TLE). In case of *n*-alkanols being present in the lipid extract, samples were derivatised with BSTFA (2.3.1.1) prior to GC, GC/MS and GC/C/IRMS analyses.

2.4 **Instrumental analysis**

2.4.1 *Gas Chromatography (GC)*

All GC analyses were performed on a Hewelett Packard 5890 series II gas chromatograph, using either autosampling or manual injections. Helium was used as carrier gas and a flame ionization detector (FID) was used to monitor column effluent. The diluted samples (1 μL) were injected into a fused silica capillary column (50 m x 0.32 mm i.d.) coated with a dimethylpolysiloxane stationary phase (0.1 μm film thickness, J&W Scientific; CP-Sil 5 CB). The temperature program was as follows: initial temperature was held at 50°C for 2 min followed by an increase to 300°C (10 min) at a rate of 10°C min^{-1}. The data were acquired and analysed with Clarity software. Peaks were identified by comparison of retention times with those of a derivatised external standard. Quantification was achieved by the internal standards method (Section 2.5.1).

2.4.2 *High Temperature-Gas Chromatography (HT/GC)*

HT/GC analyses were performed on an Agilent Technologies 7890A System gas chromatograph, using either autosampling or manual injections. The carrier gas was helium at constant flow (4.26 mL min^{-1}) and a flame ionization detector (FID) was used to monitor column effluent. Trimethylsilylated total lipid extracts (1 μL) were injected through an on-column injector, in track-oven mode onto a 15 m x 0.32 mm i.d. fused silica capillary column coated with a DB1 stationary phase (non-polar column, 100% dimethylpolysiloxane, 0.1 μm film thickness; Agilent Technologies). The GC oven temperature program was 50°C for 2 min to 350°C (10 min) at 10°C.min^{-1} (Charters et al., 1993; Evershed et al., 1990). Data acquisition and processing were carried out by the HP Chemstation software (Rev. B.03.02 [341], Agilent Technologies).

2.4.3 *Gas Chromatography-Mass spectrometry (GC/MS)*

Two GC/MS were used to analyse the extracts: (i) the GC/MS with a non-polar column for the detection of the TMS and (ii) the GC/MS with a polar column for the detection of FAMEs. The first analyses were performed on a Thermo Finnigan Trace MS operating with an ionizing energy (IE) of 70eV with a scanning range of *m/z 50*-650. Helium was used as the carrier gas. The GC interface temperature was 300°C and a source temperature of 200°C. The temperature program was 50°C (2 min) to 300°C (15 min) at a rate of 10°C.min^{-1}. Samples were introduced by on-column injection. The analytical column was a 60 m x 0.32 mm ZB-1 coated with dimethylpolysiloxane (film thickness, 0.12 μm). Data acquisition and processing were carried out using XCalibur software.

GC/MS analyses of FAME derivatives were performed using a Finnigan Trace quadrupole MS, operated in electron ionization (EI) mode operating at 70eV with interface temperature of 250°C and a source of temperature of 200°C. The scanning range was between *m/z* 50-650. The temperature

program was 50°C (2 min) to 250°C (15 min) at the rate of 10°C min^{-1}. For the detection of ω-(*o*-alkylphenyl)alkanoic acids (APAAs), the MS was operated in total ion current (TIC) and selected ion monitoring (SIM) mode acquiring at *m/z* 105, 262, 290, 318 and with a dwell time of 0.12 second per scan. Diluted samples were introduced using a PTV injector onto a 60 m x 0.32 mm i.d. fused silica capillary column coated with VF-23ms stationary phase (50% cyanopropyl-methylpolysiloxane, 0.15 μm film thickness; Varian, Factor Four). Data acquisition and processing were carried out using the XCalibur software. Due to the absence of commercial APAAs standards, the chromatogram of each sample was compared with an archaeological standard, known to contain $C_{16,}$ C_{18} and C_{20} APAAs.

2.4.4 *Gas Chromatography/Combustion/Isotope Ratio Mass spectrometry (GC/C/IRMS)*

Compound-specific stable carbon isotope ratios were performed using a GC Agilent Technologies 7890A GC coupled to an IsoPrime 100 (EI, 70eV, three faraday cup collectors *m/z* 44, 45 and 46) *via* an Isoprime GC5 combustion interface with a CuO and silver wool reactor maintained at 850°C. Fames were analysed using a VF-23ms stationary phase (50% cyanopropyl/methylpolysiloxane, 60 m x 0.32 mm i.d., 0.15 mm film thickness). Helium was used as carrier gas and the temperature programme was the same as for the GC/MS analyses.

2.4.5 *Gas Chromatography/ Thermal Conversion /Isotope Ratio Mass spectrometry (GC/TC/IRMS)*

Compound-specific stable hydrogen isotope ratios were performed using a ThermoFisher Scientific Delta^{Plus} V GC/TC/IRMS (thermal conversion reactor, 300 x 0.5 mm i.d.; Al_2O_3; 1450°C). FAMEs were introduced to the GC via Agilent PTV injector (splitless mode; 50-300°C; purge time=1 min) and later an Agilent Split/Splitless injector (splitless mode; 300°C purge time=2 min). A fused silica capillary column (30 m × 0.25 mm i.d.) with a methylpolysiloxane stationary phase (Zebron ZB-1; 0.25 μm film thickness) was used; column flow was constant at 0.8 mL min^{-1}. The temperature programme used consisted of an initial isothermal period of 1 min at 80 ºC followed by an increase to 300 ºC at a rate of 10 ºC min^{-1} and a final isothermal period at this temperature for 10 min. The MS ion source pressure was 2.2×10^{-6} mbar and the electron ionisation potential was 3 kV. Faraday cups were used for the detection of ions of *m/z* = 2 (H_2^+) and *m/z* = 3 (HD^+) with cup centring performed using the HD^+ ion beam. A retardation lens removed $^4He^+$ ions and in order to correct for H^{3+} ions a calibration was performed every day using Thermo Finnigan ISODAT 2.0 software; the H^{3+} factor was typically below 5 and had a rate of change of less than 0.1 day^{-1}.

2.5 **Data processing**

2.5.1 *Quantification of lipid residues*

In order to estimate the percentage of lipid residues recovered from the archaeological potsherds, an internal standard (IS - *n*-tetratriacontane) was added in the TLE. The integration of the GC peak

areas was compared with the IS and the following equation was applied in order to get the concentration of the lipid residues:

$$[TLE] = \frac{\frac{(100 - A_{IS} - A_{Cont})}{A_{IS}}}{m_{Sherd}} \times m_{IS}$$

[TLE]	= total lipid extract concentration (μg g^{-1})
A_{IS}	= peak area (%) of internal standard
A_{Cont}	= peak area (%) of any appreciable contamination in the sample (e.g. phthalates)
m_{IS}	= mass internal standard (μg)
m_{Sherd}	= mass of powdered potsherd (g)

2.5.2 *$\delta^{13}C$ values*

The $^{13}C/^{12}C$ ratios are expressed relative to the VPDB (*Belemnitella americana)* standard.

$$\delta^{13}C = \frac{R_{SAMPLE} - R_{STANDARD}}{R_{STANDARD}} \times 1000$$

Where:

$\delta^{13}C$ is measured in ‰ and

R_{SAMPLE}= $^{13}C/^{12}C$ in the sample

$R_{STANDARD}$ = $^{13}C/^{12}C$ in the standard

Each sample was run in duplicate and any questionable runs were repeated. An external standard consisting of a mixture of FAMEs ($C_{11:0}$, $C_{13:0}$, $C_{16:0}$, $C_{21:0}$ and $C_{23:0}$) of known isotopic composition was run regularly between sample runs to ensure the integrity of the data. Results were calibrated against a reference CO_2 standard, which was injected directly into the ion source three times at the beginning and three times at the end of each run. Instrumental precision was typically ±0.3 ‰ or better. $\delta^{13}C$ values for the individual fatty acids were determined by correcting the values obtained for the corresponding FAMEs using a simple mass balance calculation to account for the extra carbon added during derivatisation.

$$\delta^{13}C_{FA} = \frac{(no.C_{FAME} \times \delta^{13}C_{FAME}) - \delta^{13}C_{MeOH}}{no.C_{FAME}}$$

Where:

$\delta^{13}C_{FA}$ = $\delta^{13}C$ value of the fatty acid

$\delta^{13}C_{FAME}$ = $\delta^{13}C$ value of the FAME

$\delta^{13}C_{MeOH}$ = $\delta^{13}C$ value of the derivatising methanol

$n°C_{FAME}$ = total number of carbon atoms in the FAME

$n°C_{FA}$ = total number of carbon atoms in the original fatty acid

In order to make them directly comparable with the ancient fats, the $\delta^{13}C$ values for the modern reference fats were corrected for post-industrial CO_2 by adding 1.2‰ (Friedli et al., 1986).

2.5.3 *δD values*

Data were calibrated to six (three at the beginning and three at the end of each run) H_2 reference peaks injected directly into the ion source, before being normalized using the equation of a line from a plot of known against measured δD values for a standard suite of 15 *n*-alkanes ($C_{16:0}$-C_{30}; Mixture B, Arndt Schimmelmann, University of Indiana) injected after every two sample runs. Instrument error was typically less than 5‰, calculated using the same *n*-alkane standard. To condition the reactor, two early eluting compounds (pentadecane and ethyl capricate; both Sigma) were coinjected with every run. All samples were analysed at least in triplicate. Individual fatty acids were analysed as FAMEs and their δD values (in ‰) calculated by correcting for additional methyl hydrogens and any fractionations induced during methylation using;

$$\delta D_{FA} = \frac{(2N_{FA} + 2)\delta D_{FAME}}{(2N_{FA} - 1)} - 0.4N_{FA} + 29$$

Where N is the chain length of the saturated fatty acid of interest.

2.5.4 *Identification of compounds by GC/MS*

The identification of compounds was achieved by comparison of the GC/MS chromatogram and specific retention times to a known external standard, mass spectra published in scientific papers and MS database library, such as the National Institute of Standards and Technology (NIST) and Lipid library.

2.6 **Modern reference animal fats**

Few of the modern Ukrainian animals from which fats were sampled had defined diets (see Appendix A for the complete list of modern reference fats collected and analysed from Ukraine and Moldova). Thus, the $\delta^{13}C$ and δD values obtained were likely to have been significantly affected by modern farming practices (Roffet-Salque et al., 2017b), e.g. cattle reared in high cereal-based diets.

Given this, the identification of the archaeological fats was achieved by comparisons of the stable isotope composition with a global reference database of modern fats comprising compound-specific $\delta^{13}C$ values of the $C_{16:0}$ and $C_{18:0}$ fatty acids of modern reference dairy fats (n = 48), ruminant adipose fats (n = 75) and non-ruminant adipose fats (n = 24) from Europe (Copley et al. 2003; Spangenberg et al., 2006; Salque et al., 2012), Asia (Gregg et al., 2009; Outram et al., 2009; Pitter, et al., 2012) and Africa (Dunne et al., 2012) created to define a `universal` $\Delta^{13}C$ plot. The latter plot has the potential for use in distinguishing fats across a wide range of ecological zones. The $\delta^{13}C$ values of modern reference fats from Kazakhstan obtained by Stear (2008) and Outram et al. (2009) were also used as these include modern equine reference fats, which are important considering the likely presence of equine fat in the organic residues extracted from Ukrainian ceramic vessels. The combination of the two reference data sets is shown below in Figure 2.2.

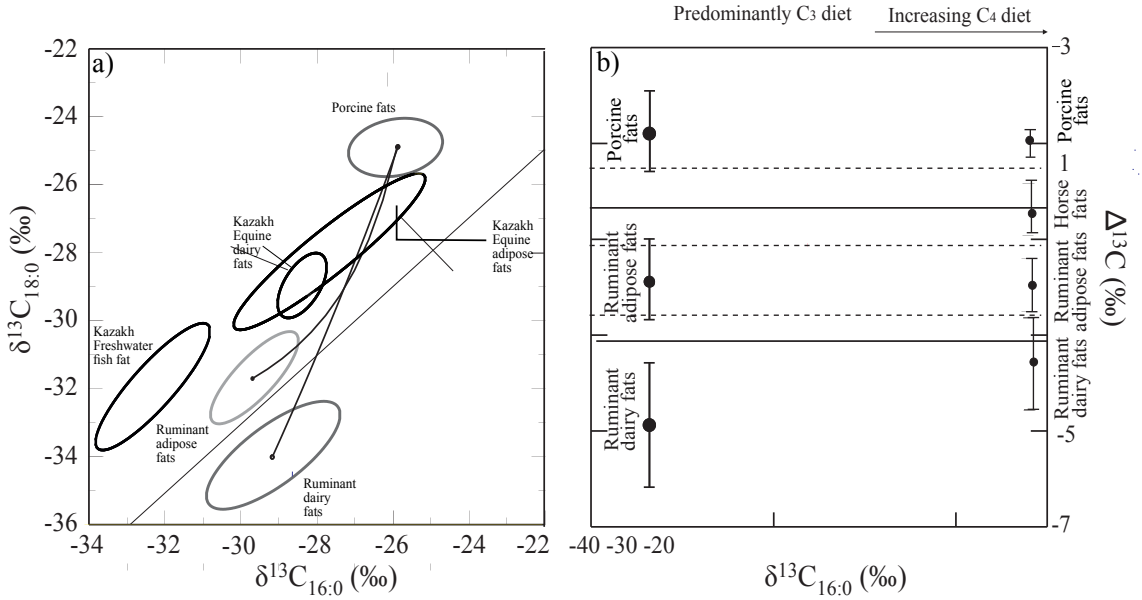


Figure 2.2. (a) Template-plot created by using the δ^{13} C values for the stearic and palmitic fatty acids of ruminant dairy fats, ruminant adipose fats, non-ruminant adipose fats and equine fats from animals raised in Britain; France; Kazakhstan; Switzerland; Turkey; Kenya and Libya. (b) Difference in the δ^{13} C values of the stearic and palmitic fatty acids (Δ^{13} C = δ^{13} $C_{18:0}$ – δ^{13} $C_{16:0}$) obtained for the same modern reference fats. By calculating the $\Delta^{13}C$ value, it is possible to separate animal fats because of the different source of $\delta^{13}C_{18:0}$ and $\delta^{13}C_{16:0}$. The ranges represent the mean ± 1 standard deviation of the Δ^{13} C values for the global database comprising modern animal fats from the mentioned studies. The δ^{13} C values obtained for the modern reference fats were adjusted for post- Industrial Revolution effects of fossil fuel burning by the addition of 1.2‰ (Friedli et al., 1986). Analytical precision is ± 0.3‰. (Adapted from Salque, 2012; Stear, 2008).

In the case of δD values, the modern Kazakh reference data of Stear (2008) has been used (Figure 2.3) as this includes equine adipose and dairy fats. However, it should be noted that the deuterium values are highly dependent on the local precipitation, as explained in Chapter 1, Section 1.6, which are different in Kazakhstan and Ukraine as discussed in Chapter 1, Section 1.1. Thus, the plot only has utility at best in a relative rather than absolute sense.

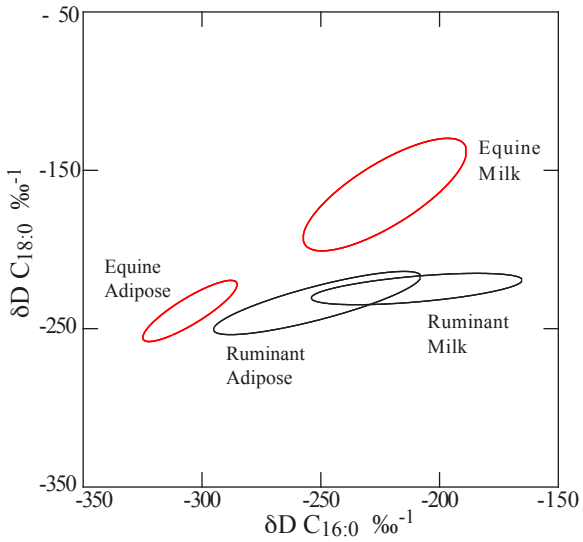


Figure 2.3. Reference-plot created by using the δD values for the stearic and palmitic fatty acids of ruminant adipose and dairy fats and equine adipose and dairy fats from animals raised in Kazakhstan (Stear, 2008).

CHAPTER 3

ARCHAEOLOGICAL BACKGROUND

3.1 **Introduction**

The 4th and the 3rd millennium BC is considered a key period for the general understanding of the prehistoric North-Pontic region; the events that have occurred between the Eneolithic of the Northern Volga region and the spreading of the Yamnaya culture are indefinite and unclear (Rassamakin, 1999, p. 68). For this reason, many archaeologists have devoted their attention addressing several questions related to ancient Eurasia and consequently numerous studies and theories have been proposed over the last decades (e.g. Anthony, 2007; Bunyatyan, 2003; Danylenko, 1974; Gimbutas, 1956; Kaiser and Schier, 2013; Kuzmina, 2003; Levine, 1999b; Merpert, 1974; Rassamakin, 1999; Schier, 2015; Telegin, 2002). However, even after remarkable discoveries (e.g. Outram et al., 2009) and a significant number of investigated archaeological sites (e.g. Kaiser, 2010), a generally accepted description of the cultural, economic and social organization of the North-Pontic societies, during the Eneolithic and Early Bronze Age, is still to be achieved.

By using the available Anglophone literature (e.g. Kuzmina, 2003; Rassamakin, 1999), in this Chapter the description of the prehistory of the North-Pontic region during the Middle, Late Eneolithic and the Early Bronze Age is presented. Hence, the general purpose is to give an introduction regarding the history of the research and to offer a first archaeological background by showing the discussions standing over the last decades together with contrasting theories and common trends. For a detailed description of the material culture and the investigated sites see Chapter 4, while a more detailed analysis of the existing zooarchaeological and botanical evidence is presented in Chapter 5.

Therefore, the specific objectives of this Chapter are to:

1) Describe the cultural models (cultural grouping) suggested by several scholars over the last decades;
2) Focus on the research carried out by Yuri Rassamakin (2006, 2002, 1999, 1994) who offered a novel cultural model that has dramatically revised the traditional pictures and theories;
3) Delineate the different hypothetical subsistence economic models proposed by the mentioned scholars over the last decades.

3.2 Cultural grouping and chronology of the North-Pontic region

3.2.1 *Introduction*

Leading archaeologists, such as Gimbutas, Danilenko, Merpert, Telegin and Rassamakin, have described the different hypothetical land-use of the Eurasian region by using the available archaeological evidence (Figure 3.1). Thus, opposing interpretations concerning the chronology of the sites, the subsistence economy and the general lifestyle of the communities lived in the vast territory of Eurasia have been drawn and are outlined in the subsequent Sections.

Two main and contrasting theories have been pondered:

1) The theory of an eastern invasion (e.g. Anthony, 2007; Gimbutas, 1956; Merpert, 1974) mainly based on four considerations: (i) The eastern communities located in the Volga area invaded and consequently socially and economically influenced the *Old Europe*; (ii) To a considerable extent, the eastern invaders exploited animals and practised nomadic pastoralism, therefore introducing the pastoralism practice in the Western Eurasia; (iii) The main reason that led to a westward migration was a climate change that caused increasing aridity and leading to difficulties for the pastoralism-based communities in adapting to the climate changes; (iv) Horse domestication firstly occurred in the eastern Eurasian steppe and it was connected to the need for long distance movements (for a more detailed description of the horse domestication phenomenon see Chapter 5, Section 5.7).

2) The theory of autochthonous societies populating the area of modern Ukraine. The latter civilizations were considered essentially independent from both the western and eastern communities (Telegin, 2002; Telegin et al., 1986).

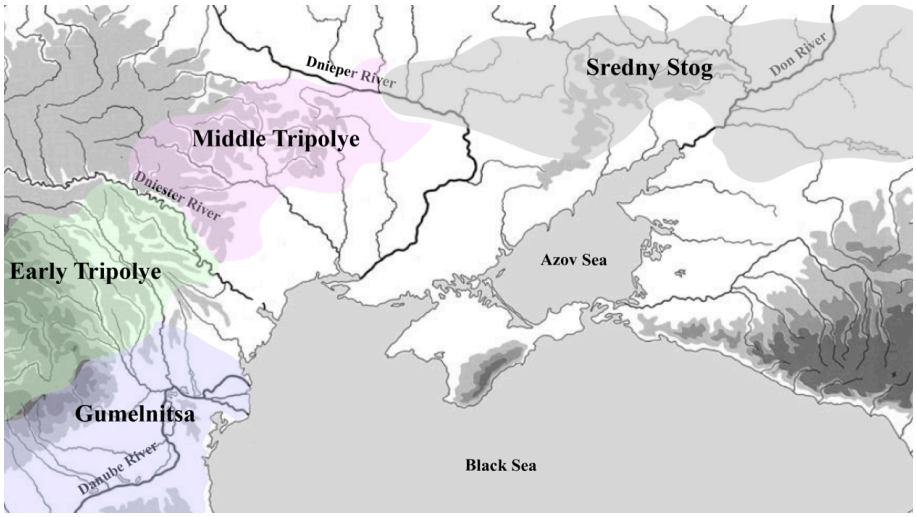


Figure 3.1. Map of Eastern Europe showing a schematic overview of the cultural distribution in the North-Pontic region; before Rassamakin (1999). Adapted from Stacul & Mallory (1989).

The recent research of Yuri Rassamakin (1999) can be considered as a third theory that has dramatically revised the previously mentioned models. Interestingly, he suggested that, during the North-Pontic Eneolithic, the major influence on the general cultural development was not the eastern world. Neither autochthonous theory was supported based on the ceramic imports that have been found in the North-Pontic region. Instead, he believed in a western influence from the Varna and Cucuteni-Tripolye culture during Tripolye B1 (around 4500-4100 BC). He based his new theory primarily on the interpretation of the burial traditions in contrast to the previous research that mainly focused on the characterization of the ceramic assemblage. Rassamakin proposed a new cultural model (Rassamakin, 1999) considering both the burials traditions (body positions and type of burial – Table 3.1) and the material cultural finds (mainly ceramics assemblages) he showed a new cultural groupings and a new chronological partition.

Table 3.1
Description of the four burial traditions recognised by Rassamakin on which his proposal of a new cultural model is based (Rassamakin, 1999, p. 73).

Burial tradition	Description
Tradition I	Extended supine burials underneath burial mounds.
Tradition II	Skeletons buried in supine positions with flexed legs both arranged in flat cemeteries or underneath burial mounds.
Tradition III	Skeletons are crouched on the side with both arms extended on the side or one arm extended and the other flexed.
Tradition IIIc	Skeletons strongly crouched on the side with arms bent.

The current project is generally based on the model and chronological structure proposed by Rassamakin, who is the contact-archaeologist; therefore, a detailed explanation of his theory is provided.

3.2.2 *Rassamakin's model*

Rassamakin subdivided the Eneolithic of the North-Pontic region to three chronological periods (Table 3.2). Although this project is mainly focused on Middle, Late/Final Eneolithic and Early Bronze Age, a brief description of the Early Eneolithic will be outlined to give a more general picture.

Table 3.2
Cultural grouping of the Black Sea region during the Eneolithic and the Early Bronze Age (EBA) (Rassamakin, 1999).

Periods	Steppe	Steppe/Forest-steppe	Forest-steppe	BC
Early Eneolithic	Skelya culture Sredny Stog II *Hiatus*			4550 (?)-4100 (4000)
Middle Eneolithic	Lower Mikhailvoka	Kvitiana	Dereivka	3800 (3700)
Late Eneolithic	Zhivotilovo-Volchanskoe type			3500 (3400)
Final Eneolithic	Repin Culture			3000 (2900)?
EBA	Yamnaya culture			2300 (2200) (?)

The Early Eneolithic dates from ca. 4550-4100 BC to ca. 3800-3700 BC. It is extremely important for understanding the prehistory of the North-Pontic region because it was a time of significant changes and cultural transformations. Although the traditional theories described the Sredny Stog communities as the main culture occupied the North-Pontic steppe and forest steppe (e.g. Telegin, 2002), Rassamakin rejects this homogeneous description claiming that the previous Neolithic cultures, characterized by large Mariupol-type flat cemeteries, were replaced by cultures "of different importance" (Rassamakin, 1999). In addition, this period is described as a time of prestigious trading between (i) the western agricultural world lived in a "peaceful egalitarian society" (Gimbutas, 1979) and mainly identified by cultures such as the Kodzhadermen-Gulmenita-Karanovo VI, Cucuteni A3-A4/Tripolye B1 and Carpathian-Balkan metallurgical province; and (ii) the Eastern communities, identified by the Skelya culture in the Dnieper region, the pre-Maikop Kuban culture in the Kuban region of the Caucasus and the Khvalynsk culture in the Volga region (Rassamakin, 1999). A fundamental statement is the new basis of the discussion that Rassamakin open up: the western influence of the two developed agricultural communities of the Balkan-Carpathian culture and the Tripolye B1-Cucuteni A3-A4, was extremely significant for the cultural and social system of the North-Pontic region. Several metal and ceramic objects from both western cultures were found in the North-Pontic territory (Rassamakin, 1999).

3.2.2.1 Middle Eneolithic (3800/3700-3500/3400 BC)

The period identified by Rassamakin as the Middle Eneolithic covers a few hundred years during which many cultural transformations occurred (Figure 3.2):

1) Tripolye-Cucuteni culture identified as a unique entity, split into Tripolye B2-C1 and Cucuteni AB (Diachenko and Menotti, 2012);
2) Economic and cultural exchanges between Tripolye sites, on the Dniester-Bug Rivers, and the adjacent eastern steppe/forest-steppe regions intensified, as demonstrated by the larger number of archaeological objects found in the North-Pontic region (Rassamakin, 1999);
3) The distinctive cultural entity of the Skelya culture disappeared from the North-Pontic region and smaller independent cultures, i.e. the Kvityana, the Dereivka and the Lower Mikhailovka cultures, took its place.

Focusing on the cultures most relevant for this research, the Lower Mikhailovka and Dereivka cultures showed greater western influences: the first one was probably the most economically developed culture of the Dnieper area. The Tripolye influence is evident in the painted ceramic potteries and kitchenware characteristic of Tripolye B2 (and also the late C1 ad C2) (Levine et al., 1999, p. 92). The Dereivka culture, commonly known because of possible horse domestication centre (Levine, 1990; Telegin et al., 1986), included two main settlements: Dereivka and Molyukhov Bugor. Findings such as the Tripolye B2 bowl and the annular copper tubular beads place the Dereivka culture in this timeline. Nevertheless the chronology of this culture is still under debate (discussed in Chapter 4).

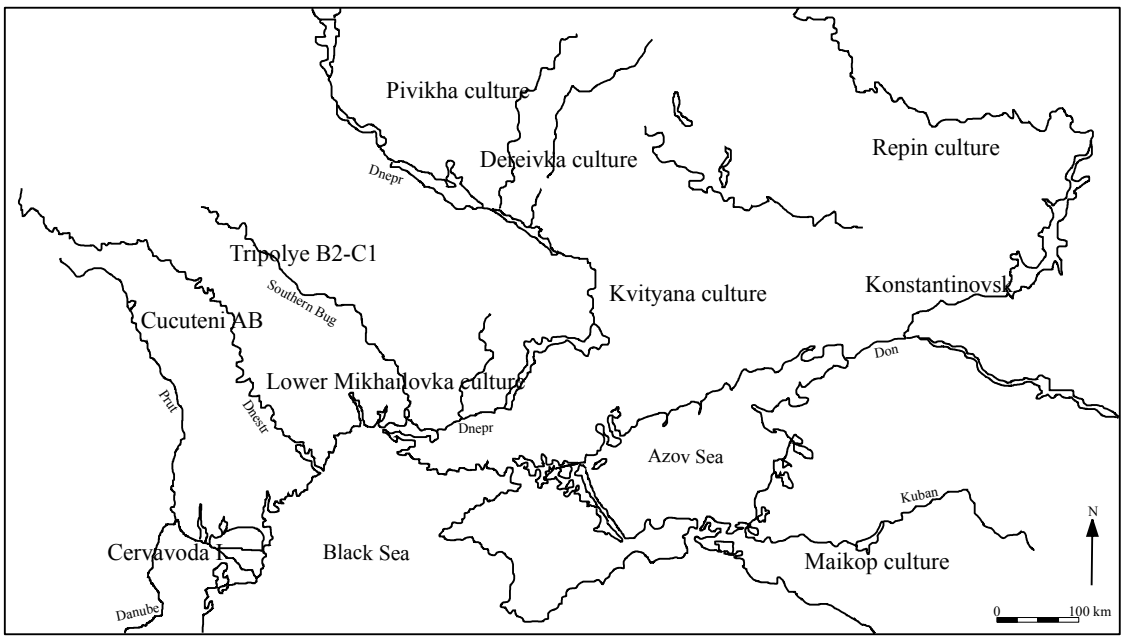


Figure 3.2. The distribution of the cultures during the Middle Eneolithic of the Northern Pontic region. (adapted from Rassamakin, 1999).

3.2.2.2 Late and Final Eneolithic (3500/3400-3000/2900 BC)

The first few hundred years of the Late Eneolithic were characterized by a strengthening of some communities such as the Lower Mikhailovka and the Tripolye cultures and an increasing western influence on Dereivka culture. Nizhnyi Rogachik settlement has to be mentioned as several ceramic samples have been analysed in the current work. It is a scarcely investigated settlement, and only few studies are available (Shaposhnikova, 1963; Spitsyna, 2010; Telegin, 1957). It appears that the ceramic vessels and additional archaeological findings were very different in respect to all the other settlements and cemeteries of the same area. According to Rassamakin, it could be considered a separated cultural entity (discussed in Chapter 4).

The second part of the Late Eneolithic is considered as a transitional stage between the Eneolithic and the Bronze Age, characterized by the collapse or weakening of the large cultural entities. Consequently, a number of new smaller regional groups formed. Some archaeologists consider certain cultures of this period as belonging to the Early Bronze Age.

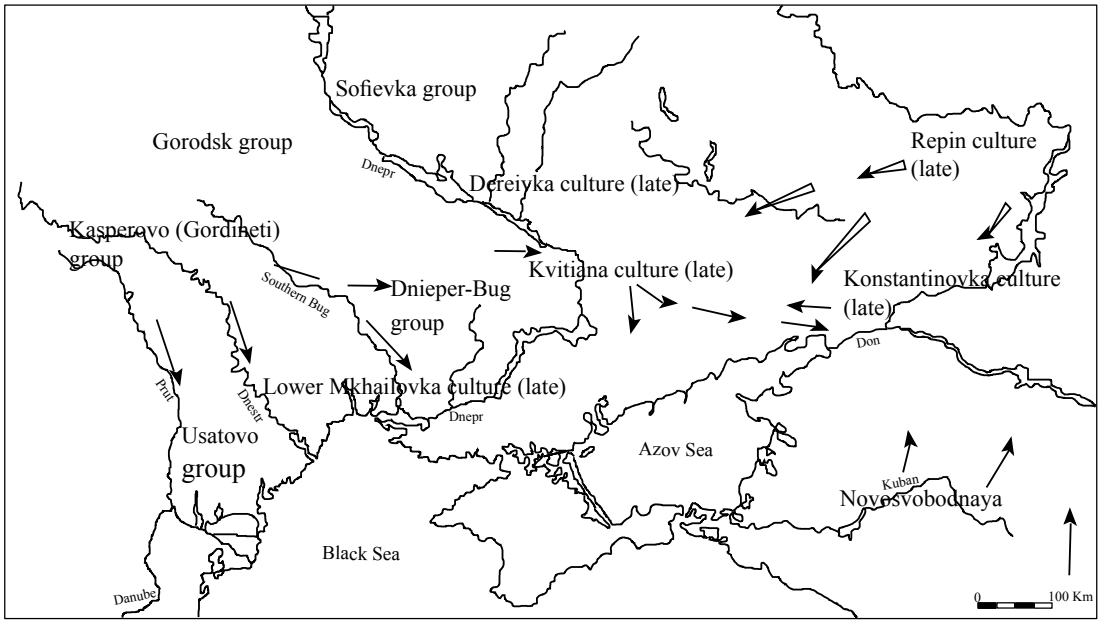


Figure 3.3. The distribution of the latest Eneolithic Pontic cultures and the sites of Zhivotilovo-Volchanskoe type (adapted from Rassamakin, 1999).

According to Rassamakin, during the Final Eneolithic, two migrations occurred. The first wave is related to the initial breaking down of the Tripolye communities; it appears that the communities of the Bug-Dnieper interfluve moved toward the territories of the Prut and Dniester, reaching the southern border of the forest-steppe in the Dnieper region (Kruts et al., 2012, pp. 71–73). The aforementioned migration involved the appearance of new cultures (i.e. Vladimirovka, Sushkovka-Dobrovody, Maidanetske, Chicherkvka, Talianki and Kosenovska). The second migration is connected with the Repin culture of the Volga area; it spread in three directions, towards the north to

the Upper Don, southwest to the Dnieper region where Dereivka and Kvityana predominance diminished, and into the lower Don and Volga. The most western appearance of Repin culture occurred in the upper horizon of the middle level of Mikhailovka settlement (Rassamakin, 1999, p. 125).

3.2.2.3 Early Bronze Age (3000/2900-2300/2200 BC)

The 3rd millennium BC of the Eurasian steppe is extremely peculiar and controversial. Two significant changes occurred in the Western Eurasia:

1) The archaeologically untraceable appearance of roughly ten thousands pit-grave burials (Rassamakin, 2004) connected with a cultural group named Yamnaya (from the Russian word *Yama* that means pit; Rassamakin, 1999); the latter is extremely impressive especially considering that the previous Eneolithic period counts not more than one thousand pit-graves (Rassamakin, 1999);

2) The increasing exploitation of domesticated animals in the form of pastoralism.

As mentioned, the traditional theory is based on the idea of a "kurgan wave" (Gimbutas, 1956), so the invasion of the western North-Pontic area by a group of pastoral stock-breeders that buried their dead in pit-graves, moving from the Volga-Don area due to a climate change, specifically a severe aridification, that forced eastern communities to move westward. In contrast with traditional theories, a group of researchers firmly criticized both the ideas of warlike invasion and the possibility of a westward migration (Ciugudean, 2011; Kaiser, 2010). The following theories are mainly based on Rassamakin's theory (1999) who suggests a cultural transformation of the pre-existing local Late Eneolithic cultures; a change in the lifestyle of each local community possibly due to climatic changes and the consequent diminishing food resources; "indeed, change to established forms of economy can cause the external appearance of a cultural group to be transformed in a fairly short time – in the course of one or two generations" (Rassamakin, 1999 ref. Gryaznov, 1955, pp. 23-24). As mentioned in Chapter 1, also the collapse of the agricultural world may have played a role in this transformation (Rassamakin, 1994; Rassamakin and Nikolova, 2008).

As for the cultural and chronological reconstruction, the social and economic events occurred during this period are very challenging to reconstruct. Zooarchaeological and archaeobotanical evidence is particularly scarce in this area and during this period, which means that the extent of animal domestication and dietary habits of the North Black Sea communities remain poorly understood. Consequently, there is an ongoing discussion concerning several aspects of the subsistence economy (Rassamakin, 1999, pp. 129–132). Thus, contrasting subsistence economic models have been proposed by a number of scholars. The latter are discussed in the following Section.

3.3 Subsistence economic models

For decades, on the trend of the traditional Eurasian archaeology (e.g. Gimbutas, 1956; Merpert, 1974), the associated traditional belief about the subsistence economy was centred on the idea that same eastern populations had influenced the lifestyles of western Eurasian people, spreading the nomadic-pastoral practise.

However, over the last few decades, the access to previously unavailable archaeological evidence and the common interest of getting reliable information about many unclear aspects of the Eurasian prehistory, led a variety of scholars to define new hypothetical Eneolithic and Early Bronze Age economic models of the Eurasian steppe (Anthony, 2007; Bendrey, 2011; Bunyatyan, 2003; Kuzmina, 2003; Levine, 1999b; Rassamakin, 1994; Renfrew, 2002; Shishlina, 2003). The debate is currently ongoing and an elaboration of commonly believed economic models for each period and/or each ecological area is one of the central unsolved aspects of modern Eurasian archaeology.

The main matters currently under discussion are the origin and developments of the pastoral economy, and its connection with other form of western settled economy such as agriculture. The idea of an economy only based on animal exploitation, supported by the traditional theories, was quickly set aside. Indeed, the exploitation of agriculture is testified, also in communities of stockbreeders, by the trade exchanges occurred between the ancient North-Pontic region communities, previously isolated, and the western farmers, which influence is evident in the neighbouring sites, such as Molyukhov Bugor and Mikhailovka (Rassamakin, 1999, pp. 147–149). Moreover, the archaeological evidence of agriculture is testified by finds of farming tools and grain imprints on vessels (discussed in Chapter 5).

Besides the increasing availability of Eurasian archaeological evidence, the extent of domestication, the nature of the economic resources, the balance between different economic activities and the general lifestyle of North-Pontic societies is still under debate. In order to better understand and get a hypothetical reconstruction of the subsistence economy and dietary habits of ancient Eurasian people, many archaeologists attempted to collect the available archaeological evidence and to suggest possible economic models. Therefore, the main goal of the current Section is to display the existing theories about economic models of the North-Pontic steppe and forest-steppe region, during the three investigated periods (Middle Eneolithic, Late Eneolithic and Early Bronze Age). However prior to showing them, it is necessary to give an explanation of two terms:

The general term *Pastoralism* refers to a specific form of economy based on the extensive herding; it implies migrations of the community according to the need of the herd (Kuzmina, 2003). There are three forms of pastoralism: *nomadic* - characterized by the absence of agriculture, *semi-nomadic* –

where agriculture is a secondary activity, and *semi-sedentary pastoralism* - where agriculture plays a predominant role. Another term that often occurs is *productive economy* (Kuzmina, 2003), which indicates the correlation between animal domestication (herding or pastoralism) and agriculture together with the capacity to interconnect two or more activities in order to be more productive.

3.3.1 *Subsistence Economy of the Eneolithic cultures*

As already mentioned at the beginning of this Chapter, during the Eneolithic, the Northern Pontic region was in contact with two opposite areas: the western world – or *Old Europe* - where the optimal climate and the more advanced technologies and social structure permitted the development of a sophisticated social-economic communities, and the eastern Eurasia, where the practices of hunting and gathering were still the more common (Kuzmina, 2003). It is generally believed (Bendrey, 2011; Bunyatyan, 2003; Kuzmina, 2003) that the abovementioned interaction between eastern Eurasian communities and agricultural world coincided with the origin of the *productive economy* (Kuzmina, 2003) in the Eurasian steppe. Kuzmina describes a complex economy characterized by both agriculture and herding of several domesticated species, that spread from the Carpathian-Danube area during the Neolithic and Eneolithic periods toward the Volga-Urals area where fishing, hunting and herding were still the major economic activities (Kuzmina, 2003, p. 208). Certainly, pastoralism was an important economic activity of these communities located in the arid Eurasia steppe zone where, it appears that, in contrast with the Southeastern Europe, "the agricultural revolution took the character of stock-breeding" (Renfrew, 2002, p. 18). However, addressing questions about the importance of pastoralism over other activities, in relation to different local regions, is challenging. Indeed, over the last decades the Eneolithic economy of the North-Pontic region was randomly described as nomadic, semi-nomadic or seasonal pastoralism economy; and a discussion about the main subsistence resources of these societies is still ongoing.

According to Bunyatyan (2003), the environmental conditions and the unsophisticated technology both very different from the *Old European area,* involved the exploitation of pastoralism activities as the major form of economy of the Northern Pontic steppe. However, because of its instability – e.g. occurrence of colder winters that could cause animal deaths or diseases - the North-Pontic populations required a secondary, concomitant subsistence economy. Therefore, Bunyatyan believes that agriculture was contemporaneously practised, probably playing a minor role. The consequences of practising both activities likely involved a conflict between the two opposite economic lifestyles: pastoralism involves at least seasonal migrations whereas agriculture is a sedentary activity. As a matter of fact, many archaeologists assert that the complicated organization of both activities was probably the reason why during the Eneolithic, the communities of the North-Pontic steppe where characterized by a slower cultural and material development, for instance visible in the ceramic production, in comparison with the Eastern Europe (Bunyatyan, 2003, p. 270).

Supporting the theory of Bunyatyan, Rassamakin (1999, pp. 147–151) believes in a variegated economy where mobile pastoralism had a significant importance; pastoralism and agriculture were both part of the economy in an interchanging balance aimed to adapt the lifestyle to the local different environments.

Summarizing, most of the recent researches (e.g. Bendrey, 2011; Bunyatyan, 2003; Kuzmina, 2003; Rassamakin, 1999; Renfrew, 2002) support the idea of an Eneolithic subsistence economy mainly based on animal exploitation together with agricultural activities that assumed an important role depending on the local environment and specific necessity of the community. Pastoralism was probably one form of animal exploitation, practising by some cultural groups depending on specific needs and the balance with other form of economy. However no further details are available in the existing Anglophone literature.

3.3.2 *Subsistence Economy of the Early Bronze Age cultures*

The majority of the modern Eurasian archaeologists (e.g. Bendrey, 2011; Bunyatyan, 2003; Kuzmina, 2003; Rassamakin, 1999) describe the general subsistence economy of the later period as similar to the previous one, but further developed.

As mentioned in Section 3.2, during the Early Bronze Age, the Yamnaya culture (ca. 3000/2900 BC – 2300/2300 BC) dominated the Northern Pontic region. The latter is traditionally considered a unique entity originated from East, however recent researches proposed a contrasting theory. Therefore, assuming that the Yamnaya culture was a cultural adaptation from the previous Eneolithic cultures, the idea of a regionally dependent and varying economic system, similar but more developed than the Eneolithic one, sounds extremely likely (Rassamakin, 1999).

Citing Shilov (1975a,b), Rassamakin describes several economic models to support the idea of a mixed and locally economy that originated in the Eneolithic and increased in the Early Bronze Age. The three models reflect three regional locations, i) the Volga-Ural model, in which sheep-breeders practised a mobile way of life; ii) the North Caucasian model, with sedentary communities of cattle/pigs-breeders; and iii) Black Sea model, divided into three zones, a northern zone where settled communities practised mainly horse-breeding; a river zone with long term settlements and cattle-breeders; and the southernmost areas occupied by sheep-breeders. Therefore, Rassamakin (1999) used the latter model as a starting point to reinforce his theory. He believes in a settled agricultural economy of the North-Pontic region that also involved a necessary seasonal pastoralism.

Also Bunyatyan (2003) suggested a similar model: the North-Pontic region communities practised a various economy according to the regional needs, developing a flexible system in which stock-breeding and agriculture were combined in an system where there were subdivisions of labours. Shishlina (2003, 2008; 2012), who mainly focused her attention on the north-western Caspian steppe, holds the opinion that the different local Yamnaya populations used a system that incorporated short distance movement, based upon seasonal changes in winter and summer pasture in the limited

environment. Anthony (2007) believes in economic differences between central and western Yamnaya groups, characterized by a more mobile pastoralism economy in the Volga compared with the western areas. Indeed, it is very important to stress the environmental and ecological difference between central and western Eurasia (Bendrey, 2011; Dolukhanov, 2002; Kremenetski, 2003) that is going to be better described in Chapter 8; considering the vast steppe belt as a unique environment can mislead, as the environmental diversity of western and eastern Eurasian steppe is very significant.

Summarizing, the majority of archaeologists support the idea that the Early Bronze Age subsistence economy was predominantly driven by the local environment, as during the previous periods. Animal exploitation and plant exploitation were both part of the flexible economic activities depending on the regional ecology.

3.4 **Conclusion**

The archaeology of Eurasia is very intriguing and intricate due to several reasons such as historical and cultural matters, concrete difficulties related with the lack of archaeological evidence and often the inconvenience to trace them. Moreover, the interpretation of Eurasian archaeology is particularly challenging because of the central geographical location and the resulting mixture of cultures and waves of migrations that occurred in this region from the Eneolithic onwards, resulting in extensive dissemination of cultural knowledge, materials and technologies. Besides the latter difficulties, from the second half of the 19th century onward, several scholars have suggested social and economic models and theories about ancient Eurasia, and specifically in relation to the Eneolithic and the Bronze Age of the North-Pontic region. Hence, the general goal of the current Chapter was to offer an idea about the ongoing discussion and unsolved issues that characterize several aspects of Eurasian archaeology. Specifically, a new archaeological theory suggested by the archaeologist Yuri Rassamakin (1999) has been presented, as his cultural and chronological reconstruction will be predominantly used in the current project. And finally, attention has been focused on cultural and subsistence economic models in order to offer a general background of the hypothetical subsistence economic practises, which is very useful for the overall comprehension of the current project. Indeed, based on the recent theories, the initial hypothesis is that the subsistence economy of the North-Pontic region, both during the Eneolithic and the Early Bronze Age, was various, in an interchanging of subsistence economic practises, including hunting, pastoralism, gathering and agriculture, depending on the diverse environments and regional ecosystems (e.g. Bunyatyan, 2003; Rassamakin, 1999). Therefore, the latter hypothesis will be tested, and possibly detailed, by the application of an interdisciplinary approach based on several tools, which is considered essential in order to give more reliable evidence and conclusions.

CHAPTER 4

SITES AND POTTERY

4.1 **Introduction**

A total of 210 ceramic potsherds have been targeted from five settlements located in the Dnieper region of Ukraine (Figure 4.1). The sites belong to three cultures: Dereivka (Dereivka and Molyukhov Bugor sites), Lower Mikhailovka (Mikhailovka I, II) and Yamnaya culture (Generalka and Mikhailovka III). The fifth settlement, called Nizhniy Rogachik, has yet to be fully assigned to any of the known cultures. Archaeologists working with Eneolithic materials have specifically named these materials as Rogachik type and dated them Late Eneolithic (contemporaneous to Late Tripolye period; Spitsyna, 2010); however, it is possibly contemporaneous with Mikhailovka II (Spitsyna, 2010).

Table 4.1
Scheme of the archaeological cultures and sites analysed in the current project.

Culture	**Sites**	**Location**	**Periods**
Dereivka	Dereivka and Molyukhov Bugor	Forest-steppe region	Ca. 3800/3700-3500/3400 BC
Nizhniaia (Lower) Mikhailovka	Mikhailovka I	Steppe region	Ca. 3800/3700-3500/3400 BC
Repin Rogachik type	Mikhailovka II and Nizhniy Rogachik	Steppe region	Ca. 3500/3400-3000/2900 BC
Yamnaya	Mikhailovka III and Generalka	Steppe region	Ca. 3000/2900–2300/2200 BC

The Eneolithic settlements were systematically compiled by Y.Y. Rassamakin (2004). Most of the settlements were excavated during the first half of the 20th century when hydroelectric stations were built. The site of Mikhailovka, which includes layers of the Eneolithic and the Early Bronze Age, was

originally a rescue excavation but afterward it changed to a systematical excavation. The excavators published a monograph, written in Ukrainian language, about the finds recovered during the abovementioned excavations (Lagodovska et al., 1962), and recently a new monograph has been written, in Russian, with new analytical results by G.F. Korobkova and O.G. Shaposhnikova (2005). The settlement of Dereivka was instead investigated by Telegin who also published a monograph in English (Telegin et al., 1986). Concerning the excavation at the settlement Molyukhov Bugor, it is still ongoing and, according to the excavator T.M. Neradenko, a comprehensive publication will be soon published. At the moment, only preliminary information are available in Russian language (Neradenko, 1995). Finally, the site of Generalka dates to the Early Bronze Age Yamnaya culture, same as the upper layers of the settlement Mikhailovka. Preliminary results, written in Russian, were published by the excavator and archaeologist O.G. Tuboltsev (2006).

The absolute dating of the settlement layers from which pottery sherds were taken for analyses is often still under discussion. Although several radiocarbon dates have been produced over the last decades, dating of materials erroneously located in a horizon do not benefit, instead it involves misinterpretation. This resulted in many dating misinterpretations and in an uncertain chronology of sites and material culture. Therefore, although radiocarbon dates obtained from bones, shells or charcoals recovered from the same layers where the investigated potsherds have been found, are also shown in the current Chapter; the expert opinion of the archaeologist Rassamakin, who dated the investigated potsherds through the observation of the ceramic features, is mainly taken into account. In general, his cultural and chronological reconstruction will be mainly considered.

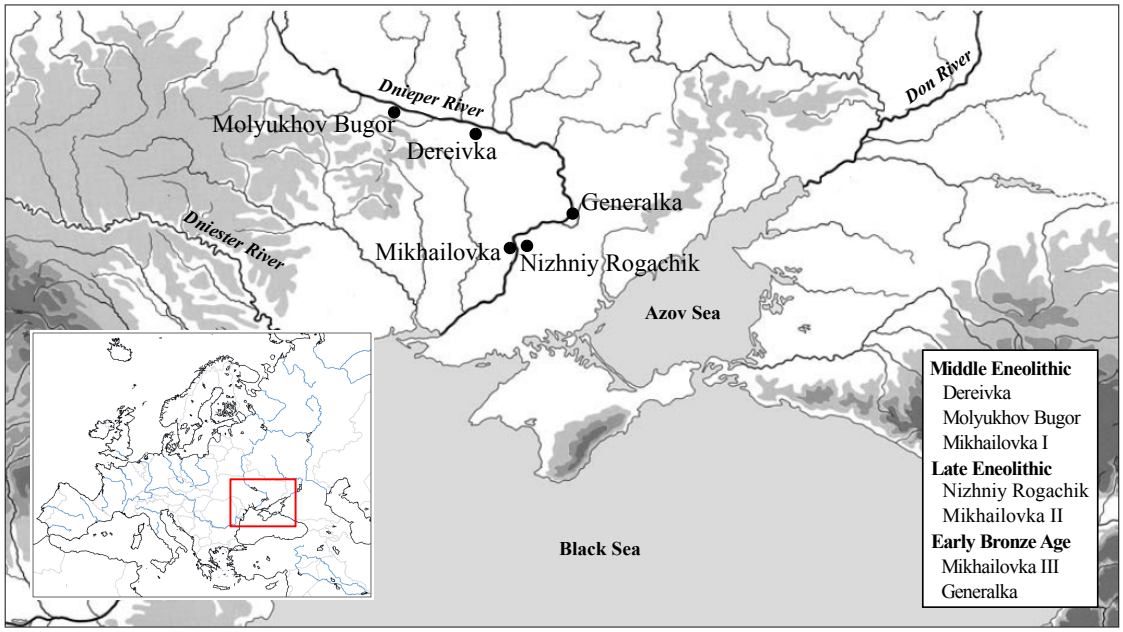


Figure 4.1. Map of the modern Ukraine and distribution of the five settlements analysed in the current study.

In this Chapter, the description of the investigated sites will be offered using the available literature. Specific aims of the Chapter are:

(i) Describe the settlement topography (when it is available);
(ii) Report the existing description of the ceramic ware assemblage;
(iii) Detail the ceramic sherds specifically recovered from each settlement and analysed in the current project;
(iv) Display the existing radiocarbon dates produced over the past decades.

Further information about archaeozoological and archaeobotanical findings will be described in Chapter 5.

4.2 **Dereivka site**

Excavator: D. Ya Telegin.
Year of discover: 1959 (Telegin, 1957; Telegin et al., 1986).
Years of excavation: 1960-61 and 1967.
Topography: The site, located on a promontory of the River Omelnik, a tributary of the Dnieper River, included a settlement, which was located 4 to 6 meters above the summer water level of the Dnieper River, and two cemeteries, a Neolithic and an Eneolithic one (Figure 4.2).

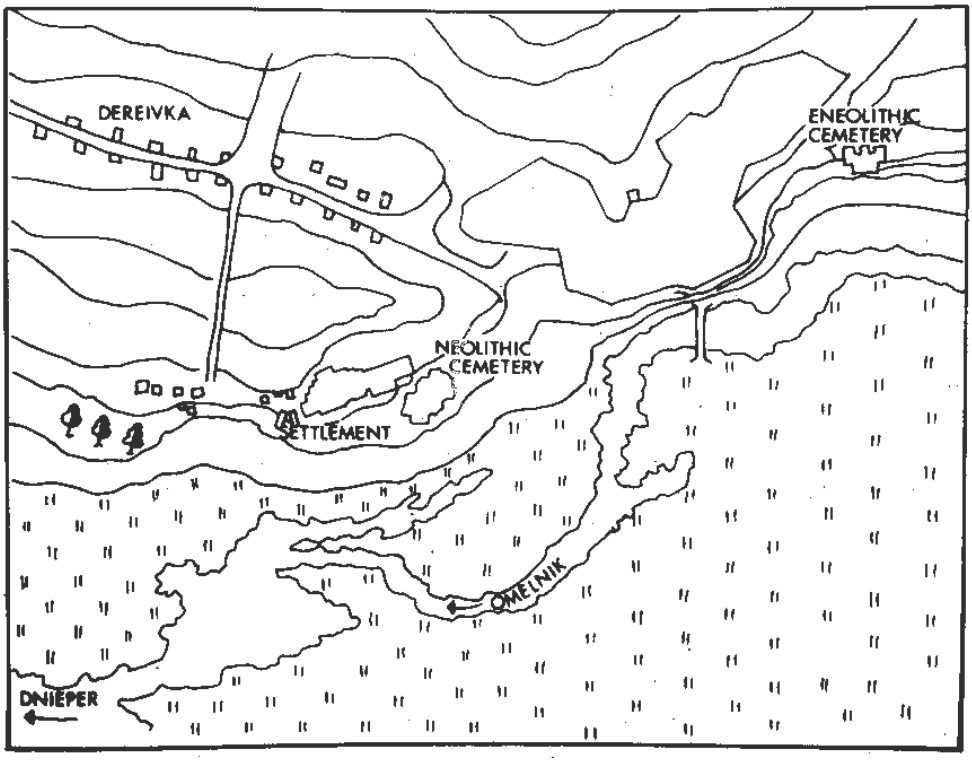


Figure 4.2. Map of Dereivka area. Extracted from Telegin, 1986.

Settlement features: The settlement site is structured and arranged as a typical Tripolye site, but is smaller in size and it has rectangular shape instead of circular (Telegin et al., 1986, p. 36). As a matter of fact, Dereivka site shows an organization that revokes Tripolye settlements. It can be divided into several areas: (i) the northern and southern parts of the settlement were occupied by two big houses and other structures that probably served as sheds; (ii) the eastern part was dedicated to ritual activities testified by buried animal skulls (Telegin et al., 1986, p. 31); (iii) the entrance was probably in the northwest of the settlement; (iv) in the central part of the settlement a high number of animal bones and shells together with a low number of ceramics suggested that this central area was devoted to livestock penning; and (v) shell accumulations around the settlement suggested a fence surrounded the site. The material culture remains collected from the excavations include pottery, artefacts of flint, bone and antler, plastic objects and many faunal remains (Telegin et al., 1986, pp. 45–70), however, in this context only the description of the ceramic wares will be outlined.

Ceramic wares: According to Telegin, the potteries from Dereivka settlement are associated with the eastern regions in the Dnieper-Don area (Telegin et al., 1986, p. 60) where similar vessel types have been found (e.g. in Aleksandriya). In contrast, Rassamakin believes in an influence from the western neighboring cultures. Indeed, many imported Tripolye potteries and plastic art have been found in the Dereivka ceramic assemblage (Rassamakin, 1999, p. 116). Common opinion is that the local ceramic material recovered during the excavations in the Dereivka settlement is unique (Rassamakin, 1999, p. 87; Telegin et al., 1986, pp. 45–70). A soft profile and an elongated pointed body characterize most vessels. The most common vessel types are pots, beakers, bowls and miniature vessels. The ceramic material is grey or yellow, however the inner core displays a dark colour suggesting a primitive firing technique (Figure 4.3). Telegin has offered very good reconstruction of the ceramic assemblage: Figure 4.4 displays the three most recurring vessel shapes.

Investigated sherds: Forty potsherds from kitchenware were selected. The fabric was usually shell-tempered clay with a dark-black core, suggesting a non-uniform heating. The identification of the vessel shape in the case of small ceramic sherds was challenging, however according to the expert observation of Rassamakin, the majority were pots rather than bowls. A complete list of all the ceramic fragments collection is given in Appendix B, Table 1.

Figure 4.3. The picture shows one of the ceramic sherds (DER2) analysed in the current study. The surface of the potsherd displays a light colour whereas the inner core is black.

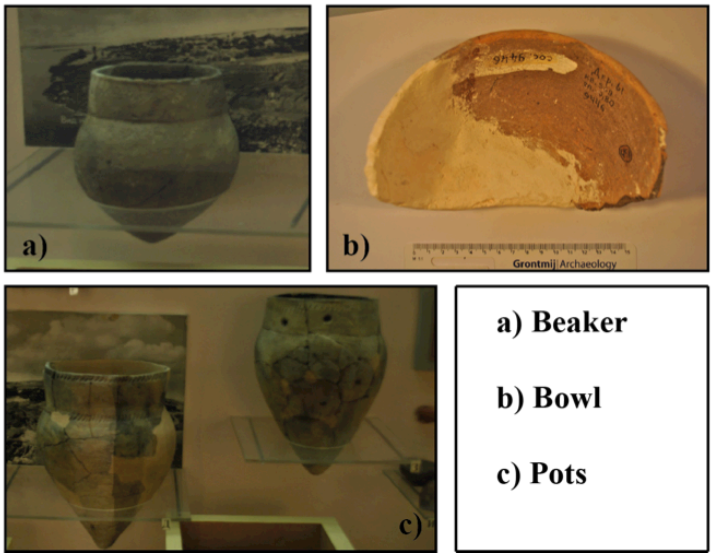


Figure 4.4. The three typical vessel shapes that have been found in Dereivka settlement. The pictures were taken in the archaeological department of Kiev (March 2013).

4.2.1 *Radiocarbon dates*

A number of radiocarbon dates produced by several laboratories (e.g. Institute of Hygiene and Medical Ecology located at Kyiv, Ukraine, Poznan Radiocarbon Laboratory (PRL); Institute of Geophysics, Departments of Geography and Anthropology, Interdisciplinary Archaeology Graduate Program, University of California, Los Angeles, California), were carried out over the last decades and showed in Figure 4.5. A list of Dereivka radiocarbon dates is showed in Appendix B, Table 8.

The chronology is highly uncertain as Dereivka stratigraphy is difficult to define and displays mixture of materials. Example of that is the famous stallion (head and left foreleg) excavated in Dereivka site (which will be better discussed in Chapter 5, Section 5.7). The latter resulted belonging to a much later period (the Iron age) (Anthony and Brown, 2003, 2000). Therefore, dating Dereivka site is very complicated and two hypothetical chronologies exist: (1) an earlier period between the 4500 and the 4000 BC; and (2) a later period (ca. 3800-3400 BC) supported by Rassamakin. The two positions are clearly observable in the radiocarbon dates showed in Figure 4.5. Considering the first three dates as obvious intrusions from a later horizon, the remaining dates are divided in two groups, which correspond to the abovementioned two periods. The majority of the sherds date 4500-4000BC; however the latter three dates display a lower uncertainty (±35y). Moreover, they correspond to the expectation of Rassamakin, so they could be considered a starting point to hypothesize that Dereivka site dated middle of the 4th millennium BC as Rassamakin suggests. A complete list of Dereivka radiocarbon dates is given in Appendix B, Table 8.

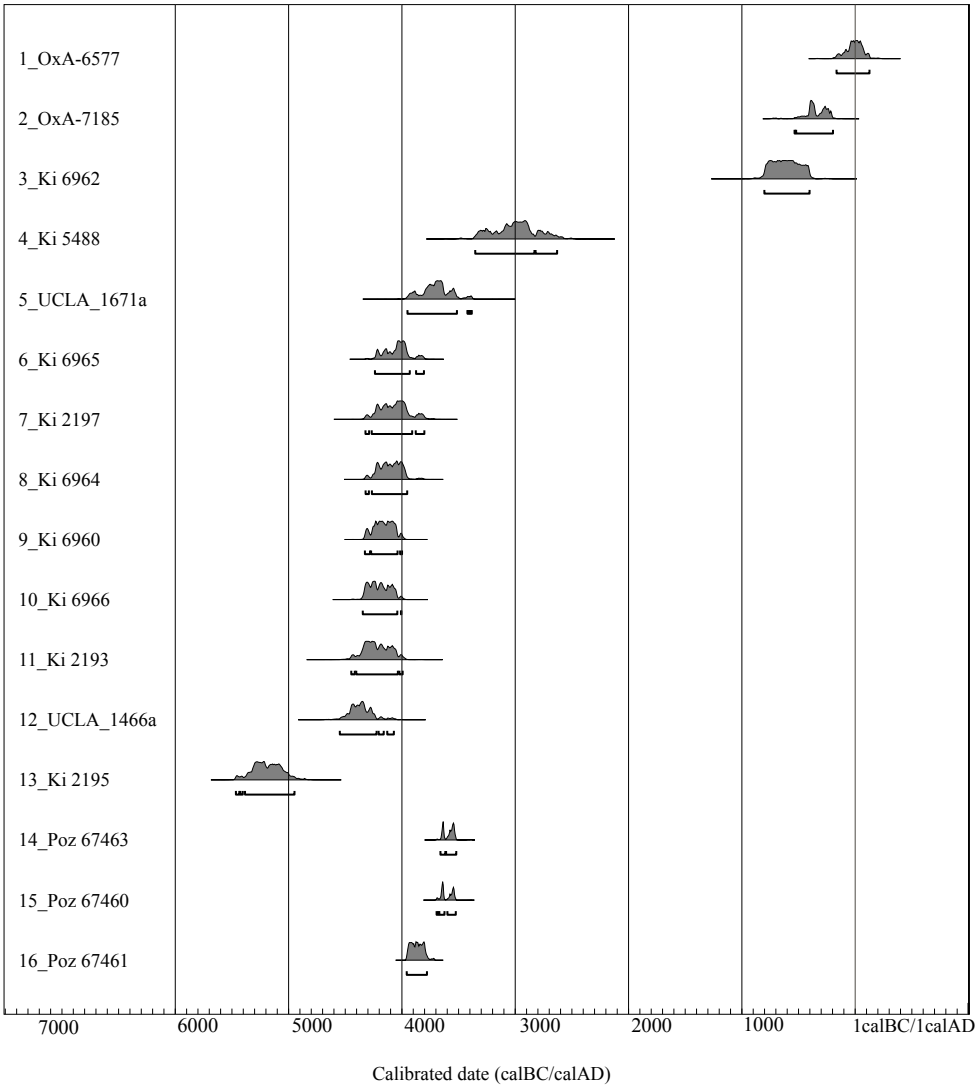


Figure 4.5. The carbon-dates diagram was produced using OxCal v4.2.4 Bronk Ramsey (2013); r:5 IntCal13 atmospheric curve (Reimer et al., 2013). The data have been processed by Kiev and Poznan laboratories (the latter under the framework '*Cluster of Excellence 264 TOPOI*') and by USA laboratories (Anthony and Brown, 2003, p. 56).

4.3 **Molyukhov Bugor site**

Excavators: D. Ya. Telegin (in 1950), V.M. Danilenko (in 1955-56) and T.M. Neradenko (from 1992).

Year of discover: 1950

Years of excavation: 1950; 1955-56 and 1992-present.

Topography: Molyukhov Bugor was located along the Dnieper River, near the village of Novoselitsa, Chigirin District, Cherkassy Region (Kotova, 2003). Specifically, the site was located on the first terrace on the right bank of the Poludenka River, which flows into the Tyasmin River, a major tributary of the Dnieper.

Settlement feature: Molyukhov Bugor belonged to Dereivka culture (Rassamakin, 1999, p. 87). As part of Dereivka culture, and according to Rassamakin (1999), Molyukhov Bugor is dated Late

Tripolye culture and indeed a high number of Tripolye C2 imports have been found in the settlement (Rassamakin, 1999, p. 87 ref. Movsha, 1981; 1993). According to Kotova (2003), at this site there are three phases of occupation dating Neolithic (*ca*. 5480-4580 cal. BC), Eneolithic and Bronze Age periods (Kotova and Videiko, 2003).

Ceramic wares: Among the European-American literature, the information related to Molyukhov Bugor is very scarce. Telegin (1986, p. 60) wrote about Molyukhov Bugor mainly in connection to Dereivka, with the aim of determining the percentage of decorated vessels with cord incisions (25% of the total ceramic assemblage). Overall, the ceramic assemblage is not described in detail; therefore the pictures of the 25 ceramic sherds (Appendix B, Table 2) that have been analysed in the current study will be the main source of information. Figure 4.6 displays a typical vessel that has been found at the site of Molyukhov Bugor.

Investigated sherds: Twenty-five potsherds from kitchenware were selected and analysed. The fabric was usually shell-tempered clay with a dark-black core and decorations on the rim. The identification of the vessel shape was not possible due to the size of the fragments.

Figure 4.6. Typical vessel that has been found in Molyukhov Bugor settlement. Picture has been taken at the archaeological institute in Kiev.

4.3.1 *Radiocarbon dates*

A lower number of radiocarbon dates from Molyukhov Bugor are reported (Figure 4.7). Five faunal bones were analysed by the Institute of Hygiene and Medical Ecology located at Kyiv, Ukraine and the Poznan Radiocarbon Laboratory (PRL). The majority of the dates (1, 2 and 3) cover the periods between the 4500 and 4000 cal. BC, whereas two dates are posterior (4000-3500 cal. BC). The case of Molyukhov Bugor is further complicated by the presence of two horizons (Neolithic and Eneolithic). Consequently, considering the numerous issues about mixing layers, it is very difficult to undoubtedly assign the material to one horizon rather than another. In such cases, the chronology suggested by the archaeologist Rassamakin (1999) by observing the ceramic features appears to be the most reliable option. A list of Molyukhov Bugor radiocarbon dates is showed in Appendix B, Table 9.

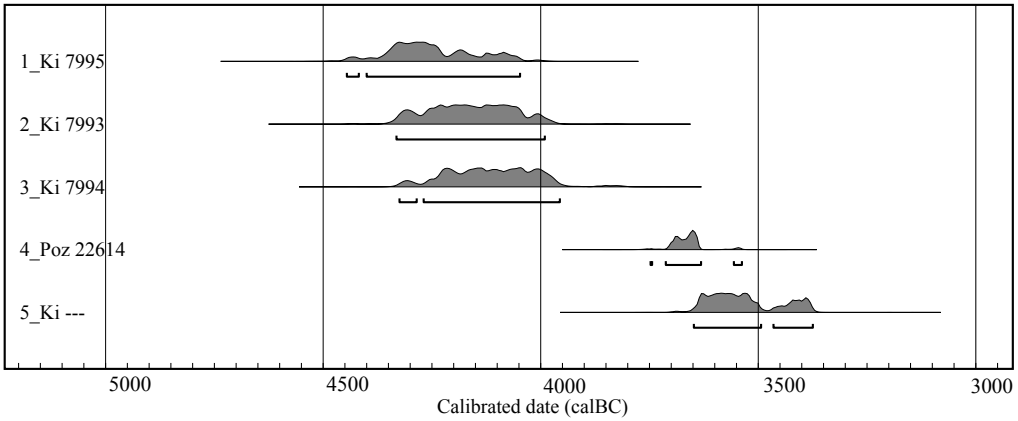


Figure 4.7. The diagram was created using OxCal v4.2.4 Bronk Ramsey (2013); r:5 IntCal13 atmospheric curve (Reimer et al., 2013). The dates have been processed by Kiev and Poznan laboratories (the latter under the framework '*Cluster of Excellence 264 TOPOI*').

4.4 **Mikhailovka site**

Excavators: O.F.Lagodovskaia, O.G. Shaposhnikova and M.L. Makarevich.

Year of discover: 1951

Years of excavation: 1952-1955 and 1960

Topography: The settlement Mikhailovka is situated on the right bank of the small river Podpolnaya, a tributary to the river Dnieper.

Settlement feature: The settlement consists of two parts that are separated by a ravine. Settlement 1 had an extension of 0.5 ha; 6,200 m² have been excavated. Settlement 2 had an extension of 0.2 ha; only 2,000 m² have been excavated. Only in settlement 1 three layers of occupation have been identified. The first layer can be dated to the Late Eneolithic and it is attributed to the Lower Mikhailovka culture (3800/3700 – 3400 BC; see Table 3.2). The second layer contained objects associated to an early phase of the Yamnaya culture; finally the third layer is attributed to a late phase of the Yamnaya culture (3100 – 2500 BC). The second and third layers partly overlap. In settlement 2 only materials from the Yamnaya culture were found. Each layer of settlement 1 include several remains of dwellings; even one stonewall was documented. The wall was constructed during the Yamnaya culture.

Ceramic wares: Mikhailovka ceramic wares have been carefully analysed and grouped according to the characteristic ceramic features and Tripolye findings (Rassamakin, 1999) allowing a distinction of the three different periods (Figure 4.8). Overall, the archaeological materials from Mikhailovka I and II demonstrate the Tripolye culture influence (Rassamakin, 1999, p. 117), indeed corded decorated vessels, together with spindle whorl and statuettes typical for Tripolye culture, were found. In contrast, the third later horizon of Mikhailovka shows original ceramic wares probably related with the Repin culture of the Volga area (Rassamakin, 1999, p. 125), which suggests a migration from the eastern area. Moreover, the ceramic findings appear to imitate both the ceramics of the local variant of the Maikop-Novosvobodnaya culture in the lower Volga area and the Tripolye culture in the west;

indeed, during the Early Bronze Age, the area of the Mikhailovka culture was a possible "zone of double influence" (Rassamakin, 2002, pp. 57–58). Several shapes of vessels were found in Mikhailovka horizons: mainly pots, amphorae and dishes. The typical shape is rounded; both the belly and the bottom are smoothed. Most of the ceramic vessels lack of ornamentations (Telegin et al., 1986, p. 60), however the most common ornaments are comb impression and cord decorations; they appear only on the rim or in the area between the belly and the neck (Telegin, 2002, p. 36). The ceramic surface is smoothed and sometimes polished.

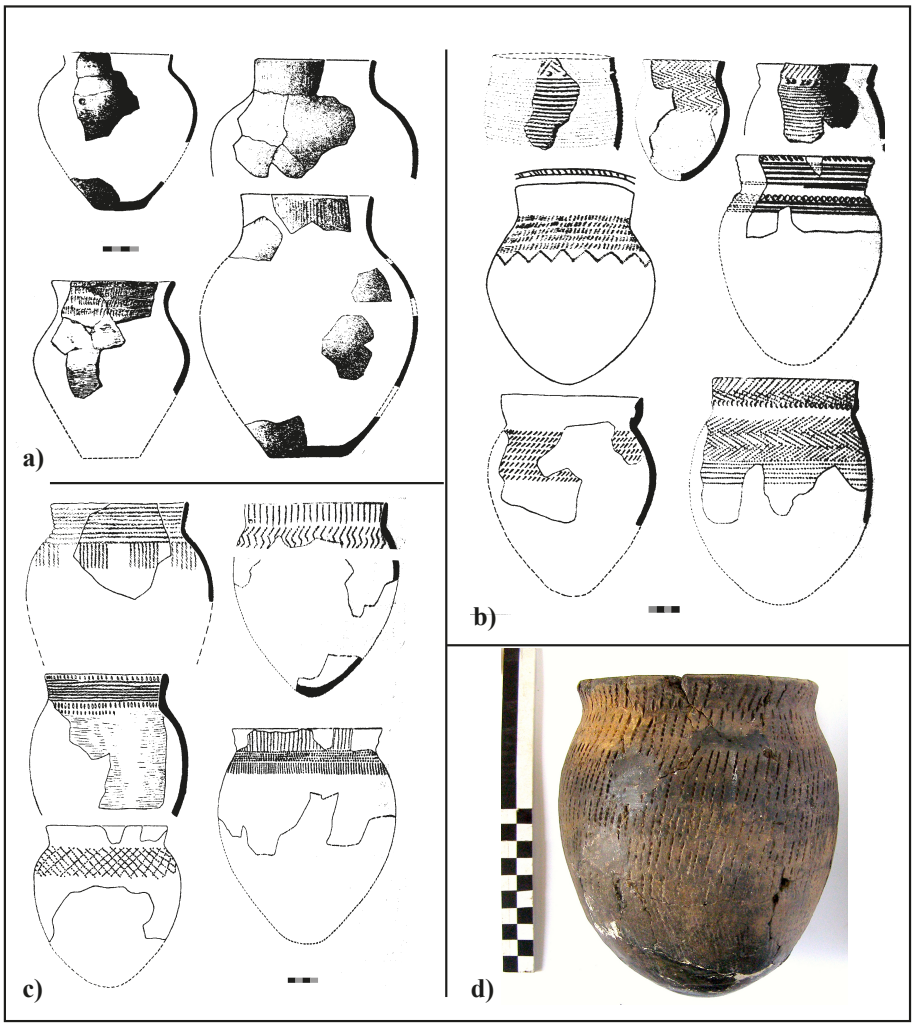


Figure 4.8. Reconstruction of vessels from the three Mikhailovka horizons; a) Mikhailovka I; b) Mikhailovka II, c) Mikhailovka III; d) shows an example of typical Mikhailovka II vessels.

Investigated potsherds: Eighty potsherds from kitchenware, of which thirty-six from Mikhailovka I, twenty-one from Mikhailovka II and twenty-three from Mikhailovka III. The majority of the analysed sherds were collected from the upper body of the vessel (see Appendix B, Tables 3, 4 and 5). They were generally decorated. The majority had a grey colour with a darker core. Some sherds were characterized by a red colour. The identification of the vessel shape was not possible.

4.4.1 *Radiocarbon dates*

Dating of Mikhailovka settlement, as for Molyukhov Bugor, is extremely problematic because of the overlapping horizons. Looking at the dates in Figure 4.9, the chronological issue is suddenly clear. Moreover, the presence of three horizons that overlapped (especially in correspondence of Mikhailovka II and III) makes the chronological identification even more complicated. The radiocarbon dates (Appendix B, Table 10) were carried out by the laboratories of Kiev and Poznan. The dated bones were found in the earlier layer (Middle Eneolithic; 3800/3700-3500/3400 BC); however, according to the chronology suggested by Rassamakin, only bones 2 and 3 are suitably dated, the remaining five bones belong to later periods, so Mikhailovka II and III (Figure 4.9).

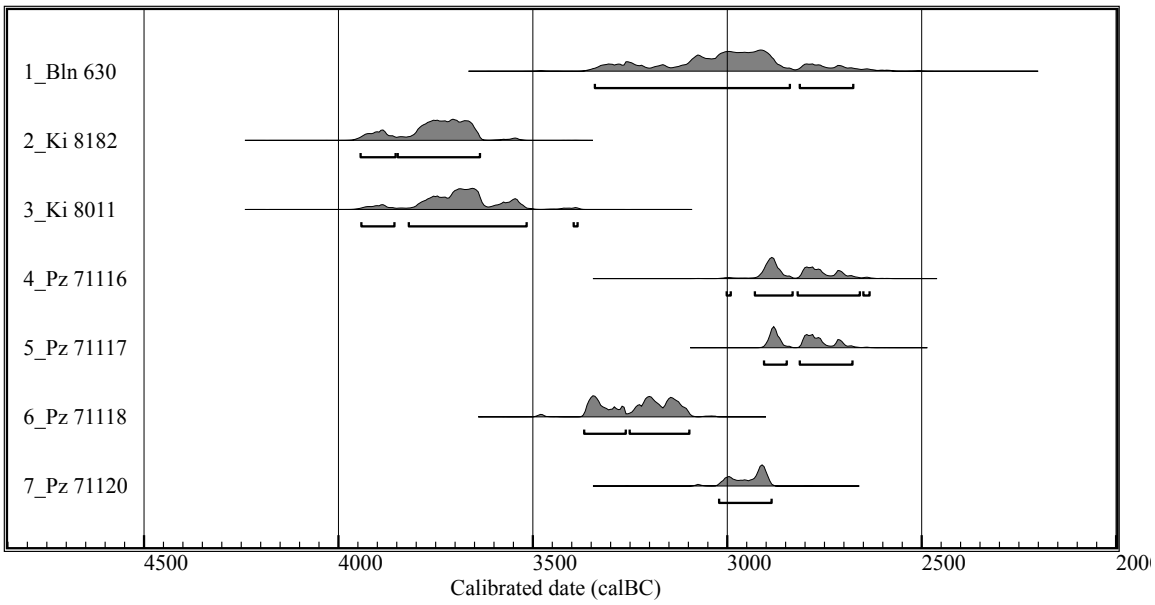


Figure 4.9. Diagram created using OxCal v4.2.4 Bronk Ramsey (2013); r:5 IntCal13 atmospheric curve (Reimer et al., 2013). The data have been mostly processed by Kiev and Poznan laboratories (the latter under the framework '*Cluster of Excellence 264 TOPOI*'), one by USA laboratories (Anthony, 2003; pp. 56).

4.5 **Nizhniy Rogachik site**

Excavators: D.Ya. Telegin and O.G. Shaposhnikova (Shaposhnikova, 1972, 1963; Spitsyna, 2010; Telegin, 1957).

Year of discover: 1957

Years of excavation: 1957

Topography: Nizhniy Rogachik was located on a plateau above River Konka and Dnieper, which several times was flood during the construction of the dyke, involving the destruction of a considerable number of archaeological sites. The information about this site comes from two unpublished excavation reports (Shaposhnikova, 1963; Telegin, 1957) and one article (Spitsyna, 2010).

Ceramic wares: Part of the ceramic fragments can be compared with those of the middle layer of Mikhailovka (Shaposhnikova, 1963; Spitsyna, 2010; Telegin, 1957). They are characterised by flat bottoms but pointed bottoms also occur. The fragments show a relatively thick wall (1 cm). The ceramic was tempered with sand, often decorated in the upper part of the vessel. They are richly ornamented using comb, twisted or simple cord. The typical decoration was realized by drawing a line on the surface of the vessel. However, according to Rassamakin, the ceramic features are very different from the other cultural groups, for this reason Nizhniy Rogachik has been considered an isolated group.

Investigated potsherds: Thirty potsherds from kitchenware. The majority of the analysed sherds were collected from the upper body of the vessel (see Appendix B, Table 6). They were not decorated except for few sherds characterized by a very simple decoration of the rim. The identification of the vessel shape was not possible.

4.6 **Generalka site**

Excavators: O.G. Tuboltsev and Peshkov.

Year of discover: 1999.

Years of excavation: 2000-present.

Topography: The site of Generalka was located on the Khortytsia Island (Figure 4.10a). The total archaeological area is 7176 m^2, however only a limited area (until 2013 only 292 m^2) have been intensively explored. Therefore, the information related to the site of Generalka is still incomplete and so the studies and the consequent interpretations have to be considered preliminary as only the data collected until 2013 have been properly analysed (Tuboltsev, 2015, in prep.). The area presents numerous ditches (Figure 4.10b); however only seven have been partly excavated until 2013. It is worth to notice that such a system of ditches does not have direct analogy with any of the known Ukrainian sites, so the interpretation remains preliminary.

Ceramic wares: A consistent amount of ceramics and bones have been found in the occupation layer of Generalka site. In the present state of research, a total number of 3286 ceramic fragments, including more than 130 collars, have been collected. Looking at the small variety of types and ornaments, the entire collection of ceramics found on the site of Generalka can be described as fairly uniform. The ceramic ware is highly dense and heavy with an average thickness of 1.2 – 1.5 cm. The colour after firing is dark, ranging from light grey to dark grey. The ceramic paste was temperate with sand, grog, debris, and lime, and rarely with organic matters such as shells. A number of fragments have been reconstructed to form a total of 12 pots, which allows the definition of the main shapes and important features of the vessels (Tuboltsev 2015, in prep.). Consequently, two main typologies of pots have been recognized (Figure 4.11): *Type A* characterized by a typical egg-body and a high neck – the transition from the body to the neck can be additionally distinguished in L-shape or S-shape –

and *Type B* characterized by a broader body and a short-neck. The base of the vessels is typically pointed or slightly flattered. The Type A vessel shape, that is also the most common in Generalka site (73.3 %), is typical of Yamnaya manufacturing (Tuboltsev 2015, in prep.).

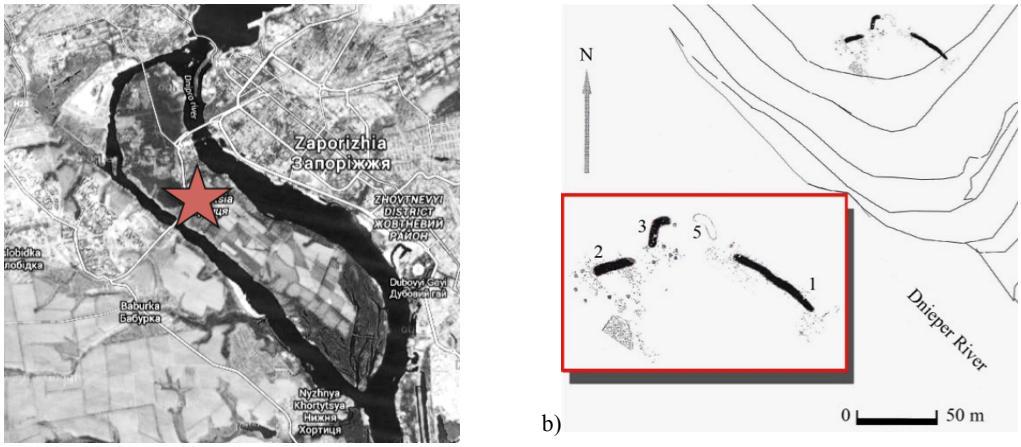


Figure 4.10. a) Khortysia Island where Generalka was located, and b) Area where the settlement is located. The red square highlights the distribution of the ditches. Extracted from Tuboltsev 2015, in prep.

Investigated potsherds: Thirty-five potsherds from kitchenware were selected. The majority of the analysed sherds were collected from the upper body (see Appendix B, Table 7). The majority of the sherds did not show any decorations. The identification of the vessel shape was not possible.

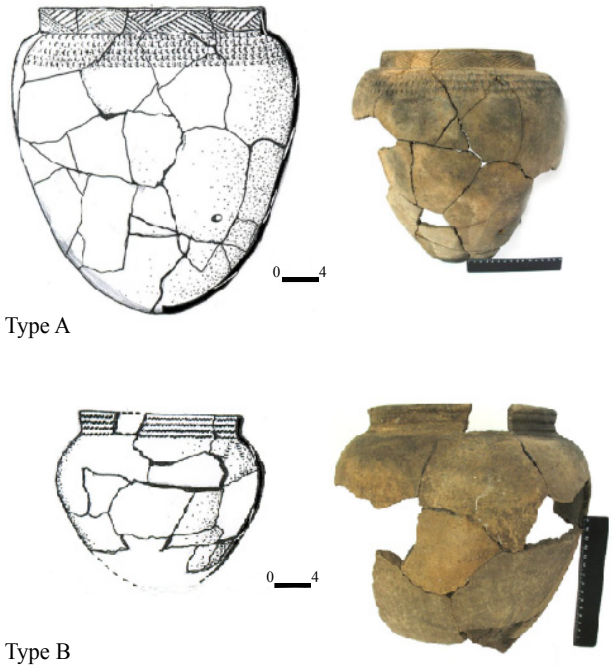


Figure 4.11. Common vessel typologies found in Generalka settlement (Tuboltsev, 2015 in prep.).

4.6.1 *Radiocarbon dates*

Only eight sample bones (of which one has not produced any data) have been analysed from Generalka so far. Looking at Figure 4.12, it appears that the majority of the sample bones date between the 3000 and the 2300 BC matching the exact date of the ceramic sherds, confirming the chronological collocation suggested by Rassamakin. A list of Generalka radiocarbon dates is showed in Appendix B, Table 11.

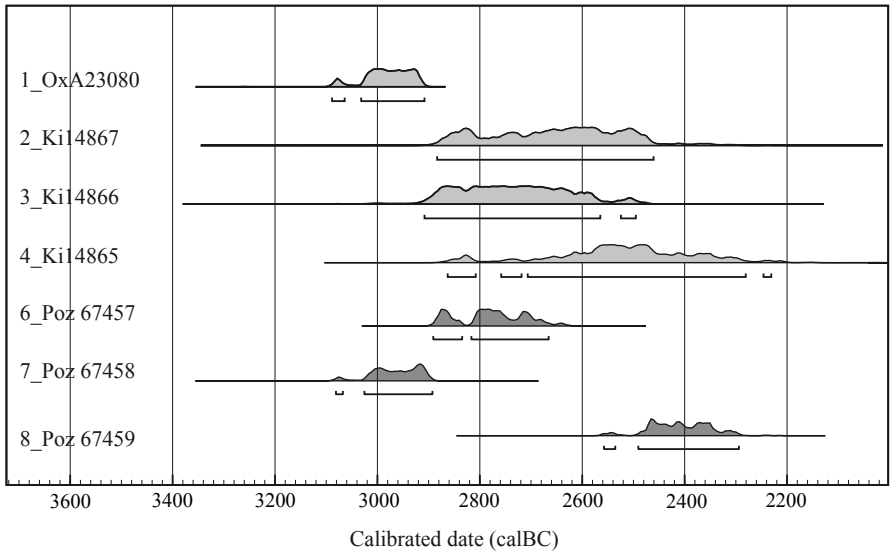


Figure 4.12. Diagram created using OxCal v4.2.4 Bronk Ramsey (2013); r:5 IntCal13 atmospheric curve (Reimer *et al,* 2013). The data have been processed by and Poznan and Oxford laboratories (under the framework '*Cluster of Excellence 264 TOPOI*').

4.7 **Conclusion**

The often-mentioned difficulties, that generally prevented the developing and understanding of ancient Eurasian events and their chronologies, have largely complicated the collection of the evidence about the five investigated archaeological sites and the ceramic potsherds. Specifically, (i) the lack of materials; (ii) the unusual overlapping of horizons due to the peculiar soil (the *chernozem*) that, apparently, prevents the proper distinction between archaeological layers; (iii) the construction of the hydroelectric station, in 1920-1940, that often allowed only surveys and no systematic excavations and (iv) the restricted European literature associated with the North-Pontic region. Nevertheless, using the available literature, a description of the settlements and ceramic wares, specifically investigated in the current project, has been drawn.

Summarizing; this Chapter together with Chapter 3, presented the description of the investigated cultures and archaeological sites (Table 4.1); two located in the forest-steppe and dated Middle Eneolithic (Dereivka and Molyukhov Bugor) and three located in the steppe area and dated Middle, Late Eneolithic and Early Bronze Age (Nizhniy Rogachik, Mikhailovka and Generalka). Specifically, the ceramic sherds analysed in the current project were described. The latter description provided

important information about the ceramic production and general manufacturing development of the prehistoric communities lived in the area of the North-Pontic region. Indeed, it is worth of note that the basic manufacture of the ceramic fragments, largely characterized by a dark core and a burned surface, is a common feature that indicates a non-uniform heating of a possible unsophisticated furnace. Additionally, great attention has been focused on the chronology both using existing radiocarbon dates, applied on bones, shells or charcoals recovered from the horizons where the investigated pottery were recovered, and the chronological partition suggested by Rassamakin, who dated the investigated potsherds by the examination of the ceramic features. Considering the complications related with the radiocarbon dates, the chronology suggested by Rassamakin is mainly considered in the current project.

CHAPTER 5

RECONSTRUCTION OF THE SUBSISTENCE ECONOMY OF THE NORTH-PONTIC REGION: EXISTING EVIDENCE

5.1 **Introduction**

The process of Neolithization, which included the introduction of agriculture and the domestication of animals such as cattle, sheep, goats and pigs (Thomas, 2003), that brought to a techno-economic shift from hunting-gathering to food production, began in several centres of the Near East at around the 9th millennium BC (Bendrey, 2011; Gerbault et al., 2011; Kuzmina, 2003; Vigne, 2011). Indeed, it is widely believed that the process of Neolithization was mainly a spreading process that from Anatolia (Figure 5.1) expanded towards Old Europe and Eurasia (Harris, 2011).

The first evidence of domestication in the western Eurasia - the productive revolution (Stanko, 2003) - is dated around the 6th millennium BC (Bunyatyan, 2003; Kotova, 2003); sheep, goats and cattle bones together with domesticated grains of wheat, barley and millet, were found in several sites of the Bug-Dniester cultures (Kuzmina, 2003, p. 203). Thus, according to the majority of the scholars (Anthony and Brown, 2003; Bendrey, 2011; Bunyatyan, 2003; Kotova, 2003; Kuzmina, 2003; Velichko et al., 2009; Vigne, 2011) by the beginning of the 4th millennium BC, the process of Neolithization, had become established in Western Eurasia, and specifically, during the Eneolithic and Early Bronze Age (ca. 4550-2300/2200 BC), animals and plants were generally domesticated in the North-Pontic region. However, other scholars have suggested to be more cautious in offering conclusions, arguing that some areas of the North-Pontic region might have been characterized by a later introduction of domesticated animals (e.g. Wechler, 2001) depending on the local-regional ecosystem (Rassamakin, 1999). Consequently, the addressing questions are about the extent of

domestication, the exploitation of secondary products, the nature of the economic resources and the balance between different economic activities in relation to each specific environment (as discussed in Chapter 3, Section 3.3).

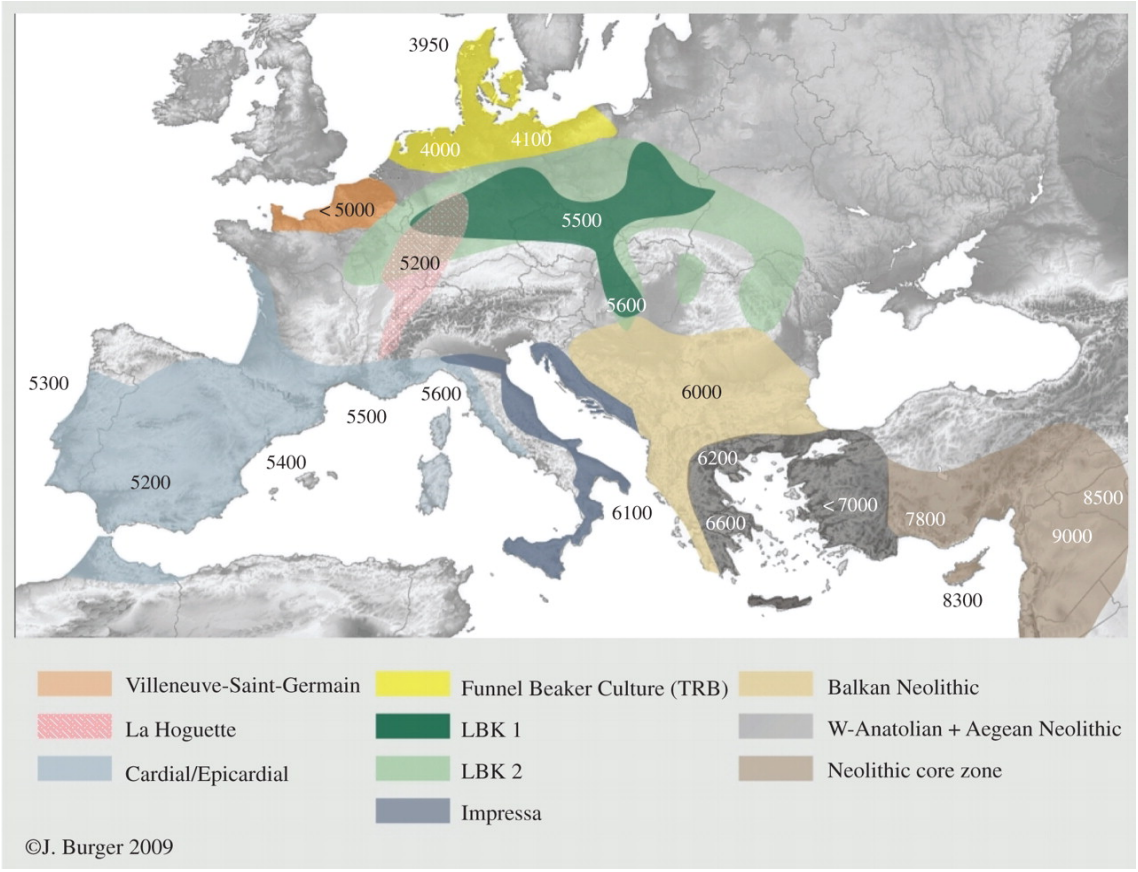


Figure 5.1. Earliest European Neolithic cultures. Dates refer to the first evidence for agriculture and/or the presence of Neolithic assemblages (in Burger & Thomas, 2011; from Gerbault et al., 2011).

As part of an interdisciplinary study, the main objective of this Chapter is to present the latest existing evidence in order to offer an updated picture of the recent researches and therefore to describe the subsistence economic strategies of people that lived in the North-Pontic region, during the Eneolithic and the Early Bronze Age, according to the existing evidence. The specific aims of this Chapter are:

(i) Report the existing archaeozoological and botanical records recovered from the investigated sites, excluding Nizhniy Rogachik for lack of faunal and botanical evidence;
(ii) Report the existing isotopic studies applied on human bones;
(iii) Discuss the hypothetical subsistence economy of people lived along the Dnieper River by integrating existing archaeozoological, botanical and isotopic evidence in relation to the reconstruction suggested by several archaeologists and discussed in Chapter 3.

5.2 Archaeological evidence

Several studies have been carried out on the archaeological materials by archaeologists interested in the understanding of the ancient Eurasian lifestyle (e.g. Bunyatyan, 2003; Kuzmina, 2003; 2006, 2002, 1999, 1996, 1994). The general belief is that the subsistence economy of the North-Pontic region, during the Eneolithic and the Early Bronze Age, was various, in an balance between plant and animal exploitation, including gathering, hunting, fishing and herding activities, in order to adapt the lifestyle to the local environment (as discussed in Chapter 3, Section 3.3). In this Section, the archaeozoological records are reported, as one of the methods to investigate domestication and consequent dietary habits of ancient populations. Indeed, the analysis of bones can provide several evidence coming from the study of the size and the shape of the bones (Mays, 2010; O'Connor and O'Connor, 2008), their location and horizon, the biological analysis such as isotopic approaches or the radiocarbon analysis.

Since one of the addressing questions of the current project concerns the horse domestication, a great attention is directed to the analysis of equine bones. At this purpose, although a more detailed explanation about the difficulties in detecting the earliest domesticated horses in Eurasia will be offered in Section 5.7, in order to better understand the faunal records discussed in the subsequent Sections, it is essential to highlight that the identification of domesticated horses is not possible by simply analysing the size or shape of the skeletons (Olsen, 2006). Indeed, unlike ruminants such as sheep/goats or cows, which lose horns or change dramatically in size, domesticated horse skeletons are not distinguishable from the wild because there is not distinct morphological change, especially in the initial domestication stages (Bökönyi, 1974; Clutton-Brock, 1999; Olsen, 2006). As a result, it is practically impossible to detect domestication from skeletal remains alone and other lines of evidence are required. For this reason, in this Section, equine bones are separately considered rather than including them in one specific category (e.g. domesticates or wild animals).

Two archaeozoological methods exist to estimate the number of bones (Klein and Cruz-Uribe, 1984): the minimum number of individuals (MNI) and the number of identified specimens (NISP). The first one is the more parsimonious because it counts the least number of individuals but, at the same time, it could involve loss of data. In contrast, the NISP method counts all the fragments recovered in an archaeological layer, being less accurate (Marshall and Pilgram, 1993). Both methods are subject to fragmentation effects (Marshall & Pilgram, 1993); however, MNI might be a less representative descriptor of relative element frequency than NISP in highly fragmented assemblages (Marshall & Pilgram, 1993).

The faunal assemblages of the investigated sites (Mikhailovka I, Mikhailovka II&III and Generalka) are characterized by a correspondence between the MNI and the NISP, therefore in this case only one method is reported (we have chosen the NISP because Generalka faunal records have been so far counted using only this method); however Dereivka and Molyukhov Bugor display a significant inconsistence between MNI and NISP values. Since it was not possible to define the degree of the fragmentation of the bones, in this case both values are presented. Therefore, in the subsequent Sections, the description of the available faunal assemblages recovered from the investigated sites will be provided.

5.3 **Dereivka faunal assemblage**

The full faunal records recovered from Dereivka determined by Bibikova, have been published in the monograph about the settlement, written by Telegin (1986) after his excavations in 1960-61 and 1967. Dereivka is considered by many Eurasian archaeologists (e.g. Anthony & Brown 1991; Anthony 2007) one of the possible centre of horse domestication; nevertheless, other studies (e.g. Levine, 1990) support the idea of a subsistence economy mainly based on hunting, where also horses were exploited as wild animals and very likely as meat source.

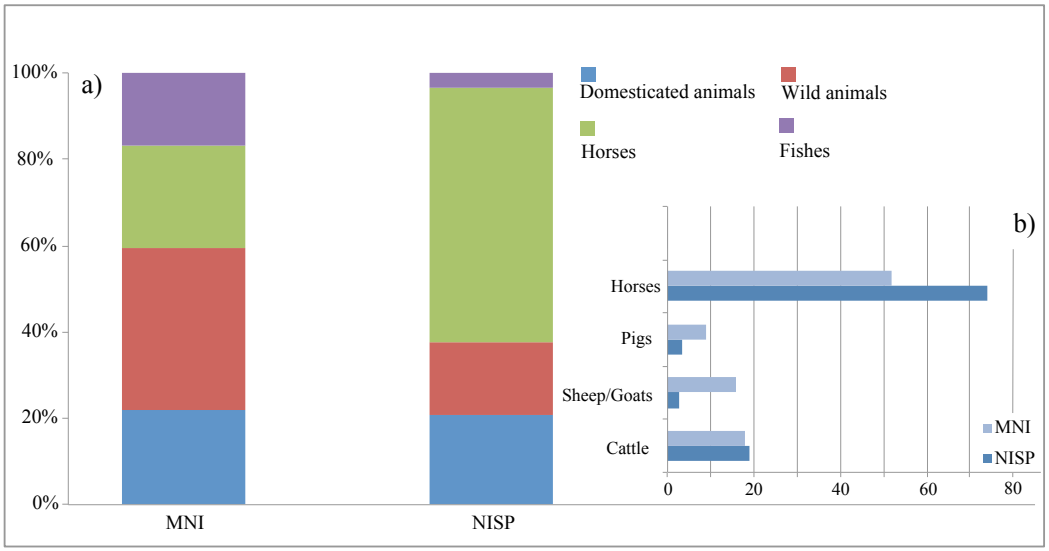


Figure 5.2. Percentages of the different classes of animals inferred from faunal records in Dereivka site. Diagram a) shows the animals grouped in broader chatergories b) shows the percentages of the domesticated animals (cattle, sheep/goats and pigs) together with horses.

The initial reason that led many scholars to believe that Dereivka horses were domesticated is related to the high amount of equine remains discovered during the excavations (Telegin et al., 1986, p. 84). However, Figure 5.2a reveals that only the NISP confirms the great percentage of equine bones (ca. 60%); in contrast the MNI is much lower, roughly 22.5% (Appendix C, Table 1). Figure 5.2a also reveals that domesticates comprised roughly the 20% of the total amount of bones, while wild animals comprised the 17-39% depending on the counting method. Fish bones were found in an appreciable

amount (3.5 to 17% depending on the counting method) indicating exploitation of aquatic resources (Figure 5.2a). Among the domesticated animals, cattle predominated over sheep, goats and pigs (Figure 5.2b).

It is worth noticing that the proportion of wild-domesticates is considerably affected by the status of the equids. Assuming that horses were wild, wild animals predominated over domesticates, using both counting methods. In contrast, if horses were domesticated, domesticates predominated over wild animals.

5.4 Molyukhov Bugor faunal assemblage

In the case of Molyukhov Bugor, three publications about faunal records exist, which are: (i) Bibikova (1963) after the excavation of V.N. Danilenko in 1955; (ii) Zhuravlev & Markova (2000), after excavations by T.N Neradenko in 1994-96 and (iii) Zhuravlev (2008), which displays the material of the last on going and not published yet excavation by Neradenko. The faunal records are displayed in Appendix C, Table 2. Figure 5.3a reveals that the percentage of equine bones is roughly 14%. Figure 5.3a also reveals that domesticates comprised the 33-48% of the total amount of bones (depending on which counting methods), while wild animals comprised the 37-65%. Figure 5.3b reveals that cattle predominated significantly over sheep/goats and pigs. Finally, no fish bones were found.

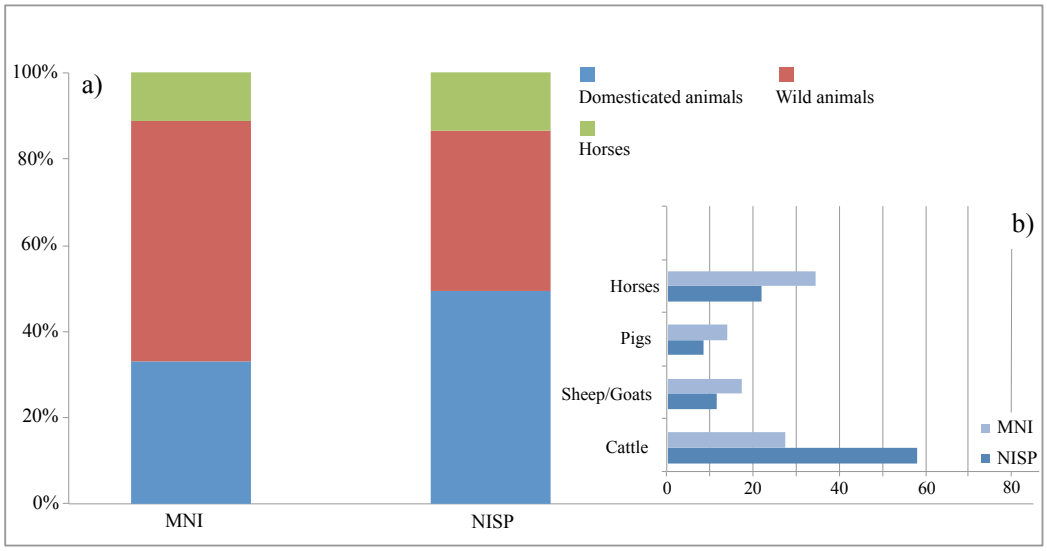


Figure 5.3. Percentages of the different classes of animals inferred from faunal records in Molyukhov Bugor site. Diagram a) shows the animals grouped in broader chatergories and b) shows the percentages of the domesticated animals (cattle, sheep/goats and pigs) together with horses.

Also in this case, it is worth noticing that the proportion of wild-domesticates is affected by the status of the equids. Interestingly, assuming that horses were wild, wild animals predominated over domesticates, using both the counting methods. In contrast, if horses were domesticated, domesticates

predominated over wild animals only looking at the NISP; the MNI value reveals that the wild animals predominated over domesticates, whether considering domesticated or wild horses.

5.5 **Mikhailovka faunal assemblage**

Faunal records from Mikhailovka I, II and III have been published by Bibikova and Shevchenko (1962) after the excavation by Lagodovskaia, Shaposhnikova and Makarevich in 1952-1960.

In the case of Mikhailovka I (Appendix C, Table 3), the faunal records counted by using both MNI and NISP methods, correspond**.** Figure 5.4a reveals that domesticates predominated over wild animals (93% *vs*. 5%). The percentage of equine bones was insignificant (ca. 2%) compared with the sites previously considered. Also in this case, the faunal assemblage did not comprise fish bones. Examination of Figure 5.4b reveals that sheep/goats predominated significantly over cattle and pigs.

As already mentioned in Chapter 4, Section 4.4, the materials of Mikhailovka II and III overlap in the same layer creating many misunderstandings. Therefore, the description of the faunal records, from Mikhailovka II and III, has always been considered together. In addition, also materials from the Middle and Late Bronze Age have been found in Mikhailovka III horizon (Rassamakin, 1999, p. 153), which could explain the general increase of faunal records in the later two horizons.

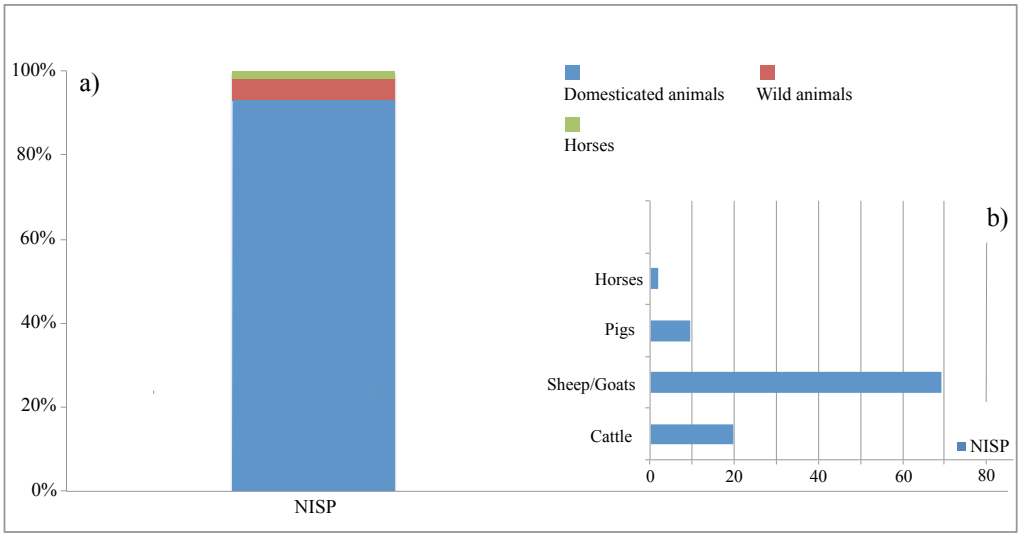


Figure 5.4. Percentages of the different classes of animals inferred from faunal records in Mikhailovka I site. Diagram a) shows the animals grouped in broader chatergories and b) shows the percentages of the domesticated animals (cattle, sheep/goats and pigs) together with horses.

The MNI and NISP also correspond in the case of Mikhailovka II and III (Appendix C, Table 4). Domesticates predominated over wild animals (Figure 5.5a), displaying a percentage of roughly 87% *vs*. ca. 2%; horses comprised the ca. 10% of the total faunal records. Figure 5.5b reveals that cattle predominated over sheep/goat and pigs. Summarizing, the faunal remains from the upper layers of

Mikhailovka reveal that domesticates predominated during both periods; cattle prevailed over sheep and goats while equine bones increased compared to the earlier horizon.

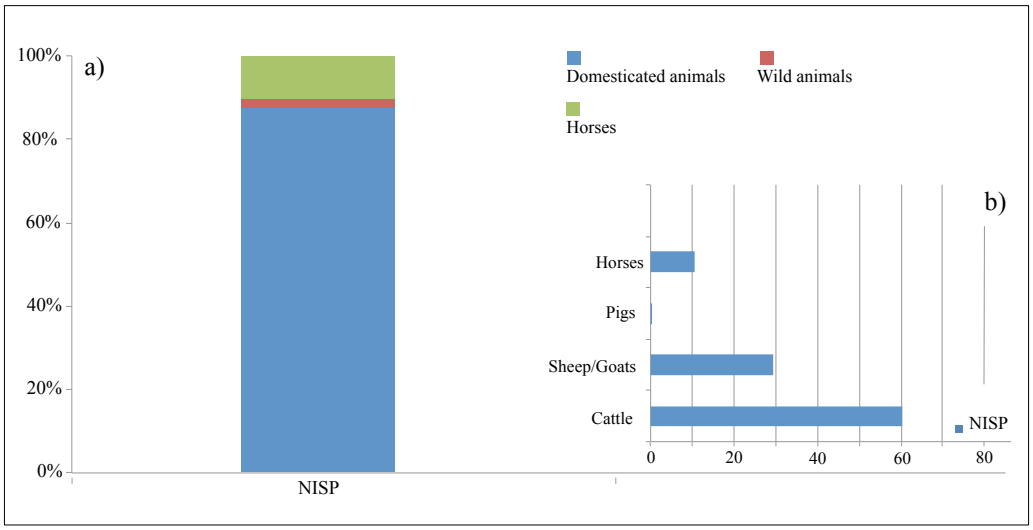


Figure 5.5. Percentages of the different classes of animals inferred from faunal records in Mikhailovka II&III site. Diagram a) shows the animals grouped in broader chatergories and b) shows the percentages of the domesticated animals (cattle, sheep/goats and pigs) together with horses.

5.6 **Generalka faunal assemblage**

Generalka was discovered in 1999 and scarce and unpublished studies have been so far carried out (Tuboltsev, 2006; Tuboltsev 2017 in prep.). In this context, the archaeozoological materials will be described using the studies carried out from the 2009 to the 2011 by M. Hochmuth and P. Morgenstern (Kaiser, 2010). All bones are fragmented and the NISP percentage is the only existing (Figure 5.6). Figure 5.6b reveals that cattle constituted the higher percentage (80%), following by sheep and goats (15%). Overall, domesticated animals (ca. 95%) predominated (Appendix C, Table 5). Among the ruminants, cows prevailed over bulls and a high number of bones attributed to animal in slaughter age (36-48 months) suggested an economy mainly based on meat and dairy fat production (Tuboltsev 2017 in prep.). The low percentage of horses (ca. 2.2%) can suggest a secondary use of these animals (maybe as transport). Also aquatic animals have been found in a very low amount (only 12 fragments).

The subsequent Section will focus on the horse domestication issue, especially in relation to Dereivka site. As mentioned, the significant percentage of equine bones recovered from Dereivka site, originated an interesting discussion about horse domestication in the North-Pontic region that is still ongoing.

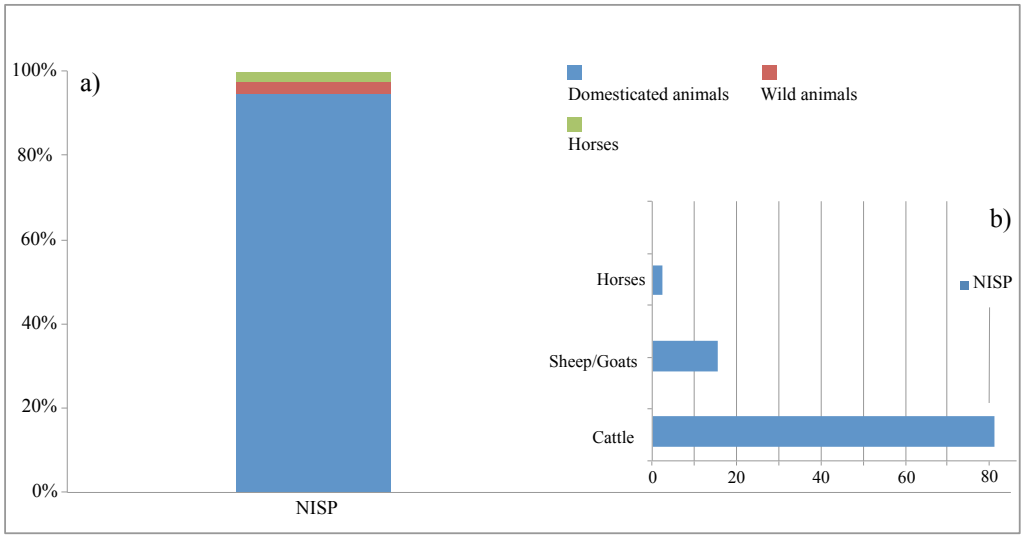


Figure 5.6. Percentages of the different classes of animals inferred from faunal records in Generalka site. Diagram a) shows the animals grouped in broader chatergories and b) shows the percentages of the domesticated animals (cattle, sheep/goats and pigs) together with horses.

5.7 Horse domestication evidence

As already pointed out in the Introduction (Section 1.2.1.1), horse domestication is a crucial matter in the archaeology of the Eurasian steppe. Indeed, it is considered a major event that changed the way of living both socially and economically. Horses were not only used as source of food but a number of other different purposes (such as transport to help in herding activities or to realize long distance trades) had surely led ancient people to exploit horses as domesticated animals (Kuzmina, 2003; Renfrew, 2002).

Many researches have been carried out on Eurasian prehistory in order to get information about this important event; unfortunately tracing horse domestication is extremely complicated. Concerning the direct evidence (Levine, 1999b, p. 9), the earliest unambiguous dateable direct evidence for horse domestication date back to the end of the 3rd millennium BC and the second half of the 2nd millennium BC (Kuzmina, 2003, p. 208; Levine, 1999b, p. 9), so to the Late Eurasian Bronze Age. Several chariot burials in southern Urals and Northern Kazakhstan, and wheeled transports buried together with complete horse skeletons, cheek-pieces and armaments, including spears, arrows and daggers, testified that the exploitation of horses for tracking purposes occurred from the Late Bronze Age onward (Anthony, 2007, 1995; Benecke and von den Driesch, 2003; Kuzmina, 2003). Therefore the focus must move on earlier periods. Unfortunately, direct evidence from earlier periods is absent. Consequently, over the last decades, Eurasian archaeologists and scholars have mainly employed numerous indirect or false direct evidence as indicators for early horse domestication.

5.7.1 *Indirect and false direct evidence in Dereivka*

Indirect evidence include the characterization of bones and artefacts and involve analytical methods such as population structure or mortality patterns, osteometrical analysis, biogeographical distribution, relative proportion in archaeological deposits, bit wear and artefact. More specifically, indirect evidence for the presence of domesticated horses are: (i) the absence of old horses in the faunal records; (ii) the presence of a high proportion of male horse skulls; (iii) the presence of objects identified as bridle cheek pieces; (iv) morphological analysis comparing the horses with other equid material and their association with other domesticates; and finally (v) the relatively high percentage of horse bones and teeth in the deposit (Levine, 2005, p. 11). Regarding the false direct evidence, only four types are conventionally accepted as proof of horse domestication: horse-head sceptres, horse burials not associated with tack, cheek pieces and bit wear. However according to Levine (2005, p. 7) false direct evidence is not usable as direct evidence because scarcely reliable.

As mentioned in Section 5.7, plenty of indirect evidence or false direct evidence (Levine, 2005) have been identified in Eneolithic sites and cemeteries of Eurasia and more significantly in Dereivka site. Dereivka has been central to discussions of horse domestication since 1967 (Anthony and Brown, 2003, 1991; Bibikova, 1969; Bökönyi, 1974; Levine, 1990; Rassamakin, 1999; Telegin et al., 1986). Unfortunately, evidence of horse domestication from Dereivka is primarily inferred from bone and artefactual evidence (Levine, 2005) and mainly from the high relative abundances of equine bones (Levine, 2006, p. 193; Telegin et al., 1986, p. 84). However, the high proportion of equine bones might be interpreted as arising through increasing horse hunting rather than its domestication (Levine, 2006, p. 193). In addition, interpretations of Dereivka equine records are further compromised by the fact that a large number of bones were lost due to ineffective curation post-excavation. After Bibikova (1986), and before the lost of part of the bones, Levine carried out zooarchaeological metrical analyses of 900 bones and teeth in Dereivka (Levine, 2005, 1990) during which she distinguished between equine bones of adult males and females discovering that the ratio between males and females was 9:1. The latter was interpreted as evidence of a selective hunting technique or ‘stalking model’, in which the pray is approached by stealth and killed (Levine, 1990, p. 736). In addition, Levine pointed out that the majority of the equine teeth from Dereivka belonged to individuals between 5 and 8 years old, which are the most productive years of a horse (Levine, 1990, p. 738). It was reasoned that if the horses from Dereivka were domesticated for meat they would have been killed at the age of 2 or 3 years old, when maximum size and hence maximum meat yield was reached, and if they were domesticated for secondary products, they would have been slaughtered after the age of 15 or 16 years old in order to exploit the secondary products as long as possible. Therefore, the faunal analysis carried out by Levine pointed to the Dereivka horses being a wild assemblage. However, worth to mention are the issues related to the archaeozoological approach. The

analysis of equine bones is not as straightforward as in the case of cows and sheep/goats that changes their morphology (e.g. horns become smaller in domestic sheep and goats). It is not possible to distinguish between wild and domesticated equine bones, especially at the first stages of domestication (Bökönyi, 1974; Clutton-Brock, 1999; Olsen, 2006). Also the mortality pattern, which is frequently used to assess early domestication of herbivores, by analysing bones and teeth (Collier and White, 1976; Meadow, 1989; Payne, 1973; Perkins Jr and Daly, 1968), is more complex in the horses (Levine, 1999b; Olsen, 2006). Usually, livestock herds are identifiable by (i) a high number of young males, which are often slaughter when they are juvenile (before 4-5 years old), in order to save grazing land and fodder, and (ii) a high number of old females necessary for breeding and milking (Olsen, 2006; Zeder, 2006a, 2006b). However, in the case of horses, the presence of robust canines in adult males do not develop until the age of 4-5 years and the horse sex can only be determined by the pelvis shape, which do not exhibit strong dimorphism (Anthony, 2007; Olsen, 2006). Unfortunately, the lost of the equine bones in the 90', does not allow repeating the metrical analysis of faunal records; therefore Levine's examination is the only existent to which refer.

Other attempts in interpreting the indirect evidence have been carried out over the past decades. In 1964, remains of a stallion, head and left foreleg, placed together with dog remains and perforated antlers tines (Telegin, 1986) were discovered in Dereivka site, and interpreted as Dereivka being centre of horse domestication. Indeed, the "Head and Hoof" deposits are well known across Eurasia from later periods and they are usually attributed to a ritual horse feast (Anthony and Brown, 2003, p. 55). The hypothesis was subsequently reinforced by the extensive evidence of bit-wear on the lower second pre-molar teeth of the stallion (Anthony et al., 1986, p. 295; Telegin et al., 1986, pp. 82–87). Later discussions rejected the above-mentioned indirect evidence (Kuzmina, 2003, p. 213; Levine, 1999b, pp. 9–14). Indeed, it has been suggested that since these artefacts have been also found in burials with no horse bones they may have had no connection with horses (Dietz, 2003, 1992; Levine, 1999a; Rassamakin, 1999). Moreover, their reconstruction as cheek-pieces has been considered unlikely because the cut marks at the end of the antler (Figure 5.7) are too small to retain the mouthpiece and reins (Dietz, 2003, p. 195). Concluding, the discussion about Dereivka stallion was finally closed after three radiocarbon analyses issued by Oxford and Kiev laboratories on the skull, bit-worn tooth and the burial surroundings, which dated the stallion to the Iron age, so to a much later period (Anthony and Brown, 2003, 2000; Levine, 1999b). Hence, while a number of indirect lines of evidence supporting Dereivka as one of the first centres of horse domestication have been offered, the question of horse domestication in Dereivka remains open.

Many complications preclude the investigation of early horse domestication in Eurasia. Sparse and contradictory evidence, lack of consistency in archaeological measurements (Olsen, 2006), small and badly preserved sample bones together with specific physiological features that do not aid in

characterizations, had led many researchers in considering an interdisciplinary approach, combining archaeological and scientific approaches, in order to develop new, direct and reliable methods to tackle the horse domestication problem.

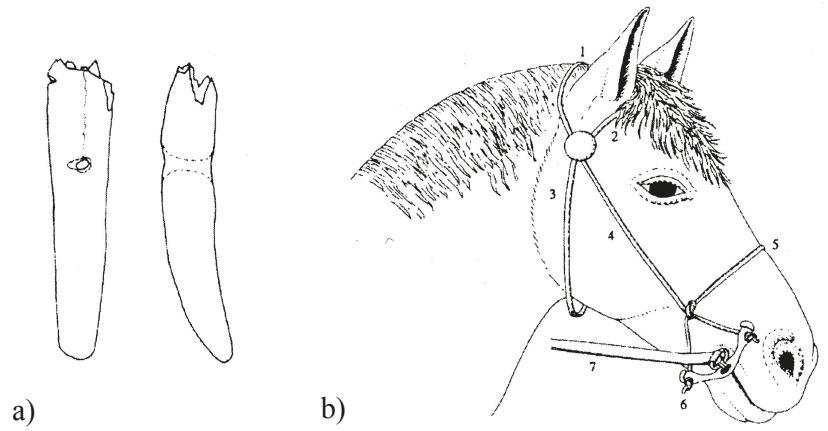


Figure 5.7. a) Shows the antler tines found in Dereivka, on the top a small cut is evident; b) shows the reconstruction of a late Bronze Age headstall in order to have a basic knowledge on how it looked like. It was structured as follow: 1) head piece, 2) browband, 3) throat lash, 4) cheek-pieces (strap), 5) noseband, 6) cheek-pieces (psalia), and 7) reins.

One of the successful examples of an interdisciplinary approach is the study carried out by Outram et al. in 2009 (also mentioned in Chapter 1, Section 1.6.2.1). It included (i) archaeozoological metrical analyses of wild and domesticated skeletons, both modern and ancient; (ii) the analysis of damage teeth possibly resulting from harnessing, such as bridle or similar restraints and (iii) compound-specific stable isotope analysis of lipid extraction from potsherds. The settlement analysed was Botai, an Eneolithic site located in the northern steppe of Kazakhstan and dated 3500-3000 BC; it was characterized by an impressive amount of horse bones, 99.9% of the total faunal bones. The first line of evidence testified a high similarity between the equine metapodia bones from Botai, the same domestic bones of modern Mongolian horses and from the Late Bronze Age site of Kent (located in Kazakhstan), where horses were already domesticated.

Concerning the analysis of damage teeth, a high number of teeth were previously analysed by the research carried out by Anthony (2003, p. 63). Of forty-two lower second premolars (that are the teeth used to brindle a horse), nineteen were relatively undamaged and came from horses more than three years old. Of the nineteen teeth, five showed bevels of few millimetres which Anthony and colleagues attributed to bit-wear, so an evidence of horse domestication (Anthony and Brown, 2003, p. 63). The study conducted by Outram brought to a similar conclusion. The analysis of fifteen teeth provided evidence of bitting damage on five of them. However, the confirmation that horses were domesticated at the Eneolithic site of Botai came from organic residues analysis applied on potteries and investigated using compound-specific stable hydrogen analysis (Outram et al., 2009). Outram and

colleagues found equine dairy products in five pots recovered from Botai and dated 3500 BC. Therefore, this research was considered the first reliable evidence of horse domestication in Eurasian steppe. A more detailed description of the organic residues analysis has been outlined in Section 1.6.2.1.

In conclusion, tracing horse domestication is complicated. However, as for the case of Botai, a similar approach has been used in the current project in order to possibly detect equine dairy products in Ukrainian pots and perhaps discover that horse domestication was part of the subsistence economy of the people lived in the North-Pontic area. These results are discussed in Chapter 6.

5.8 **Archaeobotanical evidence**

The appearance of agriculture is generally connected with the Neolithic cultures of the Bug-Dniester and linear decorated pottery culture, which occupied the forest-steppe zone of Northern Black Sea (Bibikova, 1969). As discussed at the beginning of the Chapter, the process of the Neolithization started in the Levant at around the 9th millennium BC and then reached the western North-Pontic region at around the 6th millennium BC (Velichko et al., 2009, p. 4), where signs of primitive agriculture were detected. According to Vavilov (Levine, 1999b, p. 17), North-West-Pontic region was the oldest Eurasian centre of plant cultivation. The agricultural knowledge spread afterwards into the southern-eastern steppe where "the instability of pastoralism and the need of bread forced the steppe people to develop arable agriculture as well" (Bendrey, 2011).

Supposing that cereal imprints can be used as an indication for agriculture (which possibility is discussed by Motuzaite-Matuzeviciute, 2012, 2014); only in five sites, cereal impressions in ceramic vessels have been identified during the Early Eneolithic, suggesting that agricultural activities were still insignificant (Pashkevich, 2003, p. 288). In contrast, the later periods exhibited a greater percentage of cereal impressions; plants remains were indeed recovered from roughly 80 settlements in Moldova and Ukraine (Pashkevich, 2003, p. 290).

Specifically speaking about the investigated sites, in the earlier horizon of Mikhailovka site, impressions of emmer wheat, hulled barley and millet have been identified in nine potsherds out of 2491 (Pashkevich, 2003, p. 291), suggesting that agriculture might have been part of the subsistence economic activities (Rassamakin, 1999, p. 142). Moreover, also Dereivka and Molyukhov Bugor sites displayed presence of cereal impressions, in eight vessels. In addition, at the site of Dereivka, 33 tools made of crystalline and sedimentary rock such as granite, quartzite, sandstone and shale, have been documented. Among these tools, many are related to agricultural activities (Rassamakin, 1999, p. 143; Telegin et al., 1986, p. 63): querns, grinders, pestles and stone disks, let to believe that this community was permanent settlement based on primitive hoe agriculture (Rassamakin, 2002, p. 50, 1999, p. 142).

Focusing on the later period, the evidence of agriculture decreased significantly (Pashkevych, 2012, p. 180) but it was probably important (Rassamakin, 2006, p. 456). Moreover, it appeared that millet was widely consumed in the Yamnaya populations (Bunyatyan, 2003, p. 274). Indeed, in the final stage of Mikhailovka the evidence of millet increased, suggesting an increasing presence of C4 plants in the vegetation and/or in the diet. Other types of cereal imprints, such as einkorn wheat, soft dwarf wheat and barley, have been also found (Rassamakin, 1999, p. 152).

Summarizing, the scarce archaeological and archaeobotanical evidence generally suggest that the gathering and processing of plants might have been a component in the subsistence strategies of the ancient North-Pontic people (e.g. Bendrey, 2011; Bibikova, 1969; Levine, 1999b; Pashkevich, 2003; Velichko et al., 2009); however, offering a reliable conclusion about this matter is challenging.

In the past several years, in the attempt to improve the knowledge and helping in the challenging reconstruction of the prehistoric human nutritional behaviours of the ancient Eurasian people, a number of stable isotopic studies have been carried out on human and animal bones. Unfortunately, the researches specifically applied on the North-Pontic region during the investigated periods of the Eneolithic and the Early Bronze Age, are very scarce (Gerling, 2014; Lillie, 2003; Lillie et al., 2011, 2009; Shishlina et al., 2012). However, the results presented in the subsequent Section will offer additional information and will possibly strengthen the hypothesis of a various subsistence economy, suggested by several archaeologists (Chapter 3) and indicated by both the archaeozoological and botanical evidence (discussed in this Chapter).

5.9 Existing $\delta^{13}C$ and $\delta^{15}N$ studies

5.9.1 *Introduction*

In the current Section two relevant carbon and nitrogen isotope studies specifically applied on human bones recovered from Eneolithic and Early Bronze Age North-Pontic sites (Gerling, 2014; Lillie et al., 2011), will be reported as further support to the existing archaeozoological and botanical evidence. As already mentioned in Chapter 1, Section 1.4, analyses of stable carbon isotope ($\delta^{13}C$) and stable nitrogen isotope ($\delta^{15}N$) are well-established methods that allow getting information about dietary pathways and specifically protein sources (DeNiro and Epstein, 1981; 1983; Hobson and Clark, 1992; Katzenberg, 2007; Lee-Thorp et al., 1989). Although isotopic analysis of bones may not always allow the precise reconstruction of an animal's diet, it allows the discrimination of animals belonging to particular dietary niches (Gannes et al., 1998). Thus, the reconstruction of ancient diets is possible because $\delta^{13}C$ and $\delta^{15}N$ values of fossil bones reflect the isotopic signatures of the local environment, in a trophic level distribution from the herbivores to the carnivores (Gannes et al., 1998; Hobson, 1999). Specifically, $\delta^{13}C$ values change from the predator to the prey by 5 ‰ (DeNiro and Schoeniger, 1983); in contrast $\delta^{15}N$ value in collagen is enriched by about 3‰ for every step up the

trophic level (Ambrose and DeNiro, 1986; DeNiro and Epstein, 1981; DeNiro and Schoeniger, 1983; Sealy et al., 1987). Therefore, $\delta^{13}C$ and $\delta^{15}N$ analyses are often combined because they give complementary information about the main protein source of a whole diet (Reitsema et al., 2010). Figure 5.8 displays an isotopic map produced by a PhD student worked at the University of Oxford (Dunn, 2011 ref. O'Connel, 1996), indicating both $\delta^{13}C$ and $\delta^{15}N$ typical values of different animals and plants.

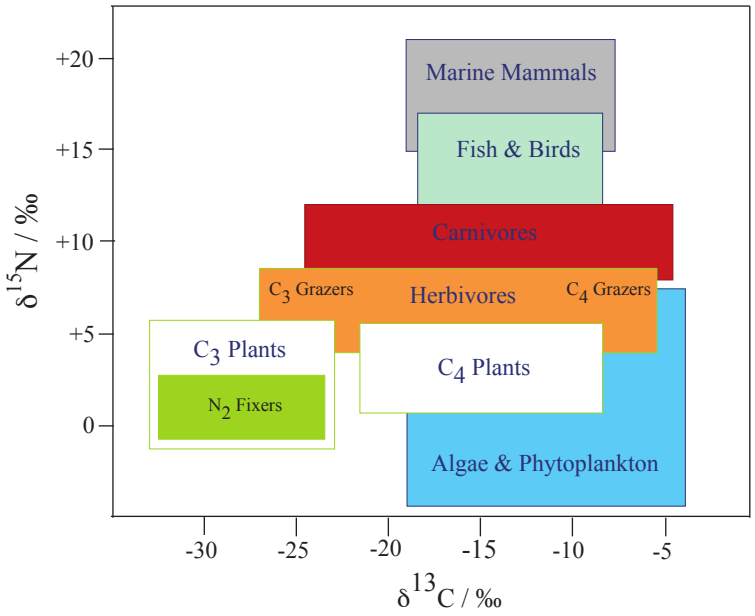


Figure 5.8. Isotope plot used for paleodietary reconstructions (Dunn, 2011 ref. O'Connell 1996).

5.9.2 *Existing $\delta^{13}C$ and $\delta^{15}N$ studies applied on the North-Pontic region*

As mentioned, two studies will be mainly considered in this context. Firstly, the research carried out by Lillie et al. (2011) on human, faunal and fish bones dated Upper Palaeolithic to Eneolithic periods and recovered from the Middle and Lower Dnieper region; lastly the analyses carried out by Claudia Gerling over her PhD project (Gerling, 2015, 2014) on faunal and human bones selected from sites in the West-Pontic, North-Pontic and Kuban regions, dated Late Eneolithic and Bronze Age periods. Only the results most relevant for this project will be presented (so only human bones).

Concerning the first research, twelve cemeteries located in the Dnieper region, were analysed, however, in this context only Dereivka and Molyukhov Bugor cemeteries will be considered (Figure 5.9). Moreover, it has to be noted that Dereivka human bones come from the Neolithic cemetery (see Chapter 4, Section 4.2 for the description of Dereivka culture). Supported by similar studies (Eriksson et al., 2003; e.g. O'Connell et al., 2003; Shishlina et al., 2012), Lillie and colleagues interpreted the depleted $\delta^{13}C$ values and the enriched $\delta^{15}N$ values of both Dereivka and Molyukhov Bugor human

bones as a suggestion of a diet mainly based on C3 terrestrial resources with supplementation of aquatic resources, such as freshwater fish (Figure 5.10a).

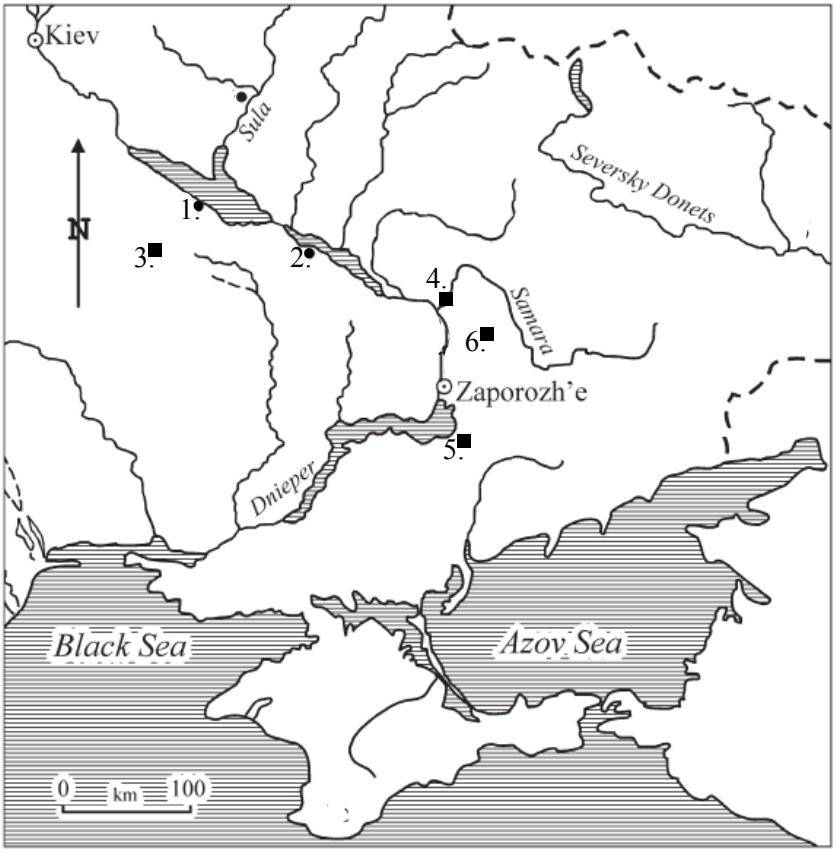


Figure 5.9. Dots correspond to the sites analysed by Lillie; (1) Dereivka, and (2) Molyukhov Bugor; squares are the sites analysed by Gerling (3) Kirovograd, (4) Peshtchanka, (5) Vinogradnoe, (6) Shakhta Stepnaya. Picture has been adapted from Lillie et al. 2011.

On the other hand, over the study carried out by Gerling et al. (2015) 20 human bones from Moldova and 30 human bones from the North Pontic area in Ukraine (Figure 5.9) – dated Eneolithic and Bronze Age - were analysed. In this context, only the Ukrainian records will be taken into account (Figure 5.10b). Examination of Figure 5.10b reveals that the bones recovered from three steppe sites (Stepnaya, Vinogradnoe and Peshtchanka) display slight enriched $\delta^{13}C$ values, compared to the samples from the forest-steppe site (Kirovograd). Also $\delta^{15}N$ values are distinctive from the steppe to the forest-steppe sites.

Generally, both groups of Ukrainian bones were characterized by carbon and nitrogen values that suggested a diet mainly based on C3 plants and terrestrial resources with some aquatic source input. Specifically, $\delta^{13}C$ values of Dereivka bones were depleted compared to Molyukhov Bugor; the latter data has been interpreted as a greater riverine fish exploitation of Dereivka people (Lillie et al., 2011), which has been explained by the earlier Neolithic period that was actually expected to show a predominance of aquatic source consumption. Also, examination of Sh. Stepnaya, Vinogradnoe,

Peshtchanka and Kirovograd (Gerling, 2014) reveals that some bones of the steppe sites are characterized by a slight enrichment of $\delta^{15}N$ that might be interpreted as a greater riverine fish exploitation of some of the people lived in the steppe sites during the late Eneolithic/EBA. Finally, the slightly enrichment in $\delta^{13}C$ values of some bones of the steppe sites could suggest a C4 plants input in the dietary habit of the steppe populations. A detailed discussion about the possible presence of C4 plants will be offered in Chapter 8.

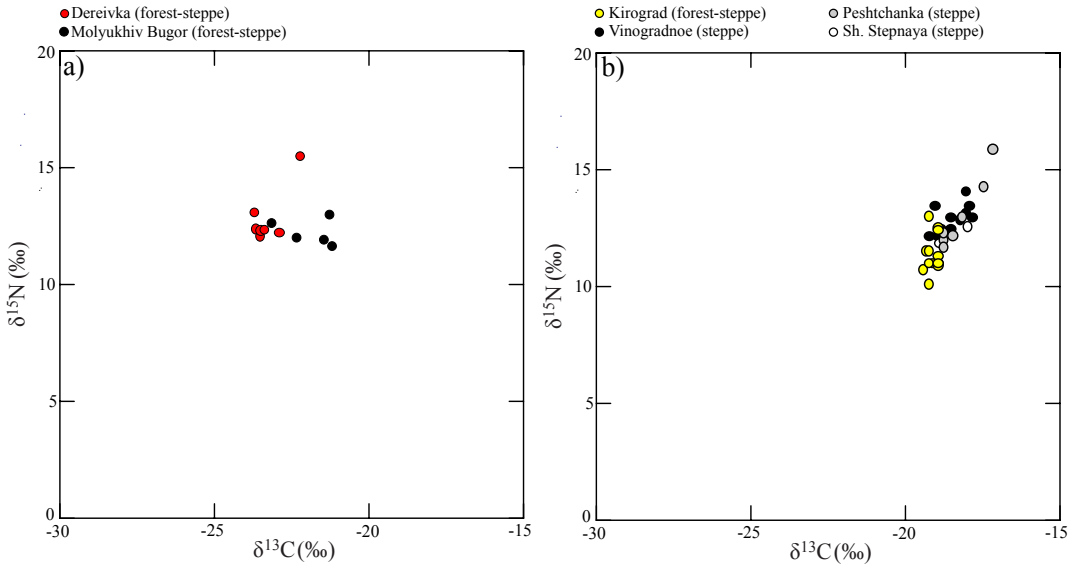


Figure 5.10. a) Plot shows $\delta^{13}C$ and $\delta^{15}N$ values of the sampled human specimen from Dereivka and Molyukhov Bugor. All means expressed as ±1σ.(Lillie et al., 2011); b) Plot shows $\delta^{13}C$ and $\delta^{15}N$ values of the sampled human specimen from the North Pontic region (Gerling, 2014).

5.10 **Summary and conclusions**

The existing faunal and botanical evidence together with existing isotopic studies applied on human bones confirm the hypothesis of a varied subsistence economy of the North-Pontic region, depending on the diverse environments and regional ecosystems.

The faunal records are schematically presented in the two triangle plots in Figure 5.11, produced by using the NISP% records. Examination of Figure 5.11a reveals that cattle bones predominated in the steppe sites of Mikhailovka II-III and Generalka followed by the forest-steppe site of Molyukhov Bugor site; in contrast the earlier horizon of Mikhailovka displayed a predominance of sheep and goats. The latter information is very difficult to explain as it might suggest a transition to a sedentary pastoral economy, as cattle are usually more exploited by settled communities (Kuzmina, 2003, p. 208; Renfrew, 2002, p. 2). However, this contradicts suggestions of an increasing nomadic pastoralist economy from the 3rd millennium BC onward (Anthony, 2007). Nevertheless, a number of interpretations will be discussed in the final overview Chapter.

The domesticates-wild-horse triangle plot (Figure 5.11b) reveals that the animal exploitation of the two steppe societies (Mikhailovka and Generalka) was similar during both Eneolithic and Bronze Age

periods, indicating a general exploitation of domesticates, and suggesting an economy based on animal husbandry. In contrast, the forest-steppe sites of Dereivka and Molyukhov Bugor plot separately (Figure 5.11b), exhibiting a higher percentage of wild animals and horses. Thus, it appears that the ancient people lived in the Dnieper area, were mainly based on two types of animal exploitation: animal husbandry (cattle or sheep/goats) and hunting, depending on the diverse environments and regional ecosystems.

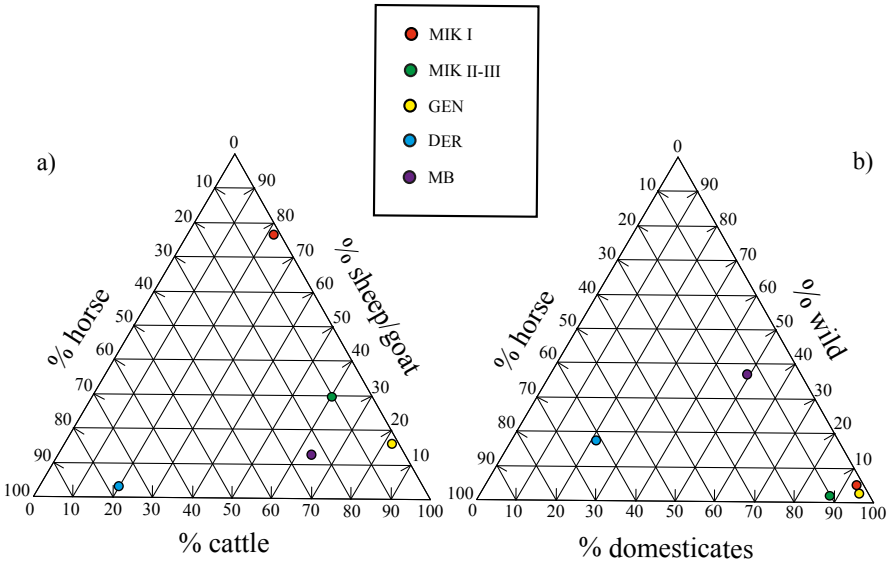


Figure 5.11. Triangle plots showing the percentages of the number of identified specimen (NISP) of the five sites analysed in the current study. Plot a) shows the domesticated animals together with horses: while b) shows the animals grouped into broader categories (wild, domesticated and horses). The plots have been produced using *Systat* software.

Furthermore, archaeological and archaeobotanical evidence from sites across the North Black Sea suggested that the gathering and processing of plants might have been a component in the subsistence strategies of both the hunter-gatherers and the pastoralists in the region (Bendrey, 2011; Bibikova, 1969; Levine et al., 1999; Pashkevich, 2003; Pashkevych, 2012; Velichko et al., 2009). However, without further evidence it is not possible to reliably confirm the latter possibility. Finally, the isotope analysis carried out over the last years (Gerling, 2015, 2014; Lillie et al., 2011) generally supports the faunal records, describing a various diet based on terrestrial animals with some aquatic input and C3 plants, with a possible C4 plants input (e.g. millet).

Concluding, the current Chapter together with Chapter 3 and 4 provided an overall archaeological background and displayed the difficulties concerning the reconstruction of the subsistence economy in an area where several hurdles occur. The evidence so far collected are extremely important as allow us to strengthen the initial hypothesis, suggested in Chapter 3: the subsistence economy of the people lived in the North-Pontic region has to be considered in relation to the specific environment as it appears clear from the evidence that there were varying economic systems and regionally dependent

communities. It is predicted that the addition of molecular and isotope evidence will further strengthen the existing evidence, and offer new and original information that will allow more refined reconstruction of the subsistence economic strategies of the people lived in the North-Pontic region.

CHAPTER 6

RESULTS (PART I): DIET AND SUBSISTENCE ECONOMY IN ENEOLITHIC FOREST-STEPPE OF THE NORTH-PONTIC REGION

6.1 Introduction

The existing evidence from the North-Pontic region (described in Chapter 5) provided a first picture of the potential subsistence economy of the people lived in this area, suggesting that the dietary habits were mainly driven by the local environment with interchangeable strategies of husbandry-hunting and gathering-agriculture depending upon the ecosystem. Therefore, following the hypothesis suggested by the existing evidence, the five investigated sites have been divided between this Chapter and Chapter 7 according to their geographical location: forest-steppe sites (Dereivka and Molyukhov Bugor) and steppe sites (Mikhailovka, Nizhniy Rogachik and Generalka). Specifically, Chapter 6 and 7 will use molecular and stable isotope techniques to investigate lipid residues from 210 archaeological ceramic vessels excavated from prehistoric Ukrainian sites (described in Chapter 4) to investigate diet and subsistence strategies in the region. Significantly, potsherds provide a valuable source of information of past economic and cultural activities thanks to their ubiquitous nature at archaeological sites even where other artefacts and remains are not present (Chapter 1, Section 1.4).

The investigation of the lipid biomarker compositions comprised the following steps:

1) Lipids were extracted using the methods outlined in Chapter 2. The TLEs were then analysed using GC, and those with appreciable lipids were also analysed by GC/MS in order to evaluate the occurrence of biomarkers (e.g. saturated and unsaturated fatty acids, *n*-alkanols, *n*-alkanes, etc.);
2) TLEs exhibiting particular lipid distributions (e.g. presence of unsaturated fatty acids and/or long-chain compounds) were investigated using GC/MS in both full scan (*m/z* 50-650) and selected ion monitoring (*m/z* 105) modes, to detect ω-(o-alkylphenyl) alkanoic acids (APAAs);
3) The $\delta^{13}C$ values of the palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) fatty acids were determined using GC/C/IRMS. Compound-specific stable carbon isotope analysis ($\delta^{13}C$) was performed on those extracts exhibiting appreciable concentrations of $C_{16:0}$ and $C_{18:0}$ fatty acids and not displaying plant biomarkers, in this instance a total of 158 lipid extracts: 27 recovered from pottery from Dereivka ceramic assemblage; 11 from Molyukhov Bugor (Chapter 6); 34, 19 and 16 respectively from Mikhailovka I, II and III; 24 extracts were analysed from Nizhniy Rogachik and, finally, 27 from Generalka (of which 6 were analysed in a previous pilot study; discussed in Chapter 7). FAMEs were prepared by the protocol described in Chapter 2, Section 2.3.1.2. and were analysed by GC/C/IRMS as described in Section 2.4.4. As explained in Chapter 2, Section 2.6 the $\delta^{13}C$ values of the reference materials collected from Ukraine resulted unusable due to commercial diets being used in rearing the animals. Therefore, in order to overcome the latter problem, the archaeological isotope carbon values have been compared with reference materials collected from Europe, Asia and Africa, which allowed creation of a comprehensive reference database (Chapter 2, Section 2.6). Kazakh reference fats were particularly important as main reference for equine fats (Outram et al., 2009; Stear, 2008) and are thus highly useful for the current research. For more details, the $\delta^{13}C$ values are reported in Appendix D, Table 1;
4) Compound-specific stable hydrogen analysis (δD) was also performed on 56 extracts of which n=24 residues were attributed to equine fats by compound-specific stable carbon isotope analysis in order to distinguish between dairy and adipose fats and n=32 were chosen among the other type of fats in order to possibly get additional information. Therefore 11 residues were analysed from the pottery from Dereivka; 20 from Nizhniy Rogachik; 15 from Mikhailovka II; and 10 from Generalka. Compound-specific stable hydrogen isotope analysis was performed by following the protocol described in Chapter 2 (Sections 2.4.5 and 2.5.3). For more details, the δD values are reported in Appendix D, Table 2.

This Chapter focuses on the forest-steppe sites of Dereivka and Molyukhov Bugor from the Middle Eneolithic (ca. 3800/3700 to 3500/34000 BC). The specific aims of this Chapter are:

(i) Determine the biomarker compositions in order to identify commodities processed in the ceramic vessels;

(ii) Identify the type of absorbed fat (e.g. ruminant dairy or ruminant adipose fats, equine fats and non-ruminant fats) by comparing archaeological and modern reference $\delta^{13}C$ values;

(iii) Assess the results of δD analysis of 56 residues to determine whether a distinction between equine adipose and dairy fats is possible and/or to determine if a distinction between different types of animals is possible.

Integration of the information obtained from molecular and stable isotope analysis together with the existing archaeozoological and botanical evidence will be detailed in Chapter 9, in order to establish a comprehensive chronology of prehistoric animal exploitation in the North-Pontic region from the Eneolithic to the Early Bronze Age.

6.2 Overall lipid preservation in Ukrainian potsherds

The potsherds (n=210) were obtained from five settlements dated from the Middle and Late Eneolithic (ca. 3800 to the ca. 3000 BC) and the Early Bronze Age (ca. 3000 to ca. 2300 BC). Two of the five sites were located in the forest-steppe (Dereivka and Molyukhov Bugor) and the remaining sites (Mikhailovka I, II and III, Nizhniy Rogachik and Generalka) were located in the steppe, along the Dnieper River (Figure 6.1).

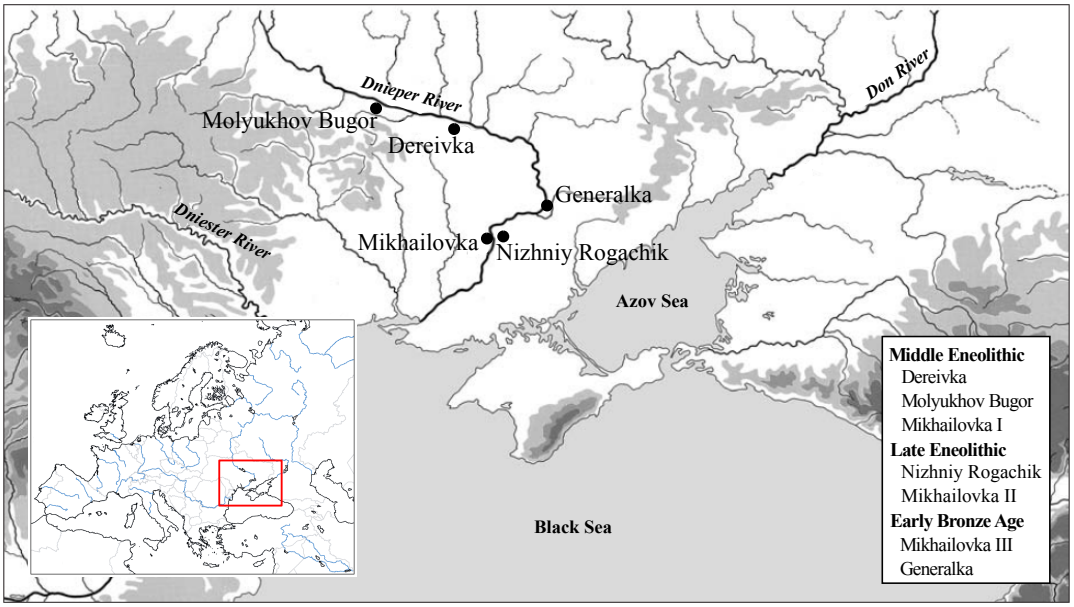


Figure 6.1. Location of the five sites analysed in the current study.

TLEs were obtained from all the archaeological potsherds using the established protocol (Section 2.3.1) that from now onward will be called Method I. It should be noted that in the case of the

Dereivka residues, the lipid recovery rate was lower than at the other sites, thus these extracts were also analysed using the new acid methanol extraction procedure (Method II; Correa-Ascencio and Evershed, 2014). This allows the higher recovery of absorbed lipid residues.

The rate of lipid recovery using Method I for each ceramic assemblage is shown in Figure 6.2. Generally lipid preservation was excellent with a total of 163 potsherds yielding appreciable lipid concentrations (>5 μg g^{-1}). This compares favourably to those recovered from British Neolithic sites (43%Copley et al., 2005a), and central/southeastern Europe (6.48%, *n*=339), northern Greece (18.4%, *n*=305), northwestern Anatolia (14.5%, *n*=703) and the Levant (6.3%, *n*=448) (Evershed et al., 2008b) and is comparable to lipid recovery from the Libyan Sahara (94% Takarkori, 76% Uan Afuda) (Dunne, 2015; Dunne et al., 2012).

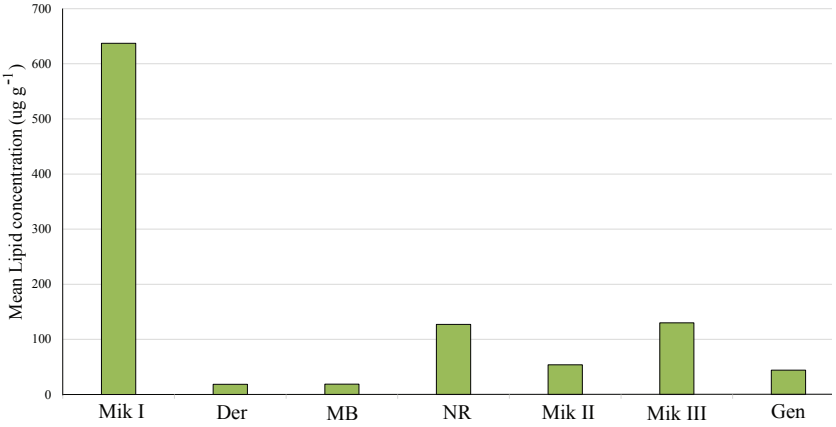


Figure 6.2. Histogram showing the mean lipid concentrations obtained from TLEs from 210 sherds from five sites (seven horizons) located in Ukraine (Dnieper region). Mikhailovka (Mik); Dereivka (Der); Moliukhov Bugor (MB); Nizhnyi Rogachik (NR) and Generalka (Gen).

The lipid concentrations obtained from the pottery from the northern two settlements (Dereivka and Moliukhov Bugor) are characterised by mean values, respectively of 18.9 μg g^{-1} and 18.7 μg g^{-1} with maximum values of 206.7 μg g^{-1} and 76 μg g^{-1}. The steppe sites exhibited greater lipid preservation. The Mikhailovka site demonstrates the maximum preservation; the earlier horizon (Mikhailovka I) reaches a mean value of 621.7 μg g^{-1}. A total of 94% of the extracts yielded an appreciable lipid concentration ranging from 5 to 3894.8 μg g^{-1}. Mikhailovka II and Mikhailovka III display a mean lipid concentration, respectively, of 53.9 μg g^{-1} and 130.1 μg g^{-1} and maximum values of 182.3 μg g^{-1} and 787.5 μg g^{-1}. The preservation of Nizhnyi Rogachik pottery was appreciable; 80% of the sampled potsherds yielded lipid concentrations ranging from 5 to 1024 μg g^{-1} with a mean value 127.1 μg g^{-1}. Finally, the Generalka pottery exhibited a lower but still appreciable lipid concentration: the mean value is 43.9 μg g^{-1} while the maximum value is 332.1 μg g^{-1}.

Therefore, the preservation of the organic residues within the Ukrainian potsherds differs according to geographical location; lipid preservation is higher in the potsherds of the steppe sites. These differences could be explained by two factors:

(i) It is possible that vessels were used differently at forest-steppe sites; as mentioned in Chapter 5, the economy appeared to depend upon local environments, so perhaps the cooking traditions were also different (e.g. food may be preferably cooked on a spit);

(ii) The strongly alkaline *chernozem* soil, mainly characteristic of the steppe environment (French and Kousoulakou, 2003), may have reduced soil microbial activity and therefore the organic residue degradation.

To date, analysis of the TLE's from Ukrainian sites with an appreciable lipid concentration (>5 μg g^{-1} of potsherd) (n=163) demonstrates that the free fatty acids, $C_{16:0}$ and $C_{18:0}$ fatty acids are the most abundant components, typical of a degraded animal fat profile (Evershed et al., 1997a). Nine different classes of compounds were identified in the lipid extracts of the ceramics investigated from Ukrainian sites: fatty acids (saturated and unsaturated), monoacylglycerol, diacylglycerol, triacylglycerol, mid-chain ketones, long-chain *n*-alkanes, long-chain *n*-alkanols, 4,8,12-trimethyltridecanoic (isoprenoid acid) and APAAs. Table 6.1 provides a summary of the TLE analyses and lipid concentrations in pottery vessels together with the number of sherds containing specific biomarkers that will be described in this and in the following chapter.

Table 6.1
Summary of TLE compositions and lipid concentrations of pottery vessels from archaeological sites across Dnieper region. In the table Middle Eneolithic (ME), Late Eneolithic (LE) and Early Bronze Age (EBA).

Archaeological site	Period	n° of sherds analysed	Proportion with appreciable lipid (%)	Mean lipid concentration (μg g^{-1})	N° of vessels containing TAGs	N° of vessels containing APAA	N° of vessels containing ketones	N° of vessels possibly containing plant waxes
Dereivka	ME	40	67	18.86	1	-	-	-
Molyukhov Bugor	ME	25	60	18.7	2	-	1	4
Mikhailovka I	ME	36	94	621.7	20	-	-	-
Nizhnyi Rogachik	LE	30	77	127.1	5	2	-	1
Mikhailovka II	LE	21	90	53.9	5	-	1	-
Mikhailovka III	EBA	23	70	130.1	3	-	-	-
Generalka	EBA	35	64	44.0	5	1	-	-

Many extracts from Dereivka and Molyukhov Bugor were characterized by long-chain *n*-alkanes with unusual distributions suggesting fossil fuel (e.g. petroleum, bitumen, oil, etc.) contamination. As explained in Chapter 1, Section 1.3.2.3, *n*-alkanes distribution together with long-chain *n*-alkanols and long-chain fatty acids might suggest the presence of plant waxes in the organic residues extracted

from the ceramic vessels. However, the *n*-alkanes can derive from other external sources. Fossil fuel contamination is recognisable by the identification of specific *n*-alkane distributions in the range C_{18}-C_{27} with no even-over-odd predominance (Figure 6.3). The carbon preference index (CPI) was used in order to assess the presence of fossil fuel compounds. The CPI equation is used to evaluate the dominance of odd-carbon number *n*-alkanes; a value equal or close to 1 indicates the presence of *n*-alkanes derived by fossil fuel compounds (Bray and Evans, 1961; Jun Li et al., 2013; Marzi et al., 1993; Wang and Liu, 2012).

$$CPI = 0.5\left(\frac{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})}{(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})}\right)+\left(\frac{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})}{(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})}\right)$$

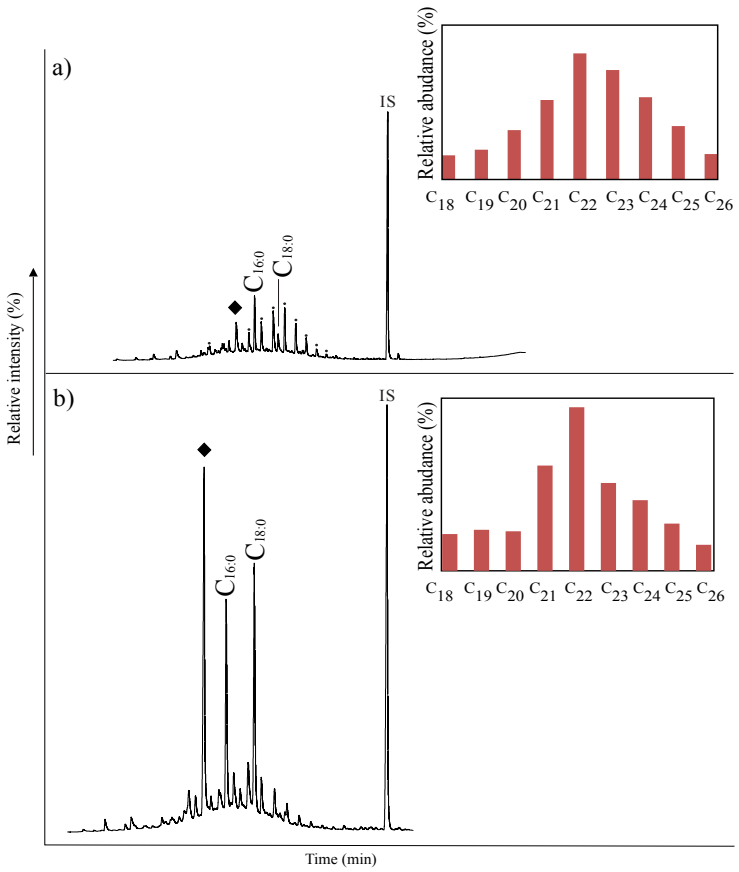


Figure 6.3. Partial gas chromatograms of TLEs from two sherds (a) DER17 and (b) MB7, showing characteristic fossil fuel contamination together with $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal fats. The image shows: fatty acids ($C_{n:0}$; with n=number of carbons), *n*-alkanes (dots), phthalate (rhombus) and the internal standard, C_{34} *n*-tetratriacontane (IS).

In contrast *n*-alkanes originating from plant waxes have a distribution in the C_{19}-C_{33} carbon number range and displaying an odd-over-even predominance (Eglinton and Hamilton, 1963; Wang and Liu, 2012). Figure 6.4 shows a typical distribution of *n*-alkanes, *n*-alkanols and long-chain fatty acids for terrestrial plants. Together with the petroleum contamination a significant number of

biomarkers were identified. The subsequent Sections and Chapters describe in detail the biomarkers observed in the TLEs of the pottery from each site.

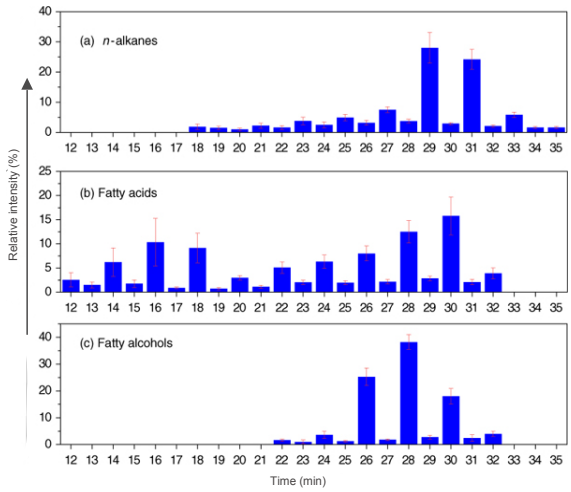


Figure 6.4. Relative abundances of *n*-alkanes (a), long-chain fatty acids (b) and *n*-alkanols (c) for terrestrial plants (Jun Li et al., 2013; Wang and Liu, 2012).

6.3 **Dereivka site**

6.3.1 *Organic residues recovered from the Dereivka pottery*

All residues from the Dereivka site were analysed using Method I (Copley et al., 2003; Evershed, 2008b). However, considering the low lipid concentration recovered from the first 30 Dereivka extracts (13.9 μg g^{-1}), Method II was also used in order to try to maximise lipid recovery. In addition, 10 further sherds were collected and analysed using the direct methanolic acid extraction (Method II). This allowed to increase the number of extracts yielded appreciable lipids concentration from 18 to 31 and to reach higher lipid concentration value 18.9μg g^{-1}. However, due to post-excavation contamination of 4 of the extracts, only 27 extracts were submitted to GC/C/IRMS.

Analysis of the TLEs from Dereivka revealed that the free fatty acids, $C_{16:0}$ and $C_{18:0}$ fatty acids, are the most abundant components indicating that the degradation of triacylglycerols, diacylglycerols and monoacylglycerols has proceeded to completion and extensive oxidation of unsaturated fatty acids has occurred. This is in sharp contrast to TLEs extracted from ceramics recovered from archaeological sites in Europe, which frequently contain a range of TAGs (e.g. Dudd and Evershed, 1998). TAGs and their degradation products (DAGs and MAGs) were observed in 3% of the residues. The TAGs exhibited an acyl carbon number ranges from C_{48} to C_{54}, dominated by C_{52}. Lower molecular weight TAGs (C_{44} to C_{46}), which characterise dairy products, were absent (Dudd and Evershed, 1998). Figure 6.5 displays the gas chromatogram of the only sherd (DER10) containing TAGs and DAGs.

Finally, some intriguing Dereivka residues, characterized by long-chain compounds, were analysed by GC/MS in SIM mode in order to screen for the presence of APAAs. No APAA's were

detected, indicating that (i) aquatic products were not processed in these vessels, (ii) the cooking temperature was typically low (Evershed et al., 2008a; Hansel and Evershed, 2009) and/or (iii) a different way of processing aquatic food was employed. Lipid biomarker analyses by GC/MS showed the residues to fall into one main category; denoted Profile I and detailed as follows:

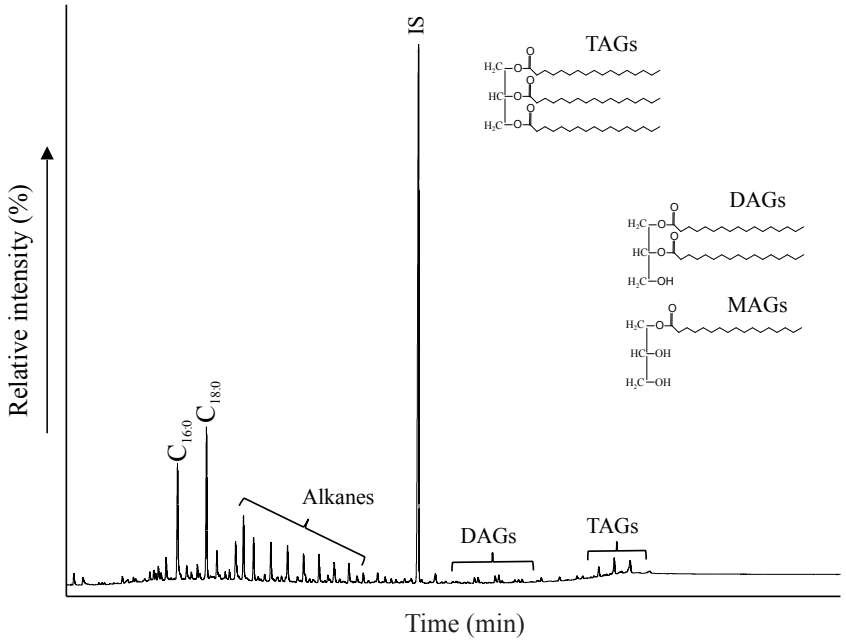


Figure 6.5. Partial gas chromatogram of TLE from sherd DER10, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products, and the distribution of DAGs and TAGs. The image shows: fatty acids ($C_{n:0}$; with n=number of carbons), triacylglycerols (TAGs), diacylglycerols (DAGs) and the internal standard, C_{34} *n*-tetratriacontane (IS).

6.3.1.1 Lipid distribution – Profile I

This profile includes residues with lipid distribution typical of animal products. Five extracts were particularly well-preserved (Figure 6.6 shows residue DER16 and residue DER25 as example): dominated by $C_{16:0}$ and $C_{18:0}$ fatty acids mainly characterized by the predominance of $C_{16:0}$ fatty acid over $C_{18:0}$ fatty acid more suggestive of equine products (Stear, 2008). Indeed, the fresh equine fat is widely characterized by a low abundance of $C_{18:0}$ fatty acid within the fatty acid profile (Malacarne et al., 2002; Shorland et al., 1952) and the differences in the ratios $C_{16:0}$:$C_{18:0}$ is very significant (Stear, 2008); therefore it is reasonable to suggest that these differences may persist in archaeological lipid residues being able to reliably identify ancient equine fat residues based only upon relative abundances, which can determined by GC analysis (Stear, 2008, p. 125). However, it must be remembered that degradative processes will likely alter fatty acid ratios and thus assignments must be verified using other techniques, such as compound-specific stable isotope analysis.

Residue DER16 (Figure 6.6a) also displays high concentration of the mystiric acid ($C_{14:0}$) Usually, dairy fats display the presence of short-chain saturated fatty acids in the C_4 to C_{14} carbon number range differing from adipose fats in their fatty acid composition (Christie, 1983; Kuksis et al., 1973).

However, short-chain saturated fatty acids are detected very rarely in archaeological pottery and thus cannot be used as reliable diagnostic criteria for milk processing. This is due to their compositional alteration during burial to a distribution more resembling adipose fats, through preferential hydrolysis of the short-chain acyl moieties as a result of reduced steric effects at ester linkages in triacylglycerols as compared with their long-chain counterparts (Dudd and Evershed, 1998). The short-chain fatty acids are also more water-soluble than their longer-chain equivalents and thus more liable to be lost through leaching in the burial environment (Bell and Razig, 1973).

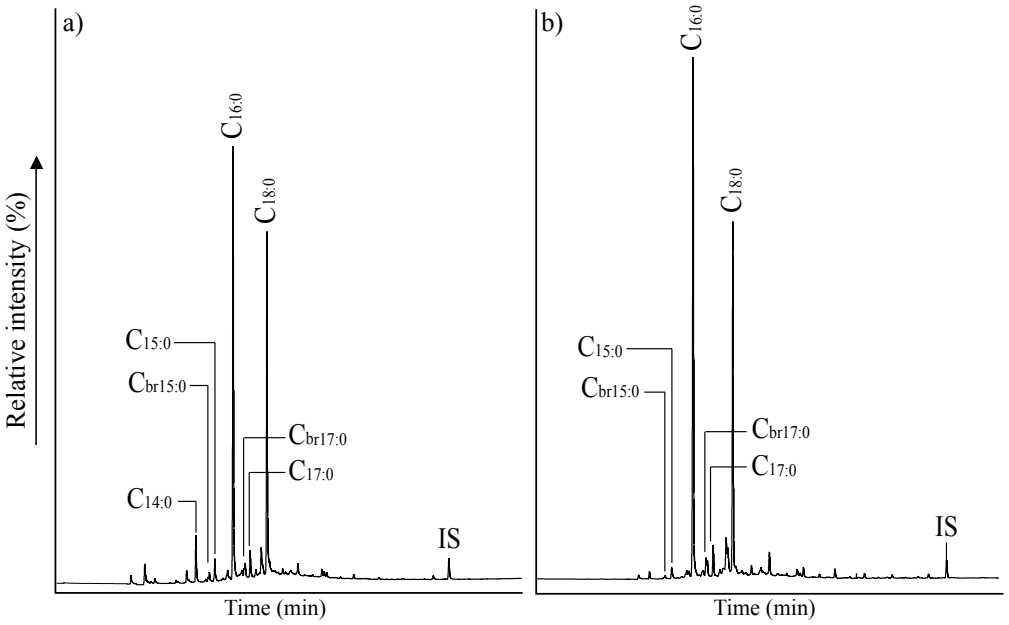


Figure 6.6. Two gas chromatograms of TLEs from sherds DER16 (a) and DER25 (b) showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products. The image shows: fatty acids ($C_{n:0}$; with n=number of carbons), branched-chain fatty acids (br), phthalate (rhombus) and internal standard C_{34} *n*-tetratriacontane (IS). Appendix D, Figure 1 displays the mass spectra of the main fatty acids.

The majority of the extracts were dominated by lower concentrations of $C_{16:0}$ and $C_{18:0}$ fatty acids and by branched-chain and odd carbon number fatty acids including $C_{15:0}$, $C_{15:0br,}$ $C_{17:0}$ and $C_{17:0br}$ suggesting that the vessels were used to process animal products. The general abundance of branched-chain fatty acids suggests bacterial origin diagnostic of ruminant animal fat (Christie, 1978). However, branched chain fatty acids (especially *iso*- and *anteiso*-$C_{17:0}$) are also detected in equine adipose fats and likely derive from similar groups of microorganism located in the hindgut of the horse (Hintz and Cymbaluk, 1994; Pond et al., 1995).

6.3.2 *$\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids*

The $\delta^{13}C$ values of $C_{16:0}$ fatty acid plotted against $C_{18:0}$ fatty acid are shown in Figure 6.7a. $\delta^{13}C_{16:0}$ range from -32.2‰ to -25.7‰, whereas $\delta^{13}C_{18:0}$ values range between -31.7‰ and -24.9‰ with mean

values, respectively, of -29.2‰ and -29.3‰. Figure 6.7b shows the $\Delta^{13}C$ plot ($\delta^{13}C_{18:0}$-$\delta^{13}C_{16:0}$), which allows separation of animal fats, by removing environmental effects (as explained in Chapter 1, Section 1.5.2).

An appreciable number of Dereivka residues (n=13) exhibit $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids characteristic of equine products (displaying mean $\delta^{13}C_{16:0}$ value of -28.9‰, mean $\delta^{13}C_{18:0}$ value of -29.0‰ and mean $\Delta^{13}C$ value of -0.1‰). Five residues plot in the range of ruminant adipose, of which only one residue might have a dairy fats origin. Examination of the raw data plot in Figure 6.7a further reveals that only one residue has characteristic isotopic composition of non-ruminant (porcine?) products (Mukherjee et al., 2007) with $\delta^{13}C_{16:0}$ =-26.7‰, $\delta^{13}C_{18:0}$ =-24.9‰ and $\Delta^{13}C$=1.8 ‰, and that five residues have possible freshwater fish origin, showing more depleted isotopic composition (Cramp and Evershed, 2014) with mean $\delta^{13}C_{16:0}$ value of -31.6‰, mean $\delta^{13}C_{18:0}$ value of -30.7‰ and mean $\Delta^{13}C$ of 1.0 ‰. However no other fish biomarkers have been identified. Three extracts have possible mixed origin (white dots).

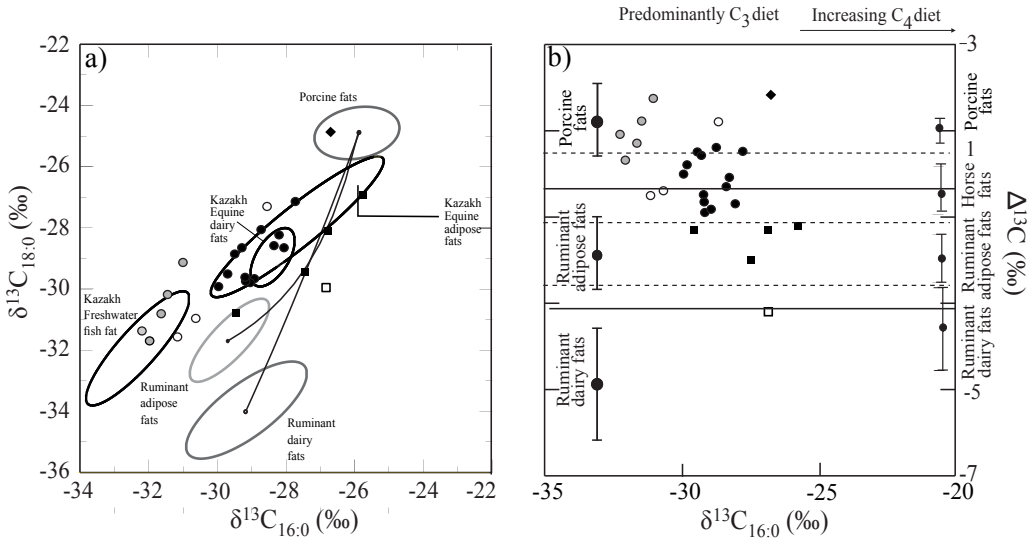


Figure 6.7. Scatterplots of (a) $\delta^{13}C$ values of $C_{16:0}$ fatty acid against the $C_{18:0}$ fatty acid extracted from 40 pottery vessels from Dereivka. In the figure, equine fats (black dots); porcine fat (black rhombus); possible freshwater fish fats (grey dots); ruminants fats (black squares); mixed fat residues (white dots). Archaeological values overlay confidence ellipses corresponding to the values obtained from modern reference fats, which enables the species classification of the ancient animal products; and (b) $\delta^{13}C$ values of $C_{16:0}$ against the $\Delta^{13}C$ values ($\delta^{13}C_{18:0}$ - $\delta^{13}C_{16:0}$).

From the compound-specific stable carbon isotope results, it appears that only 19% of the vessels analysed were used for the processing of ruminant products, which concurs with the *ca*. 20% ruminants represented in the faunal assemblage, which included cattle, sheep and goats (see Table 6.2). The carbon isotope results also suggest a near absence of ruminant dairy product processing, indicating that ruminants were not exploited for their secondary products. Forty-eight per cent of the

pottery vessels analysed were used for processing of equine products, which reflects the faunal records (Table 6.2) suggesting an economy largely based on equine exploitation.

Finally, the distribution of $\delta^{13}C_{16:0}$ values (Figure 6.7b) of the majority of the extracts range between -32.2‰ to -25.7‰, which is slightly broader that the distribution of the $\delta^{13}C_{16:0}$ values for modern ruminant fats from British animals, raised on a strict C3 diet ($\delta^{13}C_{16:0}$ values ranging from -30.9‰ and -28.6‰; Copley et al., 2003). The latter is more comparable to the $\delta^{13}C_{16:0}$ values for modern Kazakh reference fats, ranging from -29.0 to -24.1 ‰ (Stear, 2008). Similar enrichment was also observed in $\delta^{13}C$ values of lipids extracted from Near Eastern archaeological pottery (Evershed et al., 2008) where it was hypothesised to result from the animals producing the fats consuming a proportion of C4 plants in their diets and/or water-stressed C3 plants. This topic will be discussed in details in Chapter 8, Section 8.3.

Table 6.2
The different classes of animals inferred from faunal records in Dereivka site (Bibikova, 1986). Both MNI and NISP are shown. Sheep and goats are combined; the wild animals includes red deer, roe deer, boar, elk, badger, beaver, wolf, fox, hare, bear and otter.

	Cattle	*Sheep/Goats*	*Pigs*	*Dogs*	*Horses*	*Wild animals*	*Fishes*
MNI	18	16	9	5	52	83	37
MNI%	7.8	6.9	3.4	2.2	22.4	38.6	17.2
NISP	618	88	114	33	2412	673	136
NISP%	15.2	2.2	2.8	0.8	59.2	16.7	3.4

6.4 **Molyukhov Bugor site**

6.4.1 *Organic residues recovered from Molyukhov Bugor pottery*

The maximum lipid concentration of 25 extracts was 76 μg g^{-1} while the mean lipid concentration was 18.7 μg g^{-1}. A number of 18 sampled potsherds yielded appreciable lipid concentrations (>5 μg g^{-1} of potsherd), however, due to post-excavation contamination of 3 of the extracts, only 15 extracts worth to be further analysed, of which only 11 were analysed by GC/C/IRMS due to the presence of possible plant biomarkers in 4 extracts (see Section 6.4.1.2).

Generally, TLEs from Molyukhov Bugor pottery showed an exploitation of animal products denoted by the high abundance of $C_{16:0}$ and $C_{18:0}$ fatty acids.

TAGs and their degradation products (DAGs and MAGs) were observed in 8% of the residues (n=2) within the acyl carbon ranges from C_{48} to C_{54}, dominated by C_{52}. Lower molecular weight TAGs (C_{44} to C_{46}) which characterise dairy fats were absent (Dudd and Evershed, 1998). Figure 6.8 displays the gas chromatogram of one TLE (MB21) containing intact TAGs and DAGs.

In addition, three mid-chain ketones were observed in one residue (MB17), suggesting that the food was cooked at the high temperatures required for their formation (Figure 6.9). Mid-chain ketones are formed from animal fats via a ketonic decarboxylation reaction between two fatty acids in presence of an inorganic catalyst at temperatures in excess of 300°C (Evershed et al., 1995). Lipid biomarker analysis by GC/MS showed the residues to fall into two broad categories; Profile I and II, detailed as follows:

6.4.1.1 Lipid distribution – Profile I

This profile includes residues with lipid distribution typical animal products. Four extracts were particularly well-preserved (MB17, MB21, MB22 and MB23): dominated by $C_{16:0}$ and $C_{18:0}$ fatty acids mainly characterized by the predominance of $C_{16:0}$ over $C_{18:0}$ fatty acid. All of these extracts showed branched-chain and odd carbon number fatty acids, i.e. $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$ (see Figure 6.9). The remaining extracts were dominated by low concentrations of $C_{16:0}$ and $C_{18:0}$ fatty acids (e.g. Figure 6.3b) mainly characterized by a predominance of $C_{16:0}$ fatty acid over $C_{18:0}$. Fatty acids of carbon length $C_{15:0}$ and $C_{17:0}$ appeared in a few extracts.

6.4.1.2 Lipid distribution – Profile II

Four TLEs (MB3, MB5, MB8 and MB24) exhibited possible mixture between animal fats and plant wax biomarkers; they were generally dominated by well-preserved $C_{16:0}$ and $C_{18:0}$ fatty acids; two of the four extracts were characterized by the predominance of $C_{16:0}$ fatty acid over $C_{18:0}$. All of these extracts showed branched-chain and odd carbon number fatty acids including $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$. Additionally, long-chain fatty acids in the range C_{19}-C_{30} with an even-over-odd predominance and C_{26} dominating, long-chain alkanes ranging from C_{23} to C_{29} and long-chain *n*-alkanols in the range C_{22}-C_{30} were present, indicating possible presence of plant wax. In order to better highlight the FA distributions the FAMEs are displayed in Figure 6.10 together with the neutral fraction to better identify *n*-alkanes and *n*-alkanols. Long-chain *n*-alkanols including C_{24}, C_{26} and C_{28}, with C_{24} the most abundant, are evident in the neutral fraction. Unfortunately, the *n*-alkanes appear to derive from fossil fuel contamination confirmed by the CPI values of ca. 1. Figure 6.10 displays chromatograms MB3 and MB5 showing typical profile II.

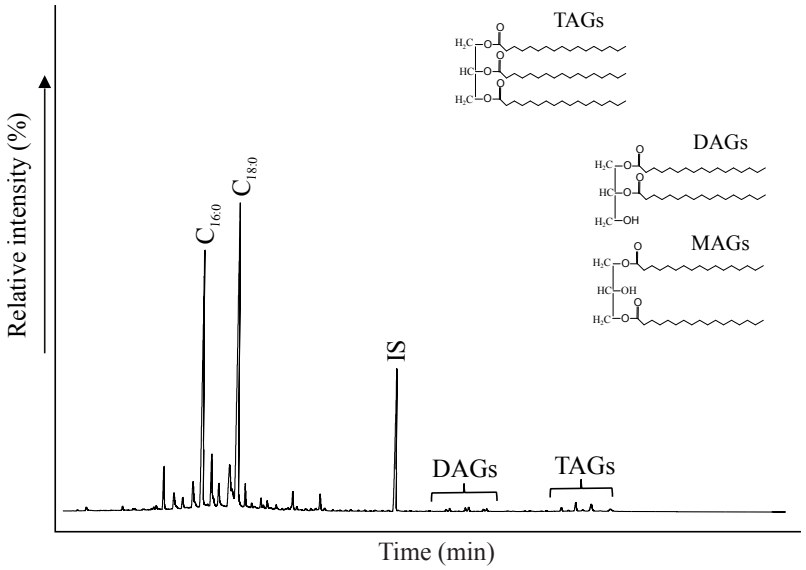


Figure 6.8. Partial gas chromatogram of TLE from the sherd MB21, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products, and the distribution of DAGs and TAGs. In the figure: fatty acids ($C_{n:0}$; where n=number of carbons), triacylglycerols (TAGs), diacylglycerols (DAGs) and the internal standard, C_{34} *n*-tetratriacontane (IS).

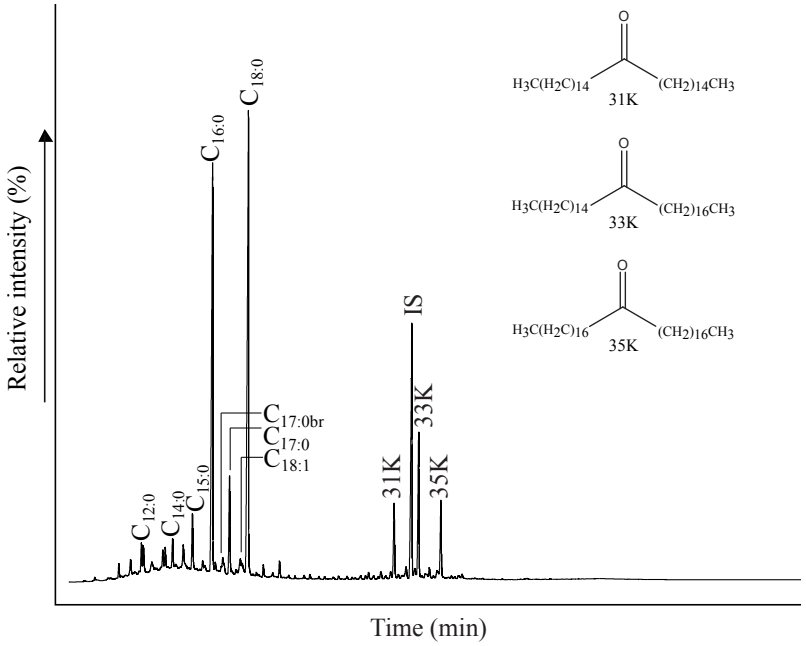


Figure 6.9. Partial gas chromatogram of TLE from sherd MB17, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products, and mid-chain ketones produced during cooking of animal products. In the figure: fatty acids ($C_{n:0}$; where n=number of carbons), branched-chain fatty acids (br), mid-chain ketones (K) and the internal standard, C_{34} n-tetratriacontane (IS).

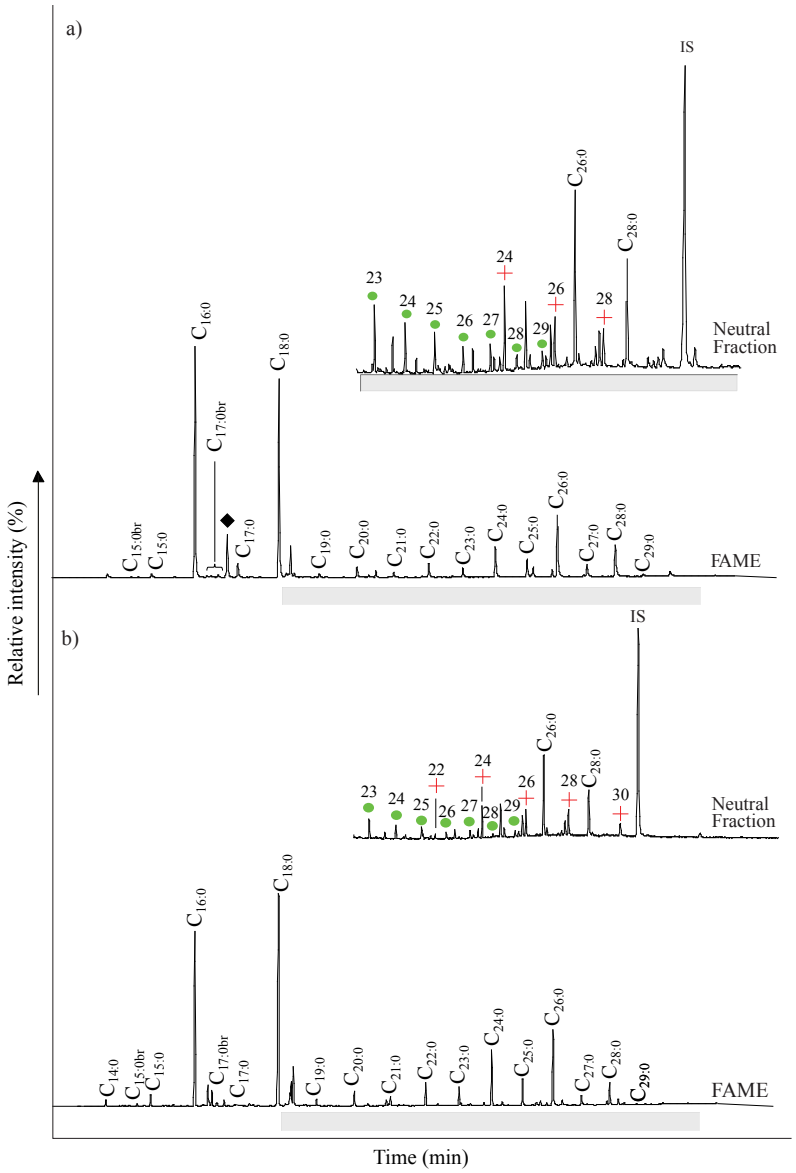


Figure 6.10. Two gas chromatograms of TLEs from sherds MB3 (a) and MB5 (b). The FAMEs show an enhanced fatty acid distribution ($C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products, and long chain fatty acids C_{19}-C_{30}); while the neutral fractions highlights the distribution of *n*-alkanes (dots), and the long-chain *n*-alkanols (crosses). In the figure: fatty acids (FA), branched-chain fatty acids (br), *n*-alkanes (dots), *n*-alkanols (crosses), phthalate (rhombus) and internal standard C_{34} *n*-tetratriacontane (IS).

6.4.2 *$\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids*

The trends seen in the carbon isotope values of $C_{16:0}$ and $C_{18:0}$ fatty acids in the Molyukhov Bugor extracts are similar to Dereivka extracts. The $\delta^{13}C_{16:0}$ values range from -29.2‰ to -26.5‰, whereas $\delta^{13}C_{18:0}$ values range between -30.7‰ and -24.3‰ with mean values of -27.7‰ and -28.5‰, respectively.

Examination of Figure 6.11 reveals that seven Molyukhov Bugor residues exhibit $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids characteristic of equine fats. Three residues plot within the range of ruminant adipose fats. Finally, only one residue plots in the range of non-ruminant fat. Examination of Figure

6.11a suggests a possible porcine origin of the only non-ruminant residue ($\delta^{13}C_{16:0}$ =-26.5‰, $\delta^{13}C_{18:0}$ =-24.3‰ and $\Delta^{13}C$=2.2‰; Mukherjee et al., 2007).

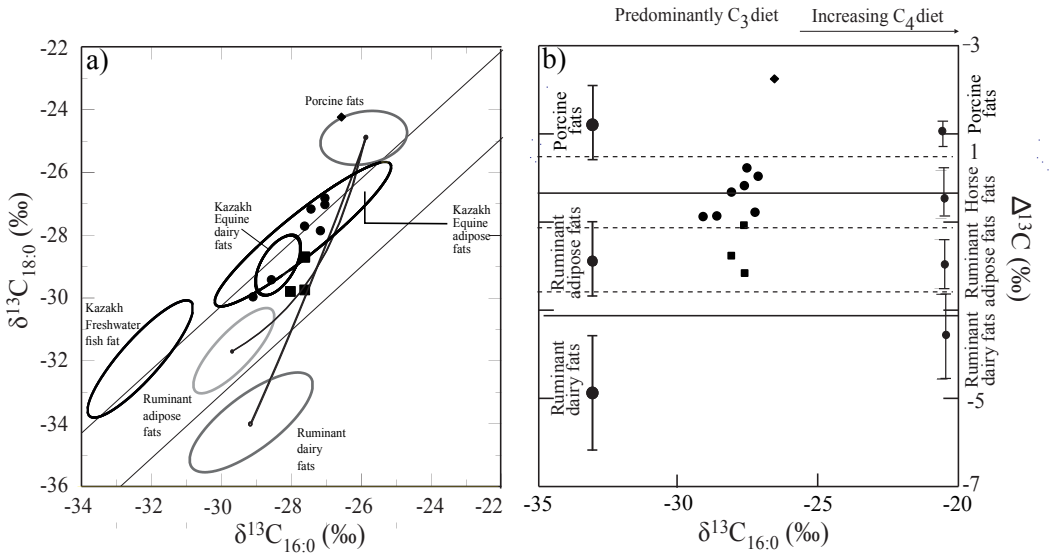


Figure 6.11. Scatterplots of (a) $\delta^{13}C$ values of $C_{16:0}$ fatty acid against the $C_{18:0}$ fatty acid extracted from 25 pottery vessels from Molyukhov Bugor. In the plots, equine fats (black dots); porcine fat (black rhombus); ruminants fats (black squares). Archaeological values overlay confidence ellipses corresponding to the values obtained from modern reference fats, which enables the species classification of the ancient animal products; and (b) $\delta^{13}C$ values of $C_{16:0}$ against the $\Delta^{13}C$ values ($\delta^{13}C_{18:0}$ - $\delta^{13}C_{16:0}$).

Table 6.3
The different classes of animals inferred from faunal records in Molyukhov Bugor site (Bibikova, 1963; Kaiser, 2010). Both MNI and NISP are shown. Sheep and goats are combined.

	Cattle	*Sheep/Goats*	*Pigs*	*Horses*	*Wild animals*	*Fishes*
MNI	8	5	4	10	50	-
MNI%	10,4	6,5	5,2	13	64,9	-
NISP	1871	367	270	704	1900	-
NISP%	36,6	7,2	5,3	13,8	37,2	-

The compound-specific stable carbon values of the fatty acids in the pottery from Molyukhov Bugor were dominated by equine products (67%), which mismatched the faunal records (Table 6.3) that revealed a lower percentage of equine bones (ca. 14%). The latter mismatch can be explained as follow: (i) the abovementioned mixture of materials might have altered the faunal record proportion or (ii) equine products were preferably processed in vessels while other animal products were processed in other manners (e.g. using a spit over an open fire). According to the faunal records hunting was a widespread activity as the 37% of the faunal assemblage comprised of wild animals. In addition, the ca. 44% were attributed to domesticated ruminants (including cattle, sheep and goats) suggesting that ruminant breeding was a significant complementary practise, also supported by the isotope results that revealed that 25% of the total residues have a ruminant origin.

Overall exploitation of equine products prevailed. Although the occurrence of residues deriving from equine fats was quite abundant (48% in Dereivka and 67% in Molyukhov Bugor), it is not possible to infer from these data whether these horses were wild or domesticated (Outram et al., 2009) since there is significant overlap of the $\delta^{13}C$ values of equine adipose and milk reference fats making it impossible to identify archaeological equine dairy fat residues based on the $\delta^{13}C$ values of the $C_{16:0}$ and $C_{18:0}$ fatty acids (Outram et al., 2009; Stear, 2008). However, the modern Kazakh equine fats were distinguishable by using compound-specific stable hydrogen analysis. Therefore, following the successful research of Outram et al. (2009), a number of lipid residues were subjected to compound-specific stable hydrogen isotope analysis (discussed in Section 6.5), in order to (i) determine if the same proxy could be used to achieve the equine adipose-milk fats distinction in the North-Pontic region and therefore (ii) establish if any of these residues demonstrate the processing of equine milk products.

Finally, the distribution of $\delta^{13}C_{16:0}$ values of the majority of the extracts range between 29.1‰ to -26.5‰, which as in the case of Dereivka, is slightly broader that the distribution of the $\delta^{13}C_{16:0}$ values for modern ruminant fats from British animals raised on a strict C3 plants diet. The latter is more comparable to the $\delta^{13}C_{16:0}$ values for modern Kazakh reference fats, ranging from -29.0 to -24.1 ‰ (Stear, 2008), and it might derive from animals consuming a small proportion of C4 plants and/or water-stressed C3 plants (Evershed et al., 2008b). The possible presence of C4 plants into the diet of the animals of the North-Pontic region will be discussed in Chapter 8.

6.5 Stable-isotope ratio of hydrogen (δD) of $C_{16:0}$ and $C_{18:0}$ fatty acids

There are several uses of the stable-isotope ratios of hydrogen (δD values) in animal tissues (Chapter 1, Section 1.6) notably in:

1) Food web delineation (Chivall, 2008; Smith and Epstein, 1971) as different digestive systems or trophic level influences the tissue δD values (Reynard and Hedges, 2008);
2) More challenging fat identification; equine adipose and equine dairy products were identifiable (Outram et al., 2009; Stear, 2008) due to the modern δD seasonal effect in Kazakhstan (of ≈100 ‰), which allowed the recognition of equine dairy fat residues from the Eneolithic site of Botai (Outram et al., 2009);
3) Palaeoclimatic reconstruction (Chivall, 2008; Cormie et al., 1994; Reynard and Hedges, 2008); δD values in meteoric water are affected by various meteorological processes, thereby providing a characteristic fingerprint of the source precipitation (Smith et al., 2013).

In order to test the abovementioned uses of the stable-isotope ratios of hydrogen (δD), a total of 56 TLEs were selected from the extracts from the settlements located in the North-Pontic region, of which n=24 residues were attributed to equine products, n=21 were attributed to ruminant adipose fats, n=6 were attributed to ruminant dairy fats and n=5 with a possible freshwater fish fats origin (all attributions were previously made by compound-specific stable carbon isotope analysis; see this Chapter and Chapter 7). The residues were selected from different settlements (11 residues were analysed from the pottery from Dereivka; 20 from Nizhniy Rogachik; 15 from Mikhailovka II; and 10 from Generalka). These were analysed by GC-TC-IRMS and recorded δD values corrected for hydrogen added during derivatisation (Chivall et al., 2012) and plotted in Figures 6.12 and 6.13.

Therefore, the main hypotheses tested in this Chapter are:

1) Different δD values are expected for different groups of animal products (e.g. equine *vs* ruminant adipose);
2) A similar but narrower (≈40 ‰ *vs* ≈100 ‰) δD seasonal effect likely occurred in Ukraine like in Kazakhstan (the seasonal effect and its role in identifying equine dairy fats in Botai extracts has been discussed in Chapter 1, Section 1.6), so it can be used to identify equine adipose-milk fats in the North-Pontic pottery as a basis for confirming (or refuting) horse domestication in the region.

As discussed above, an important use of the stable-isotope ratios of hydrogen (δD) is related to paleoclimatic reconstruction. The latter will be tackled in Chapter 8 where the environmental and climatic reconstruction of the North-Pontic region will be attempted.

6.5.1 *Results*

In order to test the first hypothesis (different δD values are expected for different groups of animal products), n=13 residues attributed to equine products, n=11 attributed to ruminant adipose fats, n=6 attributed to ruminant dairy fats and n=3 possibly attributed to freshwater fish fats (all attributed by using compound-specific stable carbon isotope analysis) were selected only from one period, the Late Eneolithic (Nizhniy Rogachik and Mikhailovka II sites) in order to remove any possible climatic/environmental variables. Despite the different attempts to alternate $\delta^{13}C_{16:0}$, $\delta^{13}C_{18:0}$ and $\Delta^{13}(C_{18:0} - C_{16:0})$ values, the distinction between different animal fats was not possible. Neither plot a, b or c allowed a separation between fats. Only the examination of Figure 6.12a allowed a slightly better distinction of fats, especially concerning the ruminant dairy fats, which displayed enriched $\delta^{13}C_{16:0.}$ Nevertheless, besides this exception, different groups of animal products did not display significant difference in δD values; therefore this hypothesis was not supported.

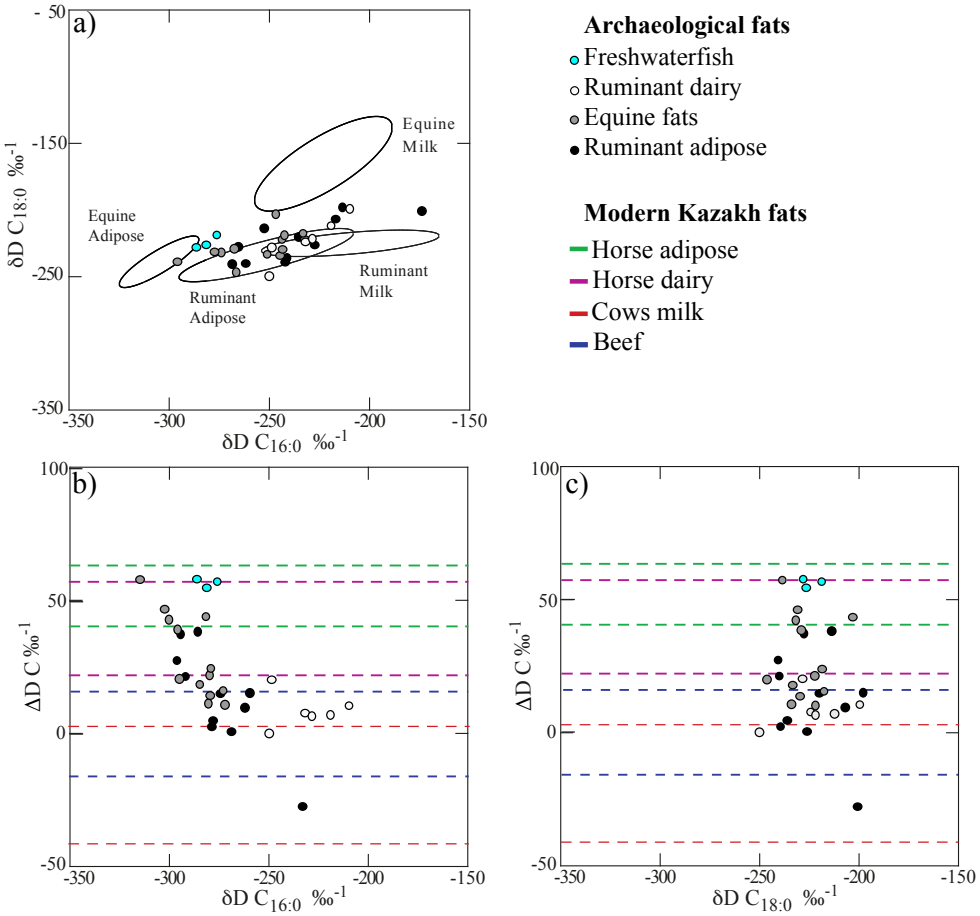


Figure 6.12. Scatterplots of (a) $\delta DC_{16:0}$ fatty acid against $\delta DC_{18:0}$ fatty acid extracted from 33 pottery vessels of which n=13 (grey dots) were attributed to equine products, n=11 (black dots) were attributed to ruminant adipose fats, n=6 (white dots) attributed to ruminant dairy fats and n=3 (blue dots) possibly attributed to freshwater fish fats. The residues were previously attributed to the specific animal products by compound-specific stable carbon isotope analysis. Archaeological values overlay confidence ellipses corresponding to the values obtained from modern Kazakh reference fats (Stear, 2008); (b) $\delta DC_{16:0}$ fatty acid against the ΔD values ($C_{18:0}$ - $C_{16:0}$) and (c) $\delta DC_{18:0}$ fatty acid against the ΔD ($C_{18:0}$ - $C_{16:0}$) values.

The second hypothesis (based on the research carried out by Outram et al., 2009) concerned the possibility to use the Ukrainian δD value shift of the meteoric water between summer and winter (≈40 ‰) in order to distinguish between equine milk and adipose fats as a basis for confirming (or refuting) horse domestication in the region. The latter hypothesis was tested by plotting Dereivka equine fats together with Botai equine fats (Figure 6.13).

As explained in Chapter 1, Section 1.6.2.1, the research carried out by Outram et al. (2009) was based on the hypothesis that the hydrogen used to biosynthesise equine fats derives ultimately from environmental water, such that carcass fat will represent an integration of hydrogen for the entire period of accumulation, probably many months, while milk fat hydrogen derives from late spring or summer precipitation. These two different fats will exhibit different averaged δD values reflecting the period of biosynthesis (Dansgaard, 1964; Rozanski et al., 1993). Significantly, Kazakhstan precipitation shows a substantial modern seasonal variation in precipitation δD value, of ca. 80‰ in

the area of Raïsovka (where Botai was located), with values of -155‰ and -80‰, being recorded in January and July, respectively (Bowen, 2009). Interestingly, the seasonal deuterium effect in Kazakhstan appear to have persisted in precipitation over the millennia, allowing the identification of equine dairy residues, enriched by roughly 100‰ (indicated by stars in Figure 6.13) compared to the main cluster of carcass fat residues. Following this idea the lipid residues from Dereivka attributed to equine fats by compound-specific stable carbon isotope analysis, were submitted to compound-specific stable hydrogen isotope analysis in order to determine if the processing of equine milk products could be detected.

Figure 6.13 displays the hydrogen isotope results of equine fat residues in potsherds from Dereivka (n=6; indicated by black dots) and Botai (n=42); indicated by white dots and stars; the data for Botai are taken from Outram et al., 2009). Examination of Figure 6.13 reveals that the 6 Dereivka residues display δD values (mean δD $C_{16:0}$ of -273‰ and $C_{18:0}$ of -229‰) plotting closer to both the modern reference and Botai horse carcass fats than to horse milk fats. Therefore, this hypothesis was also not supported (Mileto et al., 2017a).

Finally, Figure 6.14 displays the hydrogen isotope results of equine fat residues in potsherds from Dereivka, Nizhniy Rogachik and Mikhailovka II and Generalka in order to determine if the δD value shift of the meteoric water between summer and winter was present in other periods and ecosystems. In this case, the higher number of residues allowed identification of two possibly different groups of fats that have been separated by considering a hypothetical $\delta^{13}C_{16:0}$ threshold at around -260‰ (where the shift is more evident). The mean value of the two groups of residues is, respectively, -245‰ and -277‰, i.e. a shift of roughly 30‰, which would be consistent with the shift in the meteoric water between summer and winter so between equine milk and adipose. Assuming that the latter suppositions are valid, this means that ca. ten residues, attributed to equine products using compound-specific stable carbon isotope analysis, have an equine dairy fats origin. The latter data would not be surprising considering that the residues with an enriched δD come from the later sites of the Late-Eneolithic and Early Bronze Age (Nizhniy Rogachik, Mikhailovka II and Generalka). However, by performing a set of statistical methods on the distribution of $\delta DC_{16:0}$ (Program IBM SPSS statistics version 21) the difference between the two group of samples resulted to be marginal: in general the data set displayed a non-normal distribution, therefore a non-parametric test of independent samples was applied to examine the data distribution. The Mann Whitney U Test identified differences between the two group of samples but the significance level was only p=0.05 which is considered to be marginal so could go either way. In addition, the absence of reference fats from Ukraine prevents in confirming the identification of equine dairy fats and the possibility that the shift identified might simply be related to different diets of the horses perhaps due to migration has to be considered; in addition it has to be considered that the narrower Ukrainian shift between summer and winter

meteoric water might prevent clear identification of residues with enriched δD as was possible at Botai where the enrichment was greater.

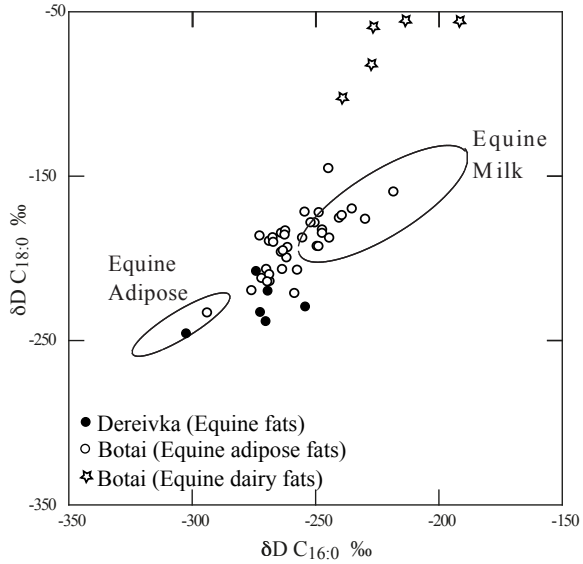


Figure 6.13. Scatterplot of δD values of $C_{16:0}$ against $C_{18:0}$ fatty acids extracted from (i) six Middle Eneolithic potsherd from Dereivka site (black dots) and (ii) 40 Middle Eneolithic potsherd from Botai site (white dots and stars). The residues were previously attributed to equine products by compound-specific stable carbon isotope analysis. Archaeological values overlay confidence ellipses corresponding to the values obtained from modern Kazakh reference fats.

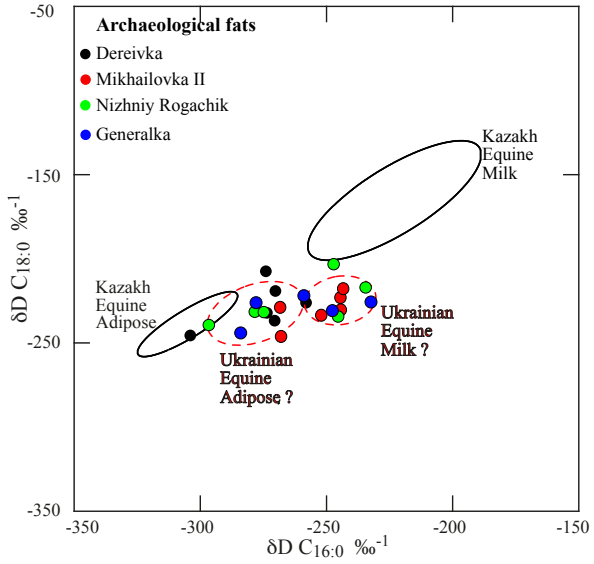


Figure 6.14. Scatterplots of $\delta DC_{16:0}$ fatty acid against $\delta DC_{18:0}$ fatty acid extracted from 24 pottery vessels from Dereivka, Mikhailovka II, Nizhniy Rogachik and Generalka, attributed to equine products using compound-specific stable carbon isotope analysis. Archaeological values overlay confidence ellipses corresponding to the values obtained from modern Kazakh equine fats (Stear, 2008). The red dotted ellipses correspond to the confidence ellipses created by dividing the residues into two groups: 1) the residues with $\delta DC_{16:0}$ values lower than -260‰ and 2) the residues with $\delta DC_{16:0}$ value higher than -260‰.

6.6 Summary and Conclusion

In this Chapter, the isotope carbon results of the lipid analysis of 65 potsherds from two archaeological sites, Dereivka and Molyukhov Bugor located in the forest-steppe of the North-Pontic region, have been presented. Lipid recovery was overall significant showing mean values, respectively of 18.3 μg g^{-1} and 18.7 μg g^{-1} with maximum values of 206.1 μg g^{-1} and 76 μg g^{-1}.

Therefore, the major conclusions that can be drawn are:

1) Analysis of the TLEs from the two forest-steppe sites demonstrates that the free fatty acids, $C_{16:0}$ and $C_{18:0}$, are the most abundant components, suggesting that the hydrolysis of triacylglycerols, diacylglycerols and monoacylglycerols has proceed to completion and that the extensive oxidation of unsaturated fatty acids has occurred;

2) The most common distribution is dominated by fatty acids that generally range from $C_{12:0}$ to $C_{24:0}$ acyl carbon atoms with high abundances of the $C_{16:0}$ and $C_{18:0}$ fatty acids, which are indicative of the presence of degraded animal products (e.g. Evershed et al., 1997a);

3) Branched-chain fatty acids ($C_{15:0}$ and $C_{17:0}$), which are components of bacterial origin diagnostic of both ruminant animal products (Christie, 1978; Hubbard and Pocklington, 1968) and equine adipose products (Hintz and Cymbaluk, 1994; Pond et al., 1995), were also abundant;

4) Additionally, a series of long-chain fatty acids and *n*-alkanols, characteristic of plant waxes, were identified in four extracts from Molyukhov Bugor.

To conclude, the application of compound-specific stable hydrogen analysis on animal fatty acids displayed an extensive overlap of residues precluding the possibility to distinguish between animal fats. Significantly, a shift of ca. 30‰ was visible by plotting the 24 residues attributed to equine products (using compound-specific stable carbon isotope analysis). The latter shift might actually correspond to the different $\delta DC_{16:0}$ value of the meteoric water between summer and winter and it might be the shift between equine dairy fats and adipose fats. However, the number of samples analysed is scarce, the absence of reference fats from Ukraine prevents in confirming the identification of equine dairy fats and the statistical methods applied did not fully support this theory. Therefore, further analysis would be necessary in order to shed light on this specific topic.

Specifically, regarding the identification of equine dairy fats in Dereivka, very likely the limited number (n=6) of residues was the fundamental problem; however, the values obtained point to these residues deriving mainly from equine carcass fats. While this might seem to contrast with the successful detection of horse milking at Botai in Eneolithic Kazakhstan, there are differences between Botai investigation and the present study of North-Pontic region that are worth emphasising: (i) most importantly a larger difference exists between the δD value of summer and winter precipitation at Botai (80-100 ‰) than in the North-Pontic region (40-50 ‰) that, given the precision of the

compound-specific δD determinations (±5 ‰), fundamentally limits the capacity to resolve milk and carcass residues, (ii) the sample size studied at Botai was very large, which necessarily increased the likelihood of detecting a low level of horse milking on statistical grounds, and (iii) the interpretation of the deuterium isotope data from the North-Pontic region is generally complicated by the limited understanding of the factors governing the fractionation of the hydrogen isotopes from the meteoric water to animal tissue (Chivall, 2008; Cormie et al., 1994) exacerbated by the lack of modern reference fats from the region (Mileto et al., 2017a).

CHAPTER 7

RESULTS (PART II): DIET AND SUBSISTENCE ECONOMY IN THE ENEOLITHIC AND EARLY BRONZE AGE STEPPE OF THE NORTH-PONTIC REGION

7.1 Introduction

As explained at the beginning of Chapter 6, the current Chapter will use molecular and stable isotope techniques to investigate additional residues extracted from 151 archaeological ceramics excavated from prehistoric Ukrainian sites (described separately in Chapter 4) and located in the steppe, to investigate diet and subsistence strategies in the region. In contrast to the forest-steppe sites, of which only two Middle Eneolithic sites were investigated (Dereivka and Molyukhov Bugor), in the case of the steppe settlements, pottery were collected for both Eneolithic and Early Bronze Age sites allowing a better reconstruction of dietary change through time.

This Chapter focuses on the steppe sites of Mikhailovka I from the Middle Eneolithic (ca. 3800 to 3500 BC), Mikhailovka II and Nizhniy Rogachik from the Late Eneolithic (ca. 3500 to 3000 BC) and Generalka and Mikhailovka III from the Early Bronze Age (ca. 3000 to 2300 BC). The investigation of the lipid biomarker compositions comprised the four steps described in Chapter 6, Section 6.1. The specific aims of this Chapter are:

(i) Determine the biomarker compositions of organic residues in order to identify commodities processed in the ceramic vessels, and;

(ii) Identify the type of absorbed fat (e.g. ruminant dairy or ruminant adipose fats, equine fats and non-ruminant fats) by comparing archaeological and modern reference $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids.

7.2 Nizhnyi Rogachik site

7.2.1 *Organic residues recovered from Nizhnyi Rogachik pottery*

The general preservation of Nizhnyi Rogachik pottery was appreciable; 77% of the sampled potsherds yielded a lipid concentrations ranging from 5 to 1024 μg g^{-1} with a mean value 127.1 μg g^{-1}. A total of 23 out of 30 potsherds contained sufficient concentrations of lipids to warrant further investigation. The TLEs were generally dominated by high abundances of saturated fatty acids including palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids, in addition to lower abundances of mystiric acid ($C_{14:0}$) acid and branched-chain and odd carbon number fatty acids, including $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$, tentatively indicating ruminant animal product processing. TAGs and their degradation products (DAGs and MAGs) were observed in ca. 20% of the residues, with the acyl carbon numbers ranging from C_{48} to C_{54}, usually dominated by C_{52}. Lower molecular weight TAGs (C_{44} to C_{46}) which characterise dairy fats were also present (Dudd and Evershed 1998). Figure 7.1 displays a gas chromatogram (NR20) containing intact TAGs, DAGs and MAGs.

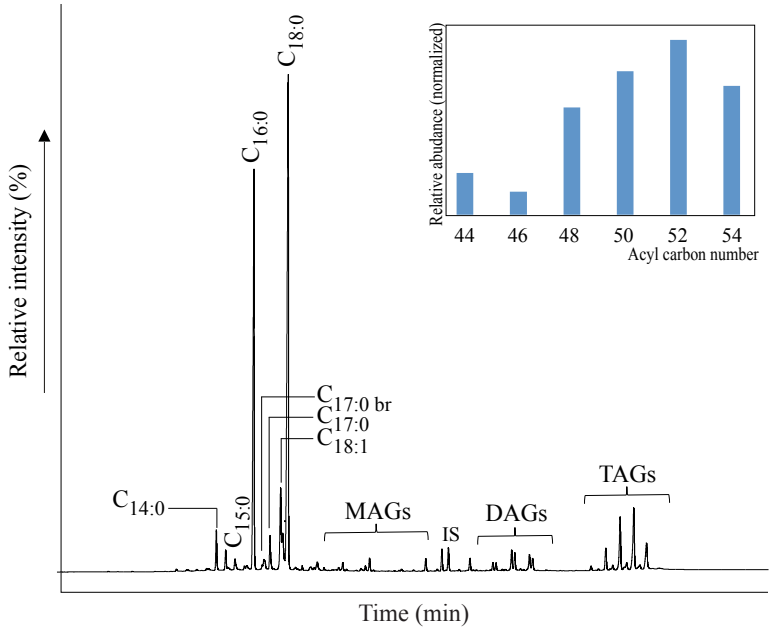


Figure 7.1. Partial gas chromatogram of TLE from sherd NR20, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products and the distribution of MAGs, DAGs and TAGs. The image shows: fatty acids (FA), branched-chain fatty acids (br), triacylglycerols (TAGs), diacylglycerols (DAGs), monoacylglycerols (MAGs) and the internal standard, C_{34} *n*-tetratriacontane (IS).

Lipid biomarker analyses by GC/MS showed the residues to fall into 3 broad categories, denoted Profile I, II and III, and detailed as follows:

7.2.1.1 Lipid distribution – Profile I

The compositions of the majority of the TLEs suggested an animal product origin as indicated by a lipid distribution mainly dominated by $C_{16:0}$ and $C_{18:0}$ fatty acids. The great majority of the extracts also displayed $C_{14:0}$ fatty acid and branched-chain and odd carbon number fatty acids, including $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$ (see Figure 7.1). The presence of branched-chain fatty acids suggests bacterial origin consistent with ruminant animal fat (Christie, 1978). However, branched-chain fatty acids (especially *iso*- and *anteiso*-$C_{17:0}$) are also detected in equine adipose fats and likely derive from similar groups of microorganism located in the hindgut of the horse (Hintz and Cymbaluk, 1994; Pond et al., 1995).

7.2.1.2 Lipid distribution – Profile II

The application of GC/MS SIM revealed the presence of ω-(o-alkylphenyl) alkanoic acids (APAAs) in two extracts from Nizhnyi Rogachik (NR9 and NR18). As discussed in Chapter 1, Section 1.3.2.5, APAAs are cyclic compounds with even carbon numbers ranging from $C_{16:0}$ to $C_{22:0}$. The two residues were otherwise dominated by a high abundance of $C_{16:0}$ and $C_{18:0}$ fatty acids, also displaying $C_{14:0}$ fatty acid and branched-chain and odd carbon number fatty acids, including $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$. Moreover, the residues displayed both APAAs (mainly C_{16} and C_{18}) and the isoprenoid acid 4,8,12-trimethyltridecanoic (4,8,12-TMTD; Figure 7.2). The APAAs are potential biomarkers for any commodities with high concentrations of unsaturated fatty acids, such as aquatic animals, plants or horse. High proportions of C_{20} and C_{22} fatty acids are particularly abundant in oily fish and fish oils (Gunstone, 2009), which lead to the formation of C_{20} and C_{22} APAAs, so the presence of only C_{18} APAAs is not a diagnostic for aquatic product processing. On the other hand, equine fat is dominated by the essential fatty acids linoleic ($C_{18:2}$) and α-linolenic ($C_{18:3}$) (Malacarne et al., 2002) acids that can produce C_{18} APAAs on heating to ca, 300^{o}C. Thus, the detection of C_{18} APAAs together a high abundance of $C_{18:0}$ fatty acid can be diagnostic of equine product processing. However, 4,8,12-TMTD is particularly concentrated in marine animals and can also be present in low concentrations in terrestrial animal fats (e.g. Christie, 2012). Therefore these two extracts can definitely be a mixture of animal products.

7.2.1.3 Lipid distribution – Profile III

One extract (NR5) showed long-chain saturated fatty acids (C_{19}-C_{30}) and long-chain *n*-alkanols (C_{24}, C_{25}, C_{26}, C_{27}, C_{28}, C_{29}, C_{30} and C_{31}), indicating possible presence of plant epicuticular wax derived from plant processing (Figure 7.3).

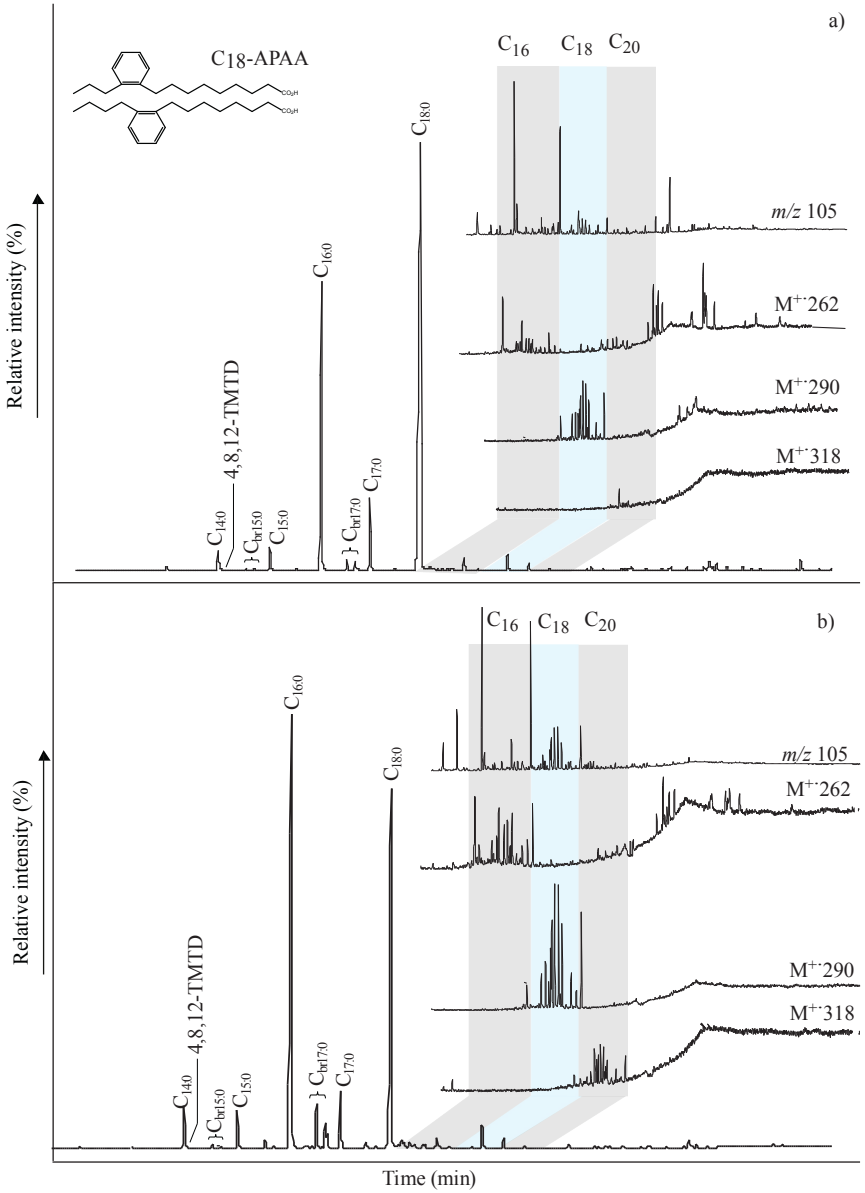


Figure 7.2. GC/MS total ion current (TIC) of TLEs from sherd NR9 (a) and sherd NR18 (b). *m/z* 105 is the common ion to all APAAs. To better highlight the APAAs, the three range masses corresponding to each C_{16}, C_{18}, C_{20} APAAs were chosen ($M^{+\cdot}$ 262, $M^{+\cdot}$ 290 and $M^{+\cdot}$ 318). Fatty acids (FA), branched-chain fatty acids (br), ω-(o-alkylphenyl) alkanoic acids (APAAs) and 4,8,12-trimethyltridecanoic acid (4,8,12-TMTD). Appendix D, Figures 3 and 4 displays the mass spectra of the C_{18}, C_{20} APAAs and the mass spectrum of 4,8,12-TMTD.

7.2.2 *$\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids*

In the case of Nizhniy Rogachik, the trend seen in the carbon isotope values of $C_{16:0}$ and $C_{18:0}$ fatty acids is significantly different from the forest-steppe sites (described in Chapter 6). Figure 7.4a displays the $\delta^{13}C$ values of both $C_{16:0}$ and $C_{18:0}$ fatty acids while Figure 7.4b displays the $\Delta^{13}C$ plot. $\delta^{13}C_{16:0}$ fatty acid varies from -31.1 ‰ to -25.3‰, whereas $\delta^{13}C_{18:0}$ fatty acid shows values between -30.5‰ and -28.3‰ with mean values respectively of -28.3‰ and -29.5‰.

The difference with the forest-steppe sites is striking. Examination of Figure 7.4b reveals that the majority of Nizhniy Rogachik residues (n=14) exhibit $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids characteristic of ruminant products, of which five residues plot well within the range of ruminant dairy products. Six residues plot well within the range of equine fats, while only two extracts (NR4 and NR6) might have a freshwater fish fat origin, with mean $\delta^{13}C_{16:0}$ value of -30.9‰, mean $\delta^{13}C_{18:0}$ value of -29.9‰ and mean $\Delta^{13}C$ of 0.9 ‰ (Cramp & Evershed, 2014). However, no APAAs or other fish biomarkers have been identified in these two extracts. The remaining one extract (NR18) might have a mixing fat origin.

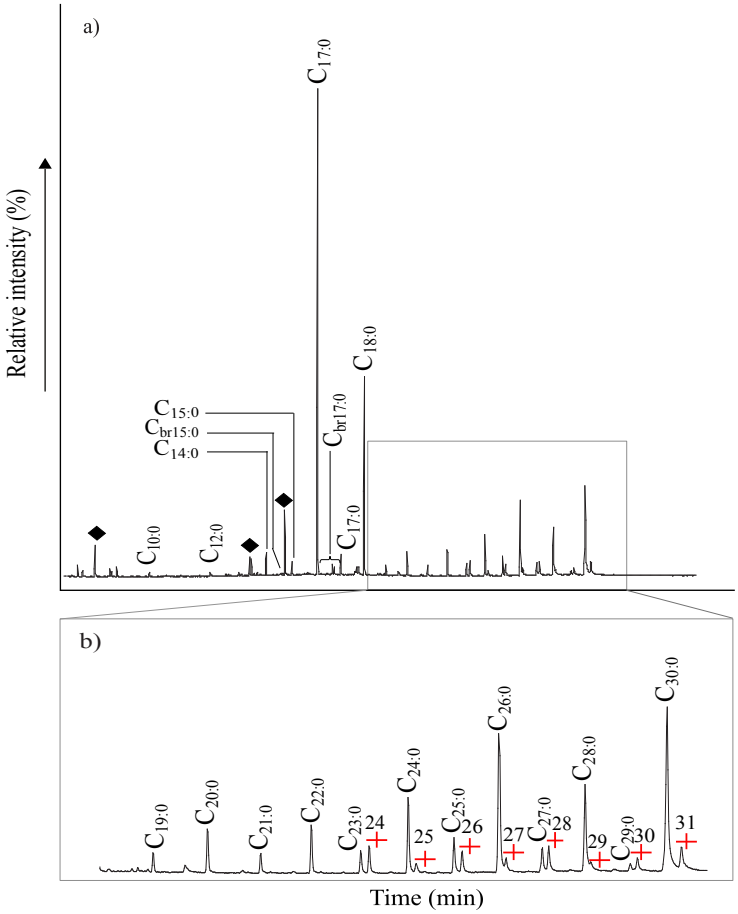


Figure 7.3. (a) Partial gas chromatogram of the TLE from sherd NR5 showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products; (b) highlights the distribution of long chain fatty acids and long-chain *n*-alkanols C_{24}, C_{25}, C_{26}, C_{27}, C_{28}, C_{29}, C_{30} and C_{31}. In the figure: fatty acids (FA), branched-chain fatty acids (br), long-chain *n*-alkanols (red crosses), internal standard C_{34} *n*-tetratriacontane (IS) and phthalic acid (black rhombus). Appendix D, Figure 2 displays the mass spectra of the *n*-alkanols distributions.

Considering the lack of faunal evidences from Nizhniy Rogachik, the results of compound-specific stable carbon isotope analysis are extremely important. From these results, it appears that the ca. 60% of the investigated pottery vessels were used for the processing of ruminant products of which the 20% were used to process ruminant dairy products. The 29% of the investigated

pottery vessels were used for processing of equine products and 8% were possibly used for freshwater fish products (n=2 residues).

Finally, also in this case, the distribution of $\delta^{13}C_{16:0}$ values (Figure 7.4b) of the majority of the extracts range from -31.1 to -25.3 ‰, which is broader that the distribution of the $\delta^{13}C_{16:0}$ values for modern ruminant fats from British animals, raised on a strict C3 diet ($\delta^{13}C_{16:0}$ values ranging from -30.9‰ and -28.6‰; Copley et al., 2003). The latter is more comparable to the $\delta^{13}C_{16:0}$ values for modern Kazakh reference fats, ranging from -29.0 to -24.1 ‰ (Stear, 2008), which animals might have been fed with a broad range of forages (Stear, 2008), comprising mainly C3 plants but with some C4 input. Significantly, some of the residues with a ruminant adipose fats and the five residues with a ruminant dairy origin, display the most enriched $\delta^{13}C_{16:0}$ values. The mean $\delta^{13}C_{16:0}$ value of the latter fats is more enriched by ca. 3-4 ‰ in comparison to modern British reference fats (Copley et al., 2003). As already mentioned in Chapter 6, similar enrichment was also observed in $\delta^{13}C$ values of lipids extracted from Near Eastern archaeological pottery (Evershed et al., 2008) where it was hypothesised to result from the animals producing the fats consuming a proportion of C4 plants in their diets and/or water-stressed C3 plants. However, this topic will be discussed in details in Chapter 8, Section 8.3.

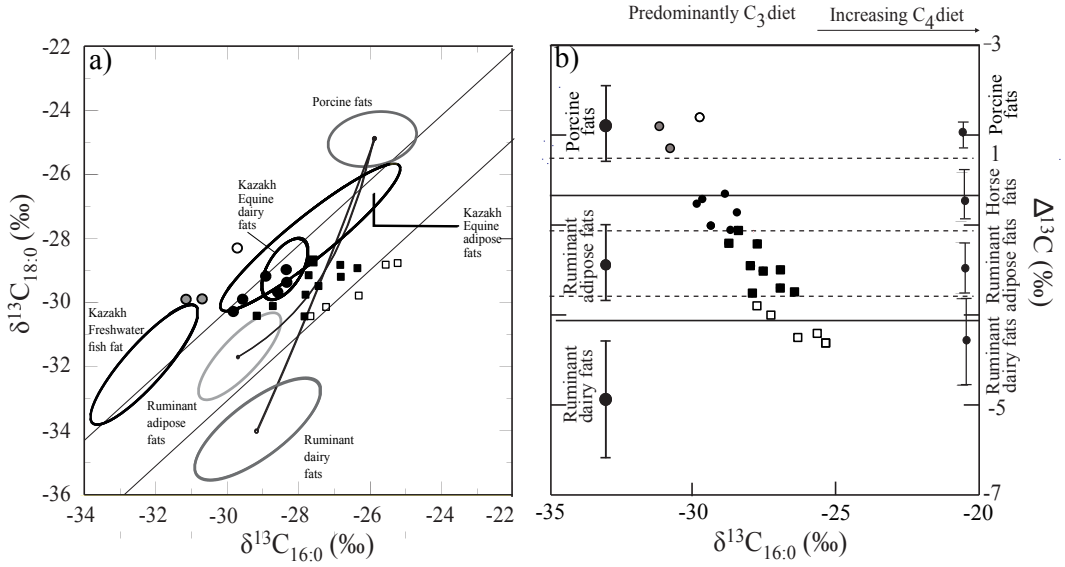


Figure 7.4. Scatterplots of (a) $\delta^{13}C$ values of $C_{16:0}$ fatty acid against the $C_{18:0}$ fatty acid extracted from pottery vessels from Nizhniy Rogachik. In the figure, equine fats (black dots); porcine fat (black rhombus); possible freshwater fish fats (grey dots); ruminants fats (black squares); mixed fat residues (white dots). Archaeological values overlay confidence ellipses corresponding to the values obtained from modern reference fats, which enables the species classification of the ancient animal fats; and (b) $\delta^{13}C$ values of $C_{16:0}$ against the $\Delta^{13}C$ values ($\delta^{13}C_{18:0}$ - $\delta^{13}C_{16:0}$) that allow a better distinction among animal groups.

7.3 **Mikhailovka site**

7.3.1 *Organic residues recovered from Mikhailovka I pottery*

A total of 36 potsherds were investigated from Mikhailovka I horizon.

The overal preservation of the organic residues was impressive. The mean lipid concentration value was 621.7 μg g^{-1}. A total of 94% of the extracts (n=34) yielded appreciable lipid concentrations ranging from 5 to 3894.8 μg g^{-1}.

$C_{16:0}$ and $C_{18:0}$ fatty acids were particularly abundant with a predominance of the $C_{18:0}$ acid in the majority of the extracts (n=24); branched-chain and odd carbon number saturated fatty acids, including $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$, were frequently present, suggesting that the ceramic vessels were generally used to process ruminant animal products.

TAGs and their degradation products (DAGs and MAGs) were observed in 55% of the residues, with acyl carbon numbers ranging from C_{48} to C_{54}, usually dominated by C_{52}. Lower molecular weight TAGs (C_{44} to C_{46}) which characterise dairy fats were also present (Dudd and Evershed 1998). Figure 7.5 displays a gas chromatogram (MIK68) containing intact TAGs, DAGs and MAGs.

The longest chain fatty acid observed was C_{22}, with no evidence of long–chain *n*-alkanes or *n*-alkanols. In addition, no APAAs or other biomarkers were detected, suggesting that the vessels were mainly committed to processing animal products.

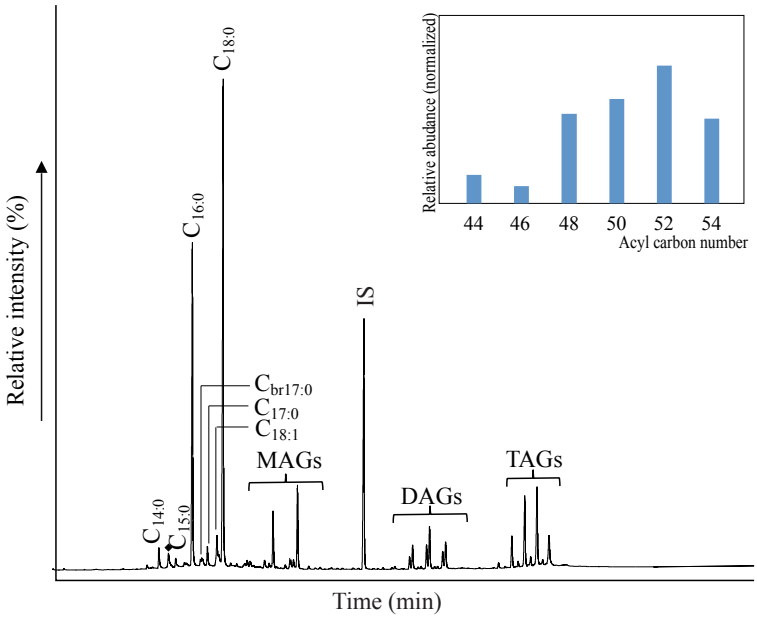


Figure 7.5. Partial gas chromatogram of TLE from sherd MIK68, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products, and the distribution of MAGs, DAGs and TAGs. In the figure: fatty acids (FA), branched-chain fatty acids (br), triacylglycerols (TAGs), diacylglycerols (DAGs), monoacylglycerols (MAGs) and the internal standard, C_{34} *n*-tetratriacontane (IS).

7.3.2 *Organic residues recovered from Mikhailovka II pottery*

The general lipid preservation was lower but still appreciable. Of a total of 21 extracts, 90% (n=19) yielded an appreciable lipid concentrations ranging from 5 to 182.3 μg g^{-1}, with a mean value of 53.9 μg g^{-1}. The great majority of the TLEs from Mikhailovka II pottery display saturated $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$ fatty acids, with a predominance of the $C_{18:0}$ fatty acid over the $C_{16:0}$ (n=18); also branched-chain and odd carbon number fatty acids, including $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$, were frequently present, indicating ruminant animal product processing.

TAGs and their degradation products (DAGs and MAGs) were observed in 21% of the residues, with the acyl carbon numbers ranging from C_{48} to C_{54}, usually dominated by C_{52}. Lower molecular weight TAGs (C_{44} to C_{46}) which characterise dairy fats were absent (Dudd and Evershed, 1998). Figure 7.6 displays the chromatogram of the best-preserved residue (MIK14) containing intact TAGs and DAGs. Moreover, the same extract displays a high concentration of the $C_{14:0}$ fatty acid showing possible presence of dairy fats (also explained in Chapter 6, Section 6.3.1.1) as the presence of short-chain saturated fatty acids in the $C_{4:0}$ to $C_{14:0}$ carbon number range is common in dairy products (Kuksis et al., 1973; Christie, 1981; McDonald et al., 1988).

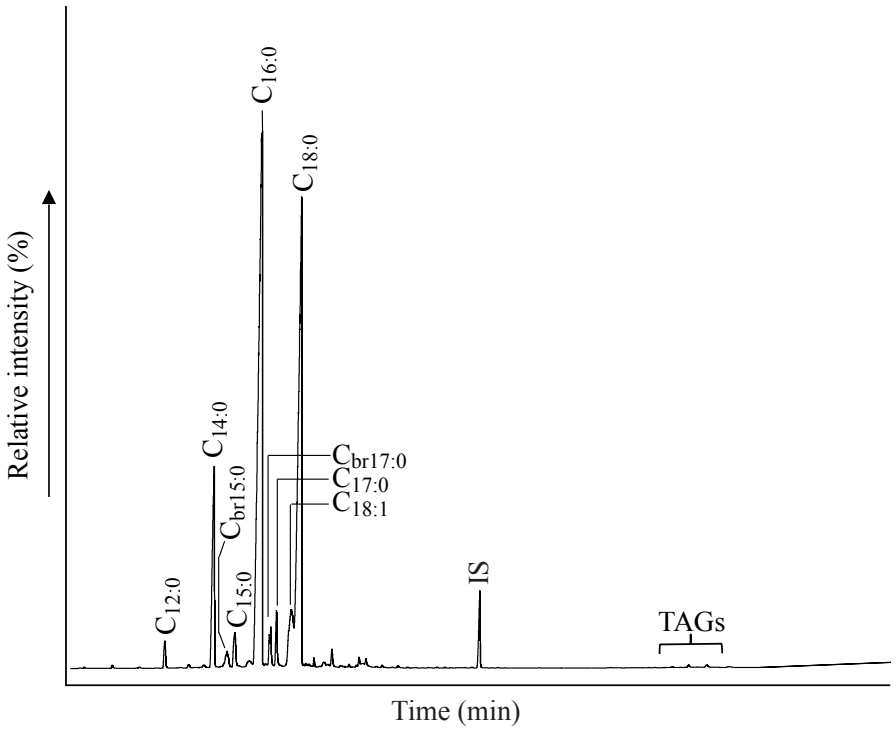


Figure 7.6. Partial gas chromatogram of TLE from sherd MIK14, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products. In the figure: fatty acids (FA), branched-chain fatty acids (br), triacylglycerols (TAGs) and the internal standard, C_{34} *n*-tetratriacontane (IS).

In addition, three mid-chain ketones were observed in one residue (MIK20), suggesting that the food was cooked at the high temperatures, required for their formation (Figure 7.7). As discussed

above, mid-chain ketones are formed from animal fats via a ketonic decarboxylation reaction between two fatty acids in presence of an inorganic catalyst at temperatures in excess of 300°C (Evershed et al., 1995; Christie, 2012b). Finally, ten TLEs displayed long-chain fatty acids ranging from C_{19} to C_{24}. No other biomarkers (e.g. *n*-alkanes, *n*-alkanols and APAAs) were detected suggesting that the vessels were mainly committed to processing animal products.

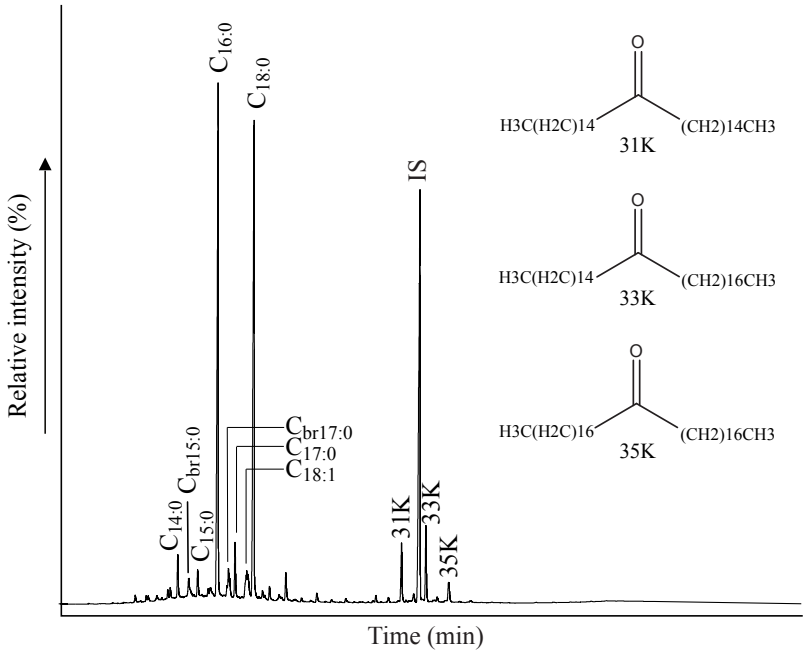


Figure 7.7. Partial gas chromatogram of TLE from sherd MIK20, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products, and mid-chain ketones produced during cooking of animal products. In the figure: fatty acids (FA), branched-chain fatty acids (br), long-chain ketones (K) and the internal standard, C_{34} *n*-tetratriacontane (IS).

To conclude, only four TLEs displayed long-chain fatty acids ranging from C_{19} to C_{24}. No other kind of biomarkers (e.g. *n*-alkanes, *n*-alkanols and APAAs) were detected suggesting that the uses of the vessels were mainly committed to process animal products.

7.3.3 *Organic residues recovered from Mikhailovka III pottery*

Sixteen out of 23 (70%) sampled potsherds yielded appreciable lipid concentrations ranging from 5 to 787.5 μg g^{-1}, with a mean value of 130.1 μg g^{-1}. The great majority of the extracts were dominated by $C_{16:0}$ and $C_{18:0}$ fatty acids with a predominance of the $C_{16:0}$ fatty acid over the $C_{18:0}$ (n=12); saturated branched-chain and odd carbon number fatty acids, including $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$ were frequently present, suggesting that the ceramic vessels were generally used to process ruminant animal products.

TAGs and their degradation products (DAGs and MAGs) were observed in 15% of the residues, within the acyl carbon numbers ranging from C_{48} to C_{54}, usually dominated by C_{52}. Lower molecular weight TAGs (C_{44} to C_{46}) which characterise dairy fats were absent (Dudd and

Evershed, 1998). Figure 7.8 also displays a gas chromatogram of one TLE (MIK35) containing TAGs. In addition, extract MIK35 displays high concentration of the $C_{14:0}$ fatty acid (Figure 7.8) showing possible presence of dairy fats as the presence of short-chain saturated fatty acids in the C_4 to $C_{14:0}$ carbon number range is common in dairy products (Kuksis et al., 1973; Christie, 1981; McDonald et al., 1988).

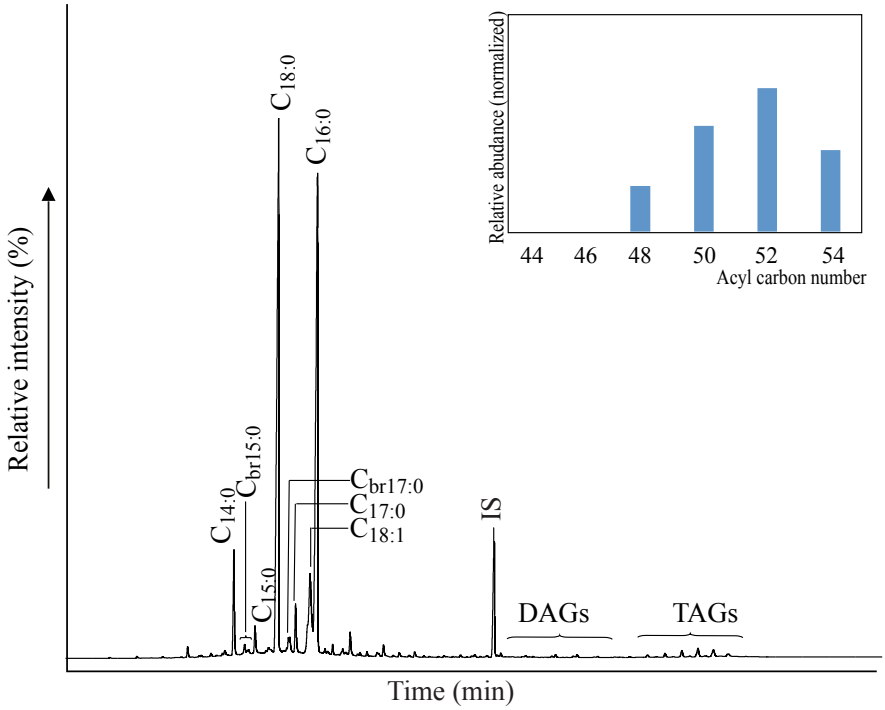


Figure 7.8. Partial gas chromatogram of TLE from sherd MIK35, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products. In the figure: fatty acids (FA), branched-chain fatty acids (br), triacylglycerols (TAGs), diacylglycerols (DAGs) and the internal standard, C_{34} *n*-tetratriacontane (IS).

7.3.4 *$\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids*

In the case of Mikhailovka I, the $\delta^{13}C_{16:0}$ values of the fatty acids range from -28.4 ‰ to -23.6‰ and the $\delta^{13}C_{18:0}$ values range from -29.1‰ and -26.6‰ with a mean value respectively of 25.9‰ and -28‰. Mikhailovka II showed more depleted $\delta^{13}C$ values; $\delta^{13}C_{16:0}$ values vary from -31.2‰ to -23.7‰, whereas $\delta^{13}C_{18:0}$ shows values ranged between -30.2‰ and -26.1‰ with a mean value respectively of -27.5‰ and -28.8‰. Finally, the trend seen in the carbon isotope values of $C_{16:0}$ and $C_{18:0}$ fatty acids in the Mikhailovka III extracts displays values in between Mikhailovka I and II: the $\delta^{13}C_{16:0}$ values range from -33.1‰ to -26.7‰ and the $\delta^{13}C_{18:0}$ values from -33‰ and -28.5‰, with a mean value, respectively of -29‰ and -30.7‰.

Examination of Figures 7.9b,d,f reveal that n=32, n=11 and n=11 extracts respectively from Mikhailovka I, II and III exhibit $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids characteristic of ruminant products, of which respectively n=7, n=2 and n=4 plot well within the range of ruminant dairy

products. Equine products were present only in one residue from Mikhailovka I, in seven residues from the second layer and two residues from Mikhailovka III. Non-ruminant products were present in one residue in both Mikhailovka I and II, while Mikhailovka III displayed 3 residues with a non-ruminant origin. These results are consistent with trends seen in the faunal records (separately discussed in Chapter 5 and summarized below; Table 7.1).

Table 7.1
Percentages of the different classes of animals inferred from faunal records in Mikhailovka site. The number of identified specimens (NISP) is shown.

MIKI	*Cattle*	*Sheep/Goats*	*Pigs*	*Horses*	*Wild animals*	*Fishes*
NISP	217	760	104	20	60	-
NISP%	18,7	65,5	9	1,7	5,2	-
MIK II-III	*Cattle*	*Sheep/Goats*	*Pigs*	*Horses*	*Wild animals*	*Fishes*
NISP	30571	14958	229	5393	1003	-
NISP%	58,6	28,7	0,4	10,3	1,9	-

From these results it appears that the majority of the investigated pottery vessels were used for the processing of ruminant products (respectively 94%, the 55% and the 55% from Mikhailovka I, II and III), of which the 21%, the 4% and the 4% were used to process ruminant dairy products. The latter result is unsurprising considering that 80-90% of the faunal assemblage was comprised of domesticates including cattle, sheep and goats. The 39% and 16% of the investigated pottery vessels, respectively from Mikhailovka II and III, were used to process equine products, which also reflect the faunal records. Only 3% of the potsherds investigated from Mikhailovka I appear to have been used to process equine products which is unsurprising as 2-8% of the faunal assemblage from this horizon comprised of equine bones. Non-ruminant products appear to have been processed only in the 3%, 6% and 8% of potsherds investigated, respectively, from Mikhailovka I, II and III. A more careful examination of the mixed plots in Figure 7.9a (Mikhailovka I) reveals that the non-ruminant residue has possible mixed origin showing slightly depleted isotopic compositions of $\delta^{13}C_{16:0}$ value of -28.4‰ and $\delta^{13}C_{18:0}$ value of -27‰ and $\Delta^{13}C$ of 1.41 ‰. Figure 7.9c (Mikhailovka II) and Figure 7.9e (Mikhailovka III) reveal that the non-ruminant residues have possible freshwater fish origin based on their depleted carbon isotopic composition (Cramp & Evershed, 2014). However, without detection of biomarkers for fish or unsaturated fatty acids it is not possible to reliable identify a fish fat origin. Finally, some of the residues had a mixing origin.

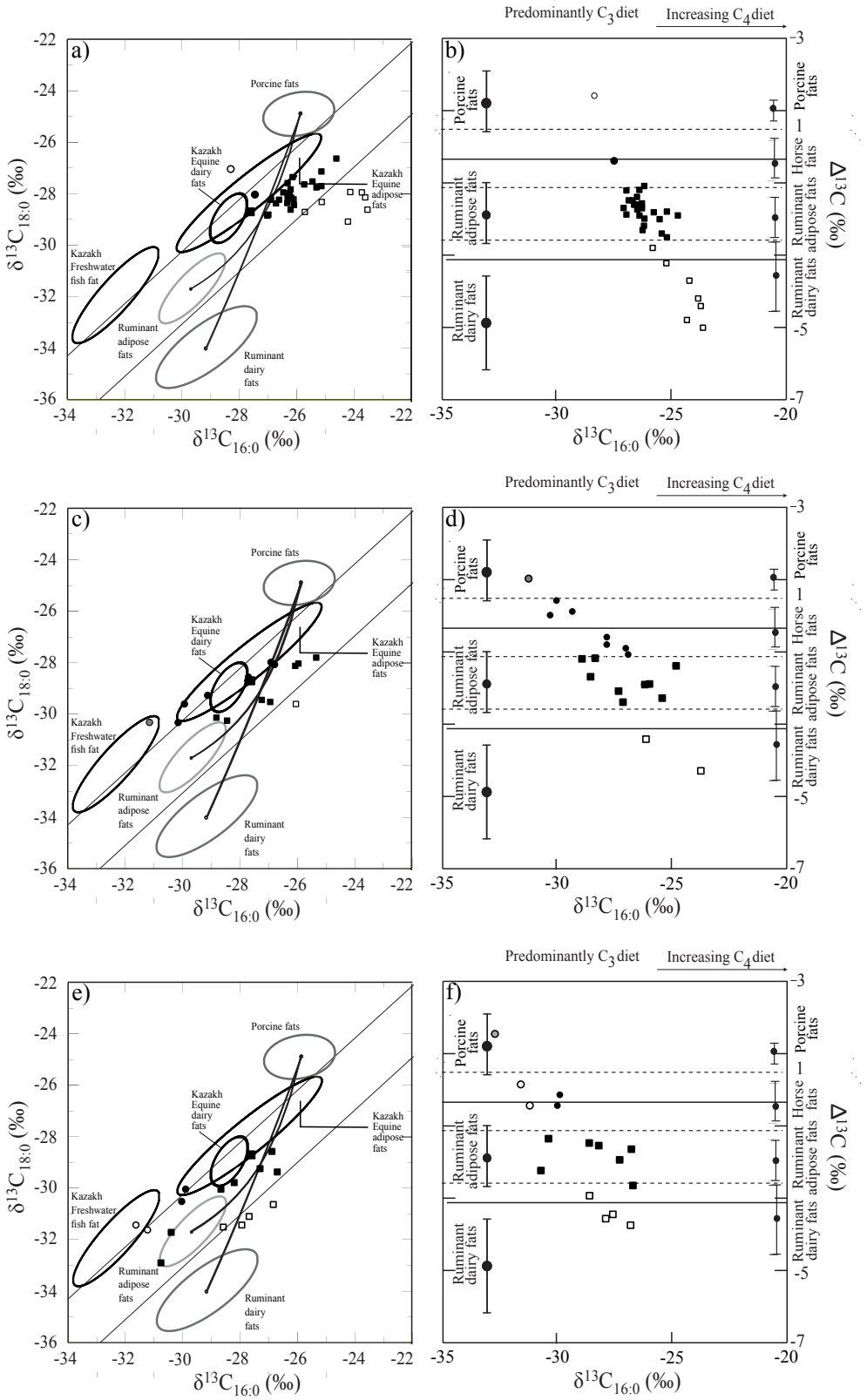


Figure 7.9. Scatterplots of $\delta^{13}C$ values of $C_{16:0}$ fatty acid against the $C_{18:0}$ fatty acid extracted from pottery vessels respectively from (a) Mikhailovka I, (c) Mikhailovka II and (e) Mikhailovka III. In the figure, equine fats (black dots); porcine fat (black rhombus); possible freshwater fish fats (grey dots); ruminants fats (black squares); mixed fat residues (white dots). Archaeological values overlay confidence ellipses corresponding to the values obtained from modern reference fats, which enables classification of the ancient animal fats; and $\delta^{13}C$ values of $C_{16:0}$ against the $\Delta^{13}C$ values ($\delta^{13}C_{18:0}$ - $\delta^{13}C_{16:0}$) from (b) Mikhailovka I, (d) Mikhailovka II and (f) Mikhailovka III.

Finally, the distribution of $\delta^{13}C_{16:0}$ values (Figure 7.9b,d,f) of the majority of the extracts from Mikhailovka range between from -33.1 to -23.7 ‰. As for the previous site, this range is broader that the distribution of the $\delta^{13}C_{16:0}$ values for modern ruminant fats from British animals, raised on a strict C3 diet ($\delta^{13}C_{16:0}$ values ranging from -30.9‰ and -28.6‰; Copley et al., 2003). The latter is more comparable to the $\delta^{13}C_{16:0}$ values for modern Kazakh reference fats, ranging from -29.0 to -24.1 ‰ (Stear, 2008). Significantly, the thirteen residues, with a ruminant dairy origin, display the most enriched $\delta^{13}C_{16:0}$ values ranging from -28.6‰ to -23.6 ‰. The mean $\delta^{13}C_{16:0}$ value of the latter fats is more enriched by c. 3-4 ‰ in comparison to modern British reference fats (Copley et al., 2003). Similar enrichment was also observed in $\delta^{13}C$ values of lipids extracted from Near Eastern archaeological pottery (Evershed et al., 2008) where it was hypothesised to result from the animals producing the fats consuming a proportion of C4 plants in their diets and/or water-stressed C3 plants. However, this topic will be discussed in details in Chapter 8, Section 8.3.

7.4 **Generalka site**

7.4.1 *Organic residues recovered from Generalka pottery*

The Generalka lipid residues revealed maximum lipid concentration of the 35 extracts of 332.1 μg g^{-1}, with a mean lipid concentration of 43.9 μg g^{-1}; 82% of the extracts (n=29) yielded appreciable lipid concentration (>5 μg g^{-1} of potsherd). However not all the twienty-nine extracts were characterized by well-concentrated $C_{16:0}$ and $C_{18:0}$ fatty acids to carry out carbon isotope analysis.

Generally, TLEs from Generalka pottery confirmed exploitation of animal products denoted by the high abundance of $C_{16:0}$ and $C_{18:0}$ fatty acids. The majority of the extracts (n=22) were characterized by a predominance of $C_{18:0}$ fatty acid over $C_{16:0}$. Many extracts showed the $C_{14:0}$ fatty acid, together with branched-chain and odd carbon number fatty acids, including saturated $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$ suggesting that the ceramic vessels were generally used to process animal products.

TAGs and their degradation products (DAGs and MAGs) were observed in 14% of the residues, within the acyl carbon numbers ranging from C_{48} to C_{54}, usually dominated by C_{52}. Lower molecular weight TAGs (C_{44} to C_{46}) which characterise dairy fats were absent (Dudd and Evershed, 1998). Lipid biomarker analyses by GC/MS showed the residues to fall into 2 broad categories, denoted Profile I and II as detailed below.

7.4.1.1 Lipid distribution - Profile I

The great majority of the lipid profiles (n=28) were characterized by the predominance of $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$ fatty acids, together with branched-chain and odd carbon number fatty acids, including saturated $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$ (Figure 7.10a). These extracts display a predominance of animal products. Long-chain fatty acids (C_{19} to C_{30}) were characteristic of n=4

extracts, whereas n=2 residues were characterized by shorter chains components (C_{19} to C_{24}) (Figure 7.10b).

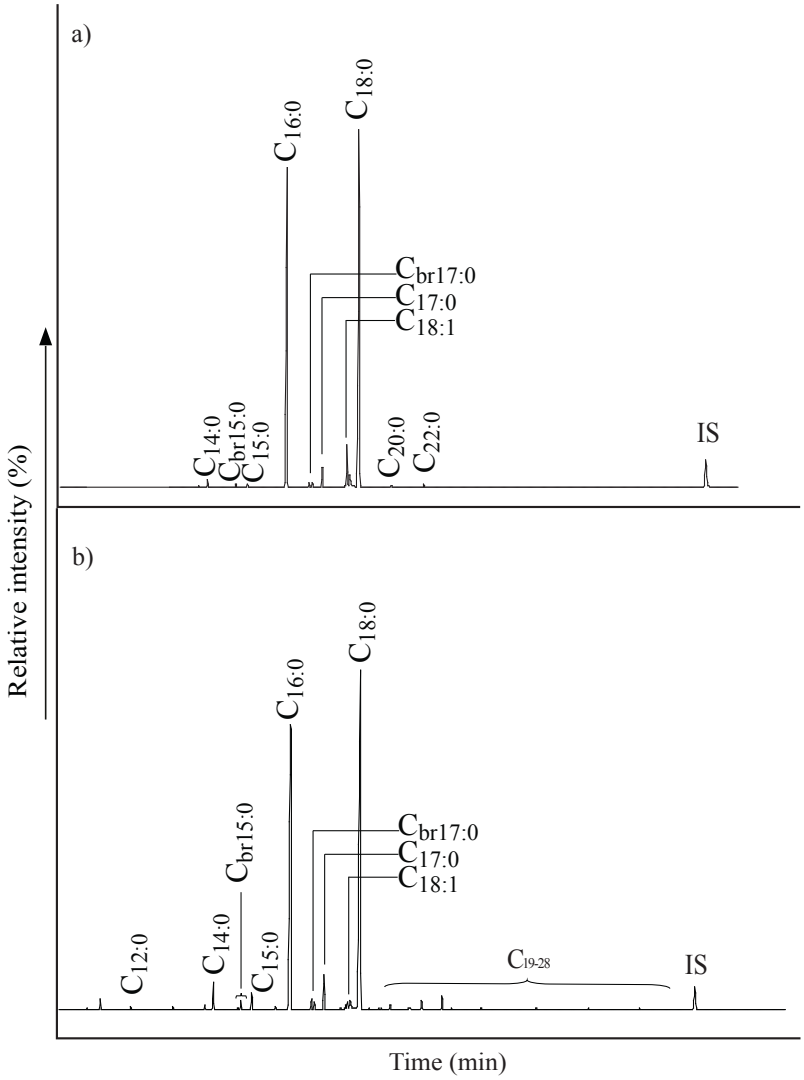


Figure 7.10. Partial gas chromatograms of TLEs from sherds (a) GEN30 and (b) GEN6, showing $C_{16:0}$ and $C_{18:0}$ fatty acids, originating from degraded animal products. In the figure: fatty acids (FA), branched-chain fatty acids (br) and the internal standard, C_{34} *n*-tetratriacontane (IS).

7.4.1.2 Lipid distribution – Profile II

Profile II refers to a single extract (GEN31 in Figure 7.11) which was dominated by a high abundance of $C_{16:0}$ and $C_{18:0}$ fatty acids together with $C_{14:0}$ fatty acid and branched-chain and odd carbon number saturated fatty acids, including $C_{15:0}$, $C_{15:0br}$, $C_{17:0}$ and $C_{17:0br}$. In addition, the application of GC/MS SIM to the extract revealed the presence of C_{18} APAAs, which, as discussed above, most likely derive from the processing of equine products, as equine fat is dominated by the essential fatty acids linoleic ($C_{18:2}$) and α-linolenic ($C_{18:3}$) (Malacarne et al., 2002) that at temperature higher than 260-270°C and in contact with a catalytic phase such as a ceramic matrix can produce C_{18} APAAs.

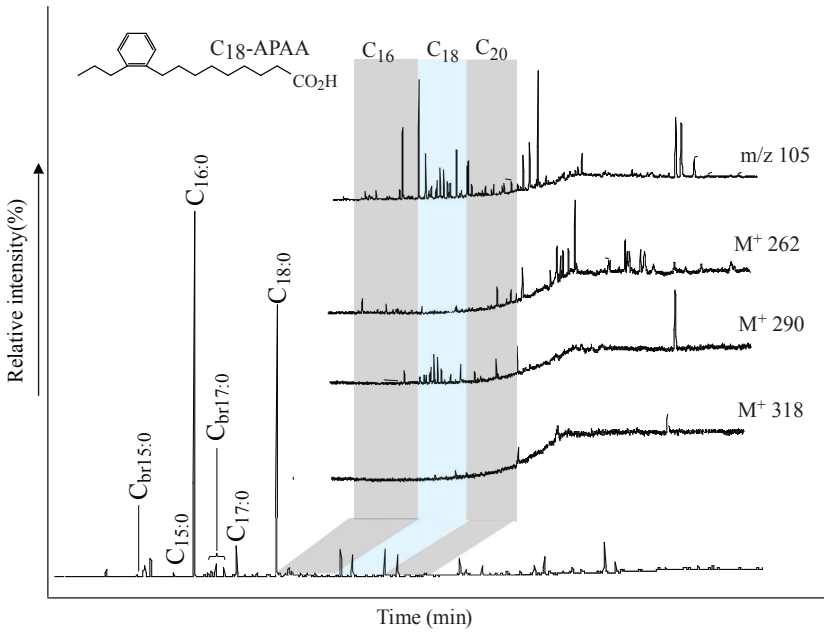


Figure 7.11. GC/MS total ion current (TIC) of TLE from sherd GEN31. *m/z* 105 is the common ion to all APAAs. To better highlight the APAAs, the three range masses corresponding to each C_{16}, C_{18}, C_{20} APAAs were chosen ($M^{+\cdot}$ 262, $M^{+\cdot}$ 290 and $M^{+\cdot}$ 318). In the figure: fatty acids (FA), branched-chain fatty acids (br), ω-(o-alkylphenyl) alkanoic acids (APAAs).

7.4.2 *$\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids*

As mentioned earlier, thirty-five potsherds from Generalka site were submitted to biomolecular and stable carbon isotope analyses. However, six potsherds were analysed in a previous pilot study aimed to valuate the degree of preservation of the organic residues in North-Pontic region potsherds (Whelton and Evershed 2012). Therefore, the results of forty-one analyses will be presented here together. In general, only twenty-seven residues out of forty-one displayed well-concentrated $C_{16:0}$ and $C_{18:0}$ fatty acids to be analysed thought GC/C/IRMS.

The Generalka $\delta^{13}C_{16:0}$ fatty acid values range from -31.5‰ to -26.3‰, whereas the $\delta^{13}C_{18:0}$ acid varies between -32.9‰ and -28.3‰ with mean values, respectively, of -28.2‰ and -29.7‰. Examination of Figure 7.12b better reveals that the majority of Generalka extracts (n=18) exhibit $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids characteristic of ruminant adipose products, of which one residues has a dairy fat origin ($\Delta^{13}C$ value = -5.9‰) and four residues might have a weak dairy fat contribution ($\Delta^{13}C$=-2.6‰). Seven residues exhibit $\delta^{13}C$ values characteristic of equine products, and only two extracts might have a freshwater fish oil origin. These results are consistent with trends seen the faunal records (separately discussed in Chapter 5 and summarized in Table 7.2).

From these results it appears that the 68% of the investigated pottery vessels were used for the processing of ruminant products, which is unsurprising considering that 94% of the faunal assemblage, comprised mainly domesticated ruminants including cattle, sheep and goats. Interestingly, only 5% of the investigated pottery vessels were likely to have been used for the

processing of ruminant dairy products suggesting that milk was not widely consumed at the site (Figure 7.12).

The estimate of 26% of the investigated pottery being used for the processing of equine products is surprising as equine bones comprised only 2.2% of the total faunal assemblage. Interestingly, 11% of the investigated potsherds (n=2) appear to have been used to process non-ruminant products. Examination of the plot in Figure 7.12a reveals that the two non-ruminant residues (GEN13 and GEN26) have possible freshwater fish origin showing more depleted isotopic composition, with mean $\delta^{13}C_{16:0}$ value of -31.4‰, mean $\delta^{13}C_{18:0}$ value of -30.7‰ and mean $\Delta^{13}C$ of 0.7 ‰ (Cramp & Evershed, 2014). However, without detection of biomarkers for fish or unsaturated fatty acids it is not possible to reliable identify a fish fat origin.

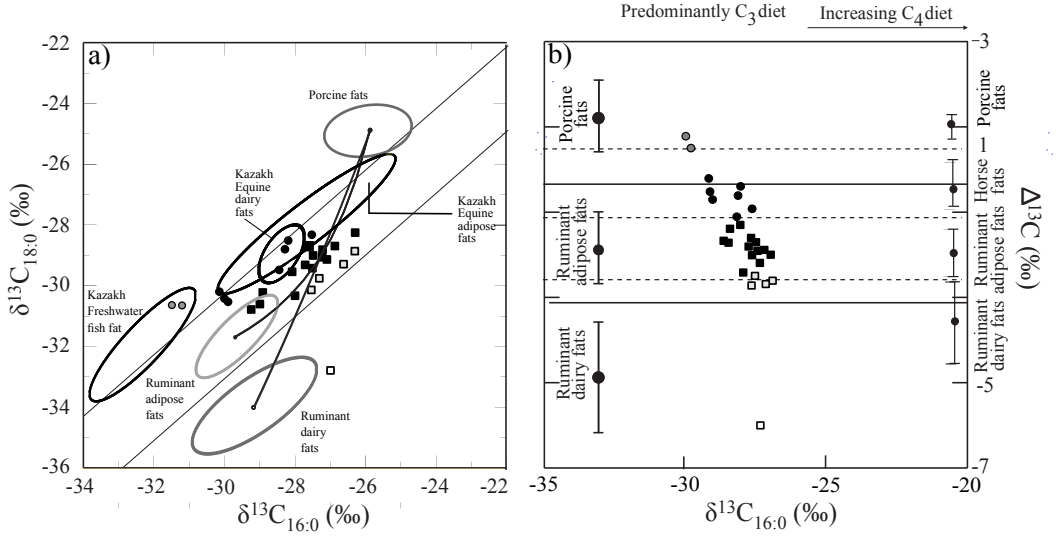


Figure 7.12. Scatterplots of (a) $\delta^{13}C$ values of $C_{16:0}$ fatty acid against the $C_{18:0}$ fatty acid extracted from pottery vessels from Generalka. In the figure, equine fats (black dots); porcine fat (black rhombus); possible freshwater fish fats (grey dots); ruminants fats (black squares); mixed fat residues (white dots). Archaeological values overlay confidence ellipses corresponding to the values obtained from modern reference fats, which enables the species classification of the ancient animal products; and (b) $\delta^{13}C$ values of $C_{16:0}$ against the $\Delta^{13}C$ values ($\delta^{13}C_{18:0}$ - $\delta^{13}C_{16:0}$) to allow a better distinction among animal species.

Table 7.2
Percentages of the different classes of animals inferred from faunal records in Generalka site. The number of identified specimens (NISP) is shown.

	Cattle	*Sheep/Goats*	*Pigs*	*Horses*	*Wild animals*	*Fishes*
NISP	1907	366	-	54	75	-
NISP%	79,4	15,2	-	2,2	3,1	-

Finally, the distribution of $\delta^{13}C_{16:0}$ values (Figure 7.12b) of the majority of the extracts range between from -31.5 to -26.3 ‰. As for the previous sites, this range is broader that the distribution of the $\delta^{13}C_{16:0}$ values for modern ruminant fats from British animals, raised on a strict C3 diet

($\delta^{13}C_{16:0}$ values ranging from -30.9‰ and -28.6‰; Copley et al., 2003). The latter is more comparable to the $\delta^{13}C_{16:0}$ values for modern Kazakh reference fats, ranging from -29.0 to -24.1 ‰ (Stear, 2008).

7.5 Summary and Conclusions

In this Chapter, the results of lipid analyses of 151 potsherds from the three archaeological sites of Nizhnyi Rogachik, Generalka and Mikhailovka I, II and III have been presented. Lipid recovery was overall significant, showing mean values of 127.1 μg g^{-1}, 43.9 μg g^{-1}, 621.7 μg g^{-1}, 53.9 μg g^{-1} and 130.1 μg g^{-1}, respectively.

Therefore, the major conclusions that can be drawn are:

1) Analysis of the TLEs from the two forest-steppe sites demonstrates that the free fatty acids, $C_{16:0}$ and $C_{18:0}$, are the most abundant components, suggesting that the hydrolysis of triacylglycerols, diacylglycerols and monoacylglycerols has proceed to completion and that the extensive oxidation of unsaturated fatty acids has occurred;
2) The most common distribution is dominated by fatty acids that generally range from $C_{12:0}$ to $C_{24:0}$ acyl carbon atoms with high abundances of the $C_{16:0}$ and $C_{18:0}$ fatty acids, which are indicative of the presence of degraded animal products (e.g. Evershed et al., 1997a);
3) Branched-chain fatty acids ($C_{15:0}$ and $C_{17:0}$), which are components of bacterial origin diagnostic of both ruminant animal products (Christie, 1978; Hubbard and Pocklington, 1968) and equine adipose products (Hintz and Cymbaluk, 1994; Pond et al., 1995), were also abundant;
4) C_{16} and C_{18} APAAs were identified in two extracts from Nizhnyi Rogachik and one from Generalka (NR9, NR18 and GEN31). In addition, the two residues from Nizhnyi Rogachik show the simultaneous presence of C_{16} and C_{18} APAAs and 4,8,12-TMTD. Examination of Figure 7.13 reveals that the isotopic composition of the fatty acid components of these two extracts confirm the mixing of aquatic and terrestrial fat (possibly horse fat) in the pots. In contrast, the C_{18} APAAs only, detected from GEN31, could indicate equine origin of the residue. Also in this case, the isotopic composition of the fatty acid components of this extract suggest a mixing of terrestrial fats in the pots (perhaps horse and ruminant fats) (Figure 7.13);
5) Finally, series of long-chain fatty acids, long–chain *n*-alkanes and *n*-alkanols were identified in one extract (NR5) from Nizhnyi Rogachik that may be indicative of epicuticular waxes originating from the processing of plants (Tulloch, 1976); however, as mentioned in Chapter 6, the low concentration or absence of *n*-alkanes limited the certain identification. Indeed,

the simultaneous presence of long-chain fatty acids, *n*-alkanes and *n*-alkanols is necessary in order to identify plant wax.

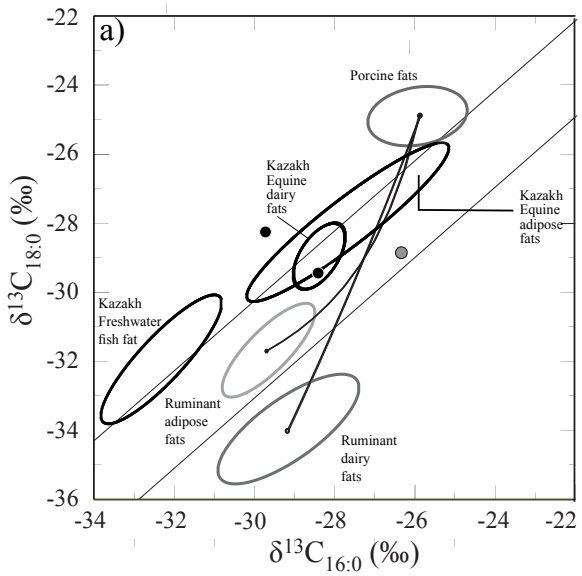


Figure 7.13. Scatterplots of $\delta^{13}C$ values of $C_{16:0}$ fatty acid against the $C_{18:0}$ fatty acid extracted from pottery vessels from two sherds from Nizhnyi Rogachik (black dots) and one from Generalka (grey dot).

CHAPTER 8

RECONSTRUCTION OF THE NORTH-PONTIC REGION ANCIENT ECOSYSTEM

8.1 Introduction

Climate and environment have already been mentioned several times in this thesis, specifically in relation to the variability of the Eurasian ecosystems. Significantly, the reconstruction of a hypothetical environmental background of the prehistoric North-Pontic region of Ukraine is critical to explaining the choices made by humans concerning their lifestyles and/or dietary habit. Moreover, an understanding of past climate and vegetation would help in the interpretation of isotopic results, allowing a better understanding of the motivations behind specific dietary choices. Therefore, this Chapter aims to offer an environmental reconstruction of the investigated area (steppe and forest-steppe of North-Pontic region of Ukraine) during the Middle Holocene, specifically from the 4th to the 3rd millennium BC (Eneolithic and Early Bronze Age). This reconstruction is built on the available literature, including (i) existing pollen analysis (e.g. Bostonalieva, 2015; Kremenetski, 2003) (ii) existing isotope analysis (e.g. Gerling, 2014; Lillie et al., 2011), and (iii) the carbon and hydrogen isotope results already discussed in the previous chapters of this thesis.

8.2 Environmental reconstruction using the pollen analysis

Concerning the pollen analysis, the research carried out by Bostonalieva (2015), a previous PhD student working at the Department of Earth Sciences Physical Geography of the Freie Universität, Berlin, is mainly considered. Interestingly, she collected roughly 200 papers that had focused on the analysis of pollens, minerals, stable isotopes, micro and macro-fossils, sediment texture-structure, and

palaeosoils, in order to offer a reliable paleoenvironmental reconstruction of the western Eurasian region. However, only few of the 200 studies (Alexandrovskiy and Chichagova, 1998; Bezusko et al., 2008; Cordova and Lehman, 2005; Dobrowolski et al., 2001; Gerasimenko, 1997; Gerasimenko et al., 2011; Huhmann et al., 2004; Kotova and Makhortykh, 2010; Kremenetski et al., 1999; Kremenetski, 2003, 1995; Pashkevych, 2012; Smyntyna, 2007) focused specifically on 18 sites located in the North-Pontic region (Figure 8.1). Due to the scarcity of sites located in the forest-steppe areas of Ukraine, a further four sites located in the western forest-steppe of Russia have also been considered from Bostonalieva's collection (Borisova et al., 2006; Sycheva et al., 2003; 2006), for a total of 22 sites. In addition to Bostonalieva's database, a few other studies that include a more extensive geographical scale surveys are also considered (Davis et al., 2003; Prentice et al., 1996; Tarasov et al., 1999, 1998; Wanner et al., 2008; Wu et al., 2007).

Moreover, the eastern area of the prehistoric Eurasian steppe (specifically the ancient area where Botai was located) is also discussed. As mentioned several times in the thesis, the Eurasian steppe has long been considered as a unique ecosystem, however, as mentioned in the previous chapters, recent scholars raised questions about the assumption of homogeneity, supporting instead the idea of a variety of ecosystems. Therefore, describing the ancient Kazakhstan environment is important in order to: (i) illustrate the differences between prehistoric eastern and western Eurasia (Kremenetski, 2003; Tarasov et al., 1999), supporting the theory of a various Eurasian environment; and (ii) to offer environmental information about an area that has been mentioned several times in this thesis especially, in relation to horse domestication and deuterium analysis.

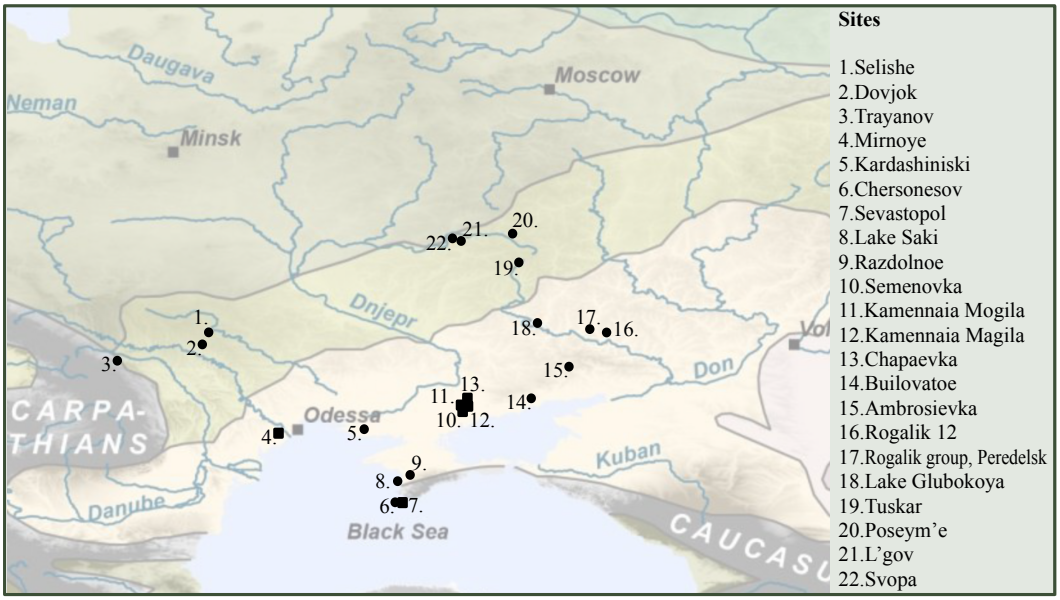


Figure 8.1. Distribution of the sites located in Ukraine (from 1 to 18) and Russia (from 19 to 22) collected from 15 pollen studies. Six sites (squares) are dated earlier than the investigated period. Extracted from Bostonalieva (2015).

8.2.1 *Pollen analysis*

Palynological science provides direct information about ancient vegetation and indirect information on the modification of ancient local conditions mainly related to climatic and geological changes (Faegri and Iversen, 1989, p. 164). However, it is necessary to be highly cautious when using this approach: "vegetation is not a meteorological universal instrument and the climate factors are only one part of the many variables that affect the vegetation" (Faegri and Iversen, 1989).

The principle on which climate reconstruction from pollen analysis is based is "to define the ecological niche(s) of the relevant taxon (taxa) and by a system of overlapping niches restrict the originally wide-ranging individual taxa down to a single defined value" (Faegri and Iversen, 1989), e.g. summer temperature and duration were the first constraints used in 1944 by Iversen to reconstruct the limit of the distribution areas of thermophilous species.

Approaches and models for the environmental and climatic reconstruction have been improved or replaced over the last decades. Indeed, traditional methods such as taxon-based modern analogues (e.g. Faegri and Iversen, 1989; Guiot, 1990; Kremenetski, 2003) together with more recent approaches that mainly exploit plant-functional-type (e.g. Davis et al., 2013; Kleinen et al., 2011; Prentice et al., 1996; Tarasov et al., 1999) are the bases of several studies applied all over the world for the purpose of reconstructing ancient ecosystems. Despite improvements in the approach, pollen analysis still contains inaccuracies mainly arising from the many variables related to the pollen survival. For example, the abundance of pollen from a particular plant species in sediment depends on transportation and pollen dispersal (Figure 8.2; Faegri & Iversen 1989), e.g. pine and spruce are readily transported by the wind (Erdtman, 1943). Moreover, pollination can be made by water or animals or/and the production of pollen can differ from plant-to-plant. Another variable is related to the resistance of pollen to degradation (Erdtman, 1943).

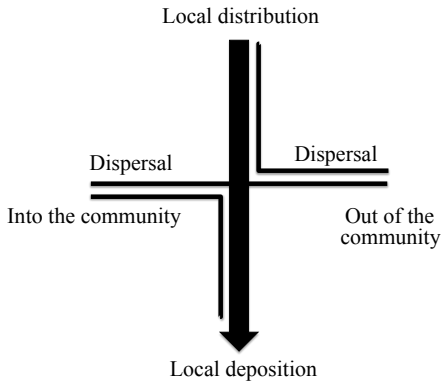


Figure 8.2. Diagram showing the potential pollen dispersion from the local distribution. Adapted from Faegri & Iversen, 1989.

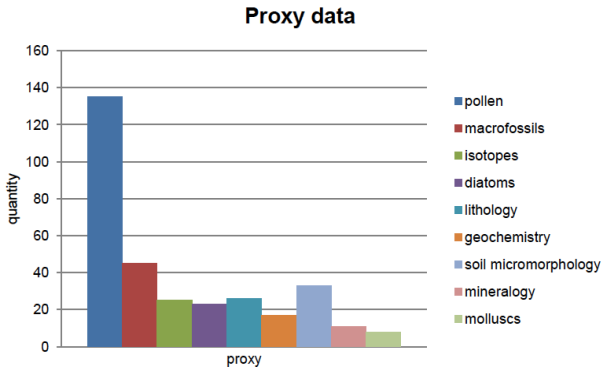


Figure 8.3. The bar-diagram displays the specific proxies applied in the vast Eurasian region in order to reconstruct the paleoclimate. The collections of proxies derive from roughly 200 articles (Bostonalieva, 2015; pp.42).

Besides the abovementioned drawbacks, pollen analysis is frequently used as a paleoenvironmental reconstruction tool; the research carried out by Bostonalieva (2015) revealed that the majority of the climate reconstructions in Eurasia are based on pollen analysis (Figure 8.3). Hence, using the available literature and existing records, the subsequent Sections aim to establish the mid-Holocene climate context of the North-Pontic region compared with the eastern Eurasia (Northern Kazakhstan mainly).

In order to focus on the periods and areas most relevant for the current project, the emphasis will be on twelve sites located in the steppe and forest-steppe of Ukraine, four located in the Russian forest–steppe and three located in the Kazakh steppe; only the sites dated 4th to 3rd millennium BC are considered (dots in Figure 8.1).

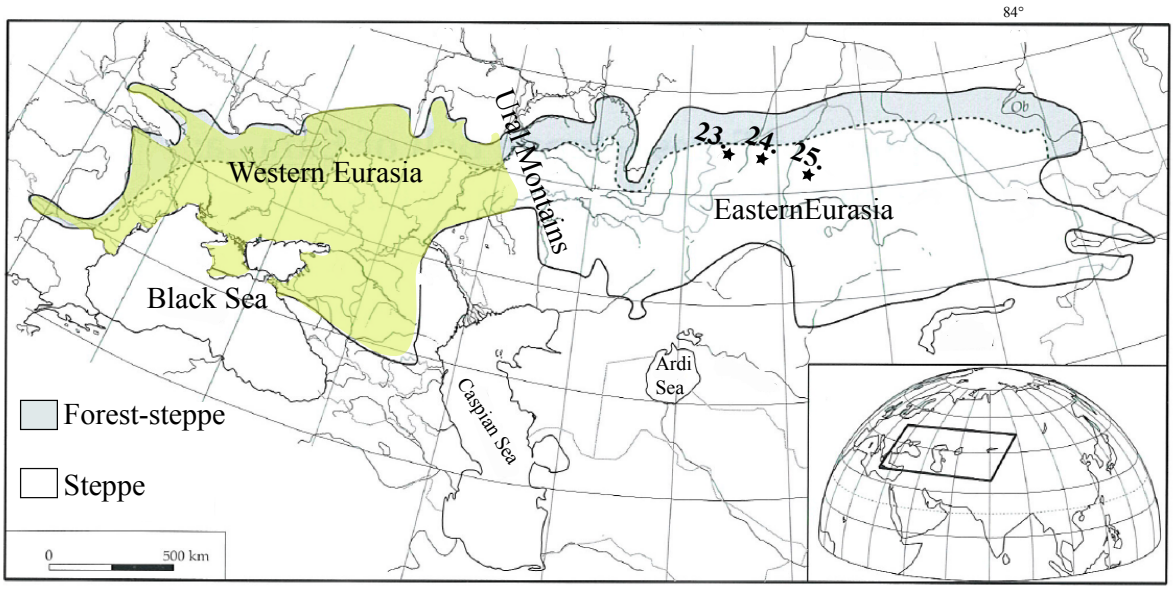


Figure 8.4. Map of the vast Eurasian region divided into western Eurasia, showed in yellow shadow and eastern Eurasia where the three sites located in Northern Kazakhstan are located: Mokhovoe (23), Karasye (24) and Pashennoe (25). Adapted from Kremenetski, 2003.

The sites considered here are located (Figure 8.1 and Figure 8.4):

1. *Western Eurasia:* Selishe, Dovjok, Trayanov, Kardashiniski, Chersonesos, Lake Saki, Razdolnoe, Builovatoe, Ambrosievka, Rogalik 12, Rogalik grupp, Lake Glubokoye (Ukraine); Tuskar, Poseym'e, L'gov, Svopa (Russia) - as showed in Figure 8.1.
2. *Eastern Eurasia:* Mokhovoe, Karasye and Pashennoe located in Northern Kazakhstan (Figure 8.4).

8.2.2 *Western Eurasia Mid-Holocene*

The mid-Holocene (Atlantic and Subboreal epochs), covered a period from the 6500 to the 1000 BC, corresponding to the Neolithic/Eneolithic and the Bronze Age periods. According to a number of studies (Bostonalieva, 2015; Cordova and Lehman, 2005; Kleinen et al., 2011; Kotova and Makhortykh, 2010; Kremenetski, 2003; Kremenetski et al., 1999; Tarasov et al., 1999; Wu et al., 2007), the North Black Sea mid-Holocene climate was characterized by strong climatic fluctuations (e.g. Figure 8.5) and changes of ecological boundaries - forests *vs*. steppe.

The Atlantic period (6500-3000BC) is universally recognized as the altithermal, the thermic maximum of the Holocene (Velichko et al., 2009). The western area of Eurasia was characterized by a "warm and humid" climate (Bostonalieva, 2015), lasting until the early Subboreal period (*ca*. 3000 BC) when precipitations decreased and a more arid conditions occurred. Specifically, during the second half of the Mid-Holocene (Late Atlantic period - 4000-2800 BC) the generally "warm and humid" climatic conditions (Bostonalieva, 2015) led to the maximum displacement of forest vegetation to the south (Khotinski, 1982; Spiridonova, 1991). The steppe region was characterized by significant abundance of broad leaves trees (BLT) that dominated the Dnieper and southern Bug valleys, possibly reaching the modern shoreline of the Black Sea (Kremenetski, 1999). Regarding the non-arboreal species, the pollen records show a variety of steppe grasses, including pollens belonging to *Artemisia genus.* According to Kremenetski, the high concentration of *Chenopodiaceae* suggests the existence of saline meadow while the presence of *Lycopodium clavatum* is significant since it suggests the presence of pine forests on the sandy terrace of the Dnieper River (Kremenetski, 1995; Thomas, 2003). The forest-steppe displayed a high abundance of pines and BLT, such as elm, hazel and birch (*Ulmus, Corylus avellana* and *Betula)*. Other thermophylous trees, none of which grow in colder present day conditions, such as oaks and lime trees (*Quercus petraea, Tilia cordifolia* or *Tilia Argentea),* were also part of the forest-steppe (Kremenetski, 1995; 1999; 2003). The non-arboreal species were quite various, consisting of *Chenopodiaceae* and *Poaceae,* together with *Cichoriaceae* and *Asteraceae.*

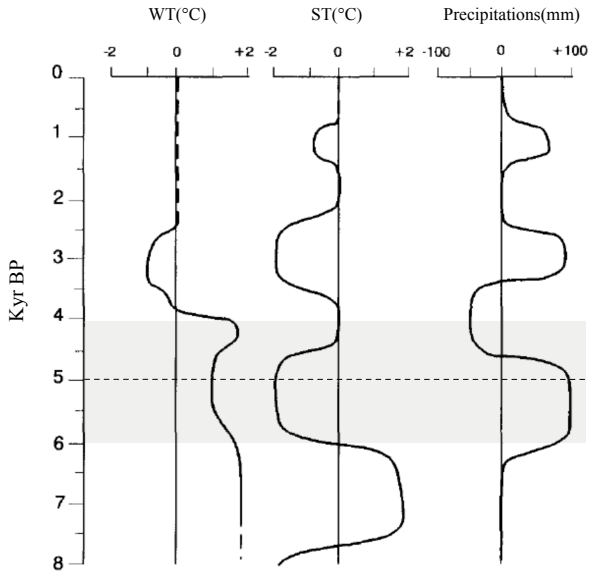


Figure 8.5. Curves of possible deviations of mean January temperatures (WT°C), mean July temperatures (ST°C) and mean annual precipitation (mm) against Kyr BP, in the steppe and forest steppe belts North of the Black Sea during the Holocene. The highlighted area represents the relevant period from the 4000BC (6000BP) to the 2200BC (4200BP). Adapted from Kremenetski (1995; pp.300).

As a whole, during the Late Atlantic period, the climate of the North-Pontic steppe and forest-steppe was optimal for the growing of temperate deciduous mixed forests (Tarasov et al., 1998), especially for BLT that grew in the southern part of the Dnieper valley. The steppe vegetation was more mesophytic than at present day. The pollen records suggest a humid and temperate climate: summer temperatures decreased by 2°C and winter temperatures rose by 1°C compared to present day (Figure 8.5), while precipitation increased to ca. 100-150 mm per annum (Kremenetski, 1995).

The subsequent Subboreal epoch (ca. 2800-1400BC), also known as "xerothermic stage" (Bostonalieva, 2015), was generally characterized by numerous climatic oscillations (Kremenetski, 2003); aridification caused the northern expansion of the steppe, while simultaneously the forest-steppe zone diminished. Pollen analysis of sedimentary layers dated around the 2800 BC display a general decrease of arboreal taxa. An evident decline in elms and hazels occurred in the forest-steppe (Kremenetski, 1995; Kremenetski et al., 1999), whereas the steppe region sites show an increase of xerophytic steppe vegetation, including *Artemisia* plants, and a decline of arboreal taxa, particularly the *Corylus* tree. This could reflect a contraction of the forests from the Dnieper valley and a simplification of the BLT forests (Kremenetski, 1995, p. 297). Consequently, the southern environment became more arid, showing a general reduction of trees, including pines and birches.

As a whole the Subboreal period is described as “warm and dry” (Bostonalieva, 2015). According to Kremenetski’s reconstruction, the mean July temperature was possibly higher by 1-2°C (Figure 8.5), the mean January temperature was lower than the previous period, while annual precipitation was 50 mm less than today (Kremenetski, 2003, p. 14).

8.2.3 *Eastern Eurasian mid-Holocene (Kazakh steppe)*

A general cool steppe environment was reconstructed for sites located in northern Kazakhstan (Tarasov et al., 1999). The western site of Mokhovoe (Figure 8.4) produced pollen records showing an increasing abundance of arboreal taxa, such as birch and pine (Kremenetski, 2003, pp. 19–22); among the steppe plants, *Artemisia* species predominate. In contrast, the two eastern sites of Karasye and Pashennoe display a predominance of non-arboreal taxa, such as *Artemisia, Asteraceae* and *Chenopodiaceae*. The analysis of the later layers (Subboreal epoch) showed pollen records dominated by non-arboreal taxa, such as *Artemisia* and *Chenopodiaceae* (Kremenetski, 2003). The western site of Mokhovoe displays a decreasing of birch and an increasing of *Artemisia* and *Chenopodiaceae*. In contrast, the eastern sites, originally dominated by steppe grasses, do not display significant changes in the pollen records, which are generally dominated by steppe grasses, such as *Artemisia, Asteraceae* and *Chenopodiaceae.*

8.3 **Environmental reconstruction using the isotope analysis**

8.3.1 *Carbon Isotope analyses*

The available pollen analysis does not offer the distinction between C3 and C4 plants (described in Chapter 1, Section 1.5.1), information which might be important in confirming the presence of certain cereals (e.g. millet which has been identified as cereal imprints in vessels; Chapter 5, Section 5.8). However, determining the spread of C3 vs. C4 plants during prehistory especially in areas where they were both present is complicated. This Section will not solve the latter matter which is a discussion that has to be tackled separately and required further investigations, however, the existing carbon isotope data (applied on human bones; Gerling, 2015; Lillie et al., 2011) together with the isotope results from the current research can add some information concerning the distribution of C3 vs. C4 plants in the North-Pontic region.

The balance between the factors (e.g. CO_2, water and temperature) that influence the growing of C3 plants and C4 plants are still unclear (Bernacki, 2012). The Ehleringer model (Ehleringer et al., 1997) showed the two main factors (CO_2 concentration and temperature) that influence the balance between C3 and C4 plants: "C4 plants grow better under low atmospheric CO_2 and/or high temperatures" (Ehleringer and Cerling, 2002). However, this model has been considered too simple as other factors can play a role (e.g. deficit of water or nitrogen). According to Collatz (1998) in the current pCO_2 (35 Pa), C4 plants tend to be favoured over C3 plants in warmer humid climates and with a mean temperature >22°C for the warmest month. However, in addition to favourable temperatures, C4 plants require sufficient precipitation during the warm growing season (Collatz et al., 1998). Figure 8.6 and 8.7 displays three images extracted from Collatz (1998) that can offer a general idea about C3 and C4 plants distribution. Figure 8.6 shows areas with a climate more

favourable for C4 plants while Figure 8.7a and b display the modern and ancient C3/C4 plants distribution reconstructed by using model calculations and analysis of the current plants distribution and considering a pre-industrial pCO_2 (27Pa) and a current pCO_2 (35Pa). According to these maps, before the industrial times (Figure 8.7b), the North-Pontic region (highlighted in the maps) was characterized by a higher percentage of C4 plants than nowadays; therefore we can assume that during the period of our interest (4000-3000BC) the presence of C4 plants might have been common.

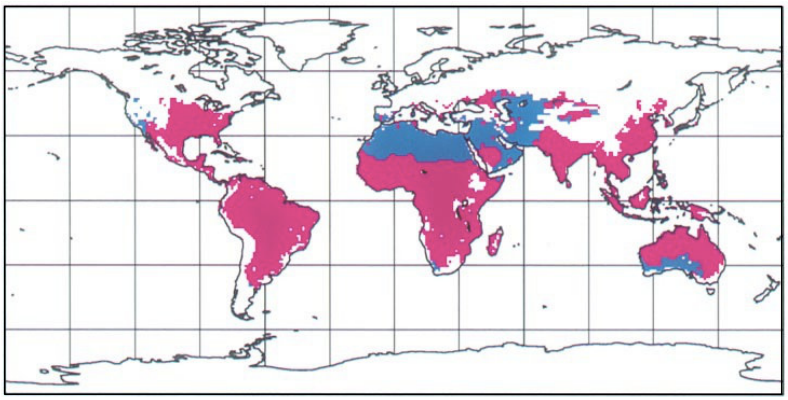


Figure 8.6. The pink areas correspond to a climate characterized by a mean temperature of the warmest month >22°C and the monthly precipitation > 25mm, optimum for C4 plants growing. (Extracted from Collatz et al., 1998)

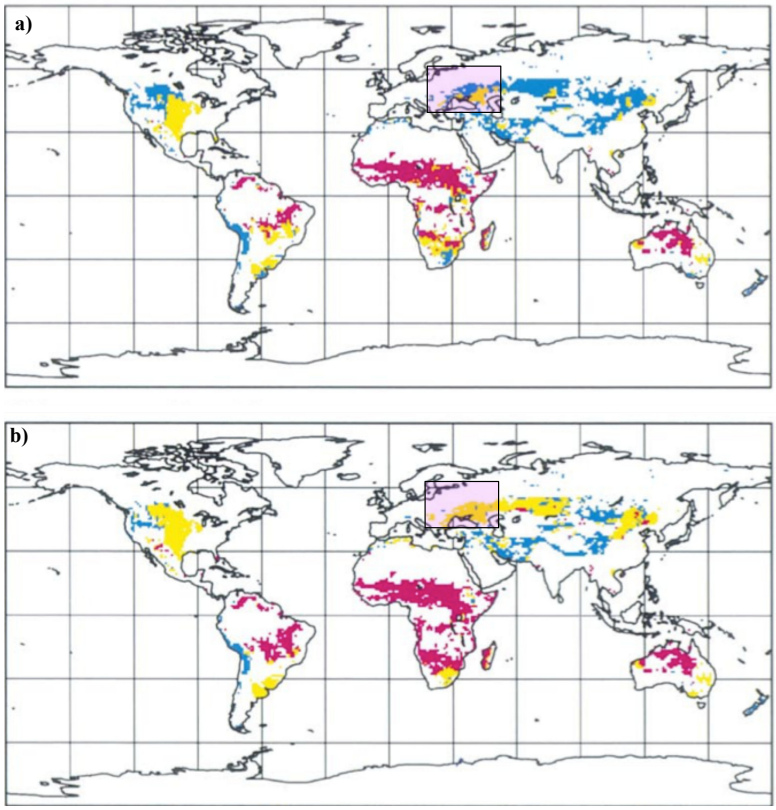


Figure 8.7. Distribution of C_3 and C4 grass extracted from Collatz (1998) and based on L&C climatology and the land classification scheme of Matthews (1983). Panel a) shows the areas corresponding to C_3 (blue), C4 (pink), and mixed C3C4 (yellow) grasslands based on the T>22°C, and pCO_2 = 35 Pa. Panel b) shows the corresponding distributions based on T>18°C, and pCO_2 = 27 Pa.

The existence of C4 plants in the ancient North-Pontic region is also supported by carbon isotope analysis. As mentioned in this Chapter, Section 8.2.1, pollen analysis is the most widely applied method in the area for environmental reconstruction, however, isotope analyses of human bones and animal fats have been applied to some areas of Eurasia (Gerling, 2014; Lillie et al., 2011; Outram et al., 2009). As explained in Chapter 1, Section 1.5, the stable carbon isotope ratio ($\delta^{13}C$) in plants is mainly controlled by the three different pathways of photosynthesis (C3, C4 and CAM; Gannes et al., 1998; O'Leary, 1988; Smith and Epstein, 1971), which are characteristic of plants living in specific environments. Therefore, the $\delta^{13}C$ value of bones or fats will reflect the plants input to the diet of the person or the animal; increasing $\delta^{13}C$ values reflect an increasing C4 plant input to the diet.

The research carried out by Lillie et al. (2011) suggested a diet mainly based on C3 terrestrial resources (discussed in Section 5.9). In contrast, the research carried out by Gerling (2014) showed a slightly $\delta^{13}C$ enrichment of human bones from three steppe sites (Stepnaya, Vinogradnoe and Peshtchanka) compared to the forest-steppe site (Kirovograd). The enrichment in $\delta^{13}C$ values of the steppe human bones (Figure 8.8) was interpreted as a possible increasing of C4 plants (and/or water-stressed C3 plants; Evershed et al., 2008b) in the dietary habit of the steppe populations (Gerling, 2014). Therefore, these data infer that C4 plants might have been present in the diet and the vegetation of the steppe area. Figure 8.8 displays the summary of the two above-mentioned researches.

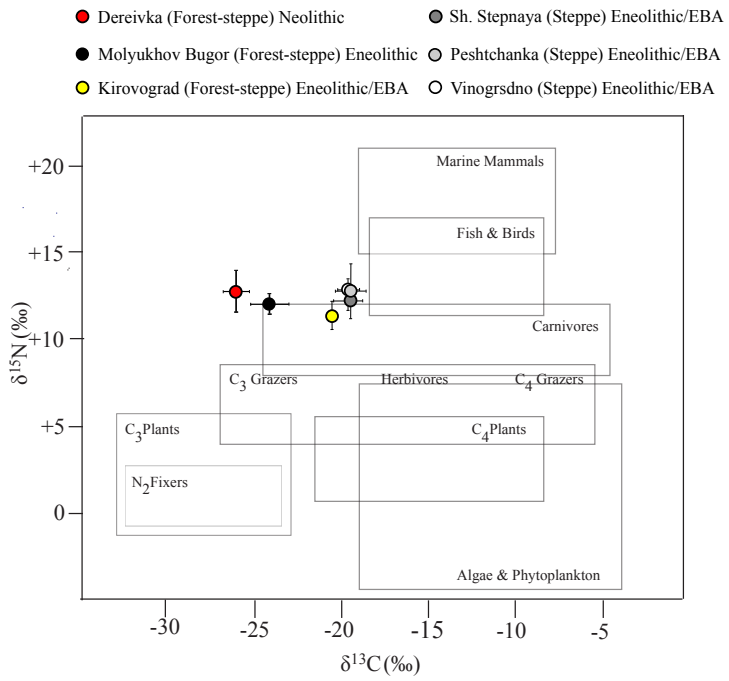


Figure 8.8. Plot showing the mean $\delta^{13}C$ and $\delta^{15}N$ values of human bones from (i) the forest-steppe sites (red, black and yellow dots) and (ii) the steppe sites (greys and white dots) overlapping on the isotope map (Dunn 2011 *ref*. O'Connell 1996). Dereivka human bones come from the Neolithic cemetery, Molyukhov Bugor dated Eneolithic and Stepnaya, Vinogradnoe, Peshtchanka and Kirovograd dated Late Eneolithic/Early Bronze age (EBA).

In the case of compound-specific stable carbon analysis, the environmental information is mainly carried by the $\delta^{13}C_{16:0}$ value of the animal fat, while $\delta^{13}C_{18:0}$ values mainly derive from the animal physiology (Mottram et al., 1999). Thus, the $\delta^{13}C_{16:0}$ value in modern animals will change according to the specific diet and therefore the specific environment. For instance, the $\delta^{13}C_{16:0}$ value of UK reference fats has a $\delta^{13}C_{16:0}$ values range from -30.9 to -28.6‰, with a mean value of -29.7‰, reflecting the strict C3 plant diet of the animals (Figure 8.9a; Copley, 2003); Kazakhstan reference fats showed $\delta^{13}C_{16:0}$ values ranging from -29.0 to -24.1 ‰ (Figure 8.9b; Stear, 2008), with a mean value of -26.9‰. In this case, the diet of the animals was unknown but the broader range of the $\delta^{13}C_{16:0}$ value compared to the UK reference, suggested that the diet was mainly comprised of C3 plants but with some C4 plant and/or water-stressed C3 plants input; finally the $\delta^{13}C_{16:0}$ value of modern African reference adipose fats range between -28.4 to -13.9 ‰ (Figure 8.9c; Dunne et al., 2012), with a mean value of -21.5 ‰ demonstrating the wide range of forages (and environments) in Africa, from C3 to C4 plants.

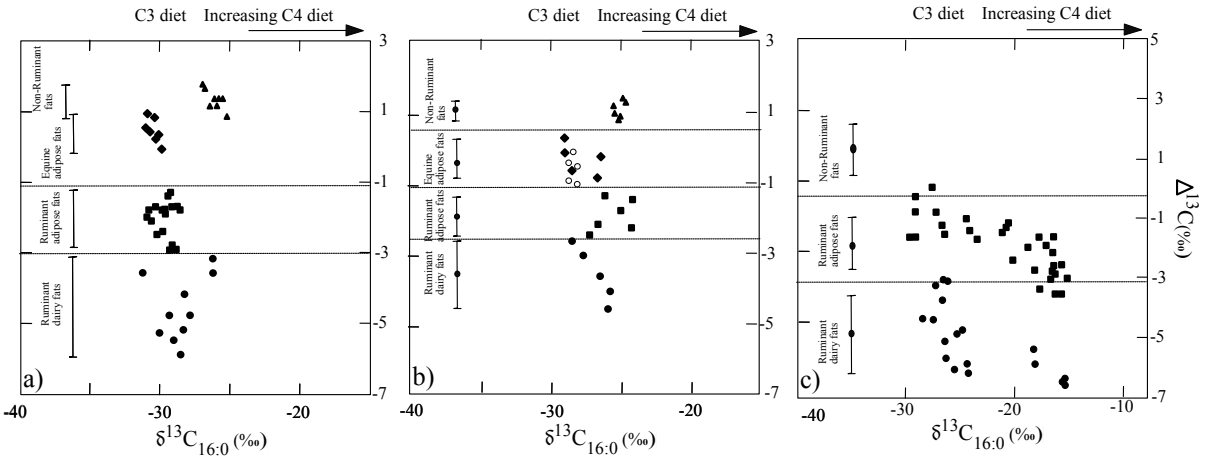


Figure 8.9 Scatterplots of $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values for (a) modern reference animal fats collected from Britain (Copley et al., 2003); (b) modern reference fats collected from Kazakhstan (Stear, 2008) and (c) modern reference animal fats collected from Libya and Kenya (Dunne, 2015). In the figure: ruminants dairy fats (black dots), ruminants adipose fats (squares), equine adipose fats (rhombus), equine dairy fats (white dots), porcine fats (triangles).

Thus, as already mentioned in Chapter 6 and 7, the carbon isotope results of the current project offered additional environmental information. Figure 8.10 displays the comparison between (a) archaeological North-Pontic forest-steppe fats, and (b) archaeological North-Pontic steppe fats, both plotted against modern reference animal fats collected from Britain and Kazakhstan. The distribution of the North-Pontic $\delta^{13}C_{16:0}$ values is broader that the one of the $\delta^{13}C_{16:0}$ values for modern ruminant fats from British animals, raised on a strict C3 diet ($\delta^{13}C_{16:0}$ values ranging from -30.9‰ and -28.6‰; Copley et al., 2003). Instead, it is more comparable to the $\delta^{13}C_{16:0}$ values for modern Kazakh reference fats that ranges from -29.0 to -24.1 ‰ (Stear, 2008), which animals diet was unknown but a C4 plants input was hypothesized. Significantly, the residues with a ruminant dairy origin display the most

enriched $\delta^{13}C_{16:0}$ values suggesting that the addition of some C4 plants to the ruminant diet might have been particularly associated with summer grazing; ruminants give birth in spring so the production of milk is strongly connected to the spring and summer. However, the slightly increased $\delta^{13}C$ values can also be explained by greater aridity, so they might derive from water-stressed C3 plants (Evershed et al., 2008b). Finally, seasonal pastoralism can also be hypothesised as the population of the North-Pontic steppe are believed to have practised this (Rassamakin, 1999).

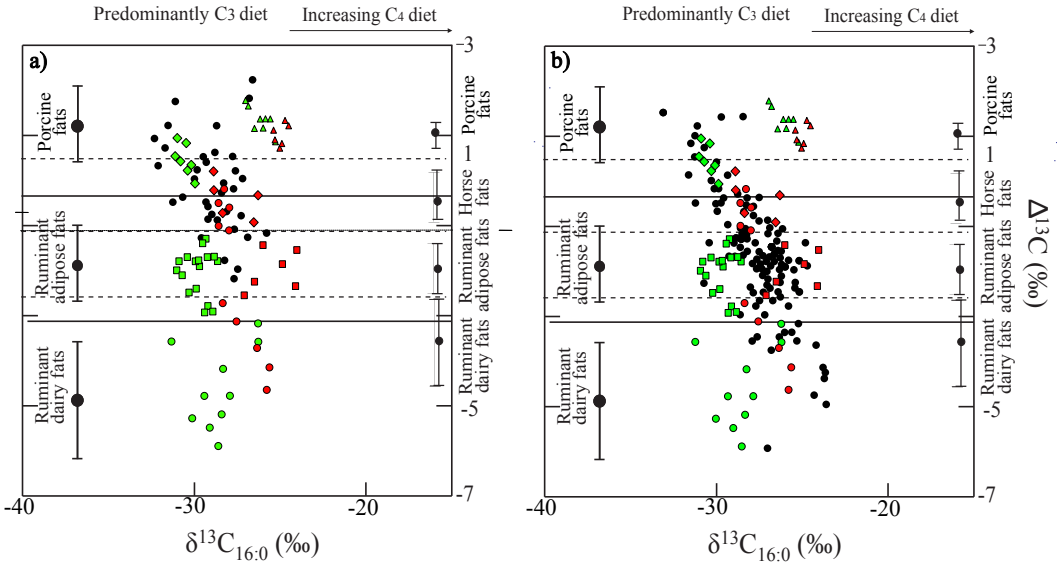


Figure 8.10 Scatterplots of $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values for (a) archaeological forest-steppe fats (black dots), modern reference animal fats collected from Britain (green dots) modern reference fats collected from Kazakhstan (red dots); and (b) archaeological steppe fats (black dots), modern reference animal fats collected from Britain (green dots) modern reference fats collected from Kazakhstan (red dots).

8.3.2 *Hydrogen Isotope analyses*

Whereas carbon isotope analysis offers information mainly about vegetation and indirectly about climate, determination of the stable-isotope ratio of hydrogen (δD values) in animal tissues can be a powerful tool in paleoclimatic reconstruction (Cormie et al., 1994). As already mentioned in Chapter 1, Section 1.6 establishing the hydrogen isotope fractionation in animal tissues is complicated by a number of factors (Sharp et al., 2003) including the fact that the bulk stable hydrogen isotope content of animal tissue depends (i) upon the δD value of both diet and drinking water (Alexander et al., 2006; Hobson, 1999; Sehoenheimer and Rittenberg, 1936), and (ii) upon different digestive systems or trophic levels (Reynard and Hedges, 2008). However, as discussed in Section 1.6.2, the PhD research carried out by Chivall (2008) suggested that hydrogen isotope analysis of extracted fats could offer climatic information. Indeed, a strong distinction in δD values between Kazakh and British animal fats was detected (Figure 8.11a); the Kazakh fats were more depleted relative to their UK analogues, reflecting the depletion of meteoric water in Kazakhstan (ca. -115 ‰) compared to that in UK (ca. -55‰).

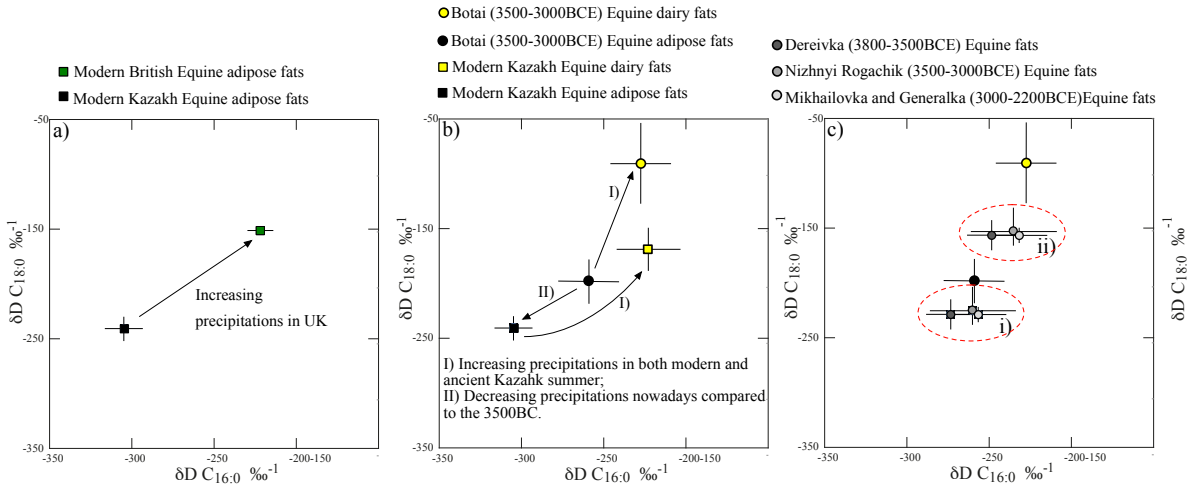


Figure 8.11. Scatter plots of mean δD values of the $C_{16:0}$ and $C_{18:0}$ fatty acids of animal fats from a) Modern equine adipose fats from Kazakhstan (black square) and United Kingdom (green square); b) Modern equine adipose and dairy fats (black and yellow squares) and Botai equine adipose and dairy fats (black and yellow dots); and c) Botai equine adipose and dairy fats (black and yellow dots) and Ancient North-Pontic region equine fats (grey dots) where i) represents the real results and ii) the expected results.

The research carried out by Outram et al. (2009) also showed the possibility of using this proxy for climate reconstruction. Indeed, by analysing modern reference fats from Kazakhstan and by identifying equine dairy fats in five pots from Botai (3500BC), the research also showed that the seasonal effect (discussed in Chapter 1, Section 1.6.1) could be used to provide information about ancient seasons (Figure 8.11b). Hydrogen used to biosynthesise equine dairy fats derives only from late spring and summer precipitation, while the hydrogen used to biosynthesise equine adipose fats will be an integration of hydrogen for the entire period of accumulation (ca. many months to 1 year). Therefore, the increasing δD value of the extracts identified as equine dairy fats reflects the increasing summer precipitations in Kazakhstan. Significantly, the years during which the reference fats have been collected from Kazakhstan (from 2002 to 2005) were characterized by a mean summer precipitation (mm) greater than the mean precipitation of the whole year (Table 8.1). Therefore, the archaeological fats, reflecting the modern fats, suggest a similar increase in the summer precipitation during the Late Atlantic period in Kazakhstan (I in Figure 8.11b). Furthermore, the depleted δD values of the modern equine adipose fats compared to the Botai equine adipose fats (II in Figure 8.11b) suggest that the modern precipitation was less abundant than that at Botai in Eneolithic times. The latter data also reflect the prevalence of the "warm and humid" Atlantic period.

Finally, Figure 8.11c shows the extracts of equine fat origin from the archaeological North-Pontic region extracts. Only equines have been considered in order to compare same animal fats. According to the pollen results discussed in Section 8.1, the ancient equine fats from the North-Pontic region were expected to display increasing precipitation (i.e. enriched δD values) compared to the ancient Kazakhstan equine adipose fats (Figure 8.11c, ii). Instead, the groups of fats from the three North-

Pontic sites displayed depleted δD values (Figure 8.11c, i). The latter data is difficult to interpret; it is very likely that other external factors influenced the values, including the possibility that the horses in the North-Pontic region came from other areas, perhaps due to migration of the horse herds. As a consequence, the hydrogen isotope results did not contribute to the environmental reconstruction of the overall North-Pontic steppe climate.

Table 8.1. Mean rainfall (mm/month) during the years when the modern reference fats where collected from Kazakhstan. The data have been extracted from the Climate Change Knowledge Portal (CCKP) of the World Bank.

	Rainfall (mm)			
Years	**2002**	**2003**	**2004**	**2005**
June-July-August	28.5	33.7	24	29
Whole year	25	24.5	22.5	19

8.4 **Conclusions**

The reconstruction of palaeoclimate is extremely challenging; a number of proxies must be used in order to achieve reliable interpretations. In the case of Ukraine, the necessary records are scarce so the paleoclimatic reconstruction is even more complicated.

In this Chapter the main purpose was to provide a general background of the climate and environment of the area of the North-Pontic region. Although a climatic change at around the 3rd millennium BC is generally believed, the extent of the climate change, its impact on North-Pontic region vegetation and consequently the ancient people is more difficult to understand.

Primarily relying on the detailed research carried out by Bostonalieva (2015) and on the pollen records described by Kremenetski (1995, 1999, 2003), an attempt to provide a general environmental background of the North-Pontic steppe and forest-steppe of Ukraine, compared with the Northern Kazakh environment, has been conducted. From the existing palynological analyses (Alexandrovskiy and Chichagova, 1998; Bezusko et al., 2008, 2000; Borisova et al., 2006; Bostonalieva, 2015; Cheddadi et al., 1996; Cordova and Lehman, 2005; Davis et al., 2003; Dobrowolski et al., 2001; Gerasimenko et al., 2011; Gerasimenko, 1997; Huhmann et al., 2004; Kotova and Makhortykh, 2010; 2003, 1995; 1999; Mauri et al., 2014; Smyntyna, 2007; Sycheva et al., 2003; Sycheva, 2006; 1999, 1998) we are able to discuss:

1) The occurrence of forest-steppe and steppe ecosystems in prehistoric times as well as in present day, and significantly the different impact of climate change on steppe compared to the forest-steppe areas;
2) The environmental difference between eastern and western Eurasia.

Concerning the first point, the North-Pontic region pollen records (Bostonalieva, 2015) revealed that the environmental difference between forest-steppe and steppe ecosystems was significant in prehistoric times as well as in present day; indeed the southern areas displayed a general predominance of steppe grasses over trees (Kremenetski, 2003, 1995; Kremenetski et al., 1999). However, during the "warm and humid" Atlantic period, the steppe zone comprised abundant temperate deciduous trees (Tarasov et al., 1998) showing milder conditions than the present day. At the same time, the decrease of arboreal taxa due to the "warm and dry" Subboreal period appeared to have had a milder impact on the forest-steppe, while the southern region experienced more drastic environmental change (Kremenetski, 2003, 1995; Kremenetski et al., 1999), showing increasing steppe grasses including *Artemisia*, *Poaceae* and *Chenopodiaceae*. Generally, the pollen analysis does not reveal a drastic aridification of the north-Pontic region during the Subboreal epoch.

The description of the pollen analysis allowed a better picture of the vegetation and changes in the balance between arboreal and non-arboreal taxa over the two different periods of the Eneolithic (Late Atlantic) and Bronze Age (Subboreal). The latter suggested increasing precipitation and/or humidity during the Eneolithic period and a more arid/cold environment during the later period. The pollen analysis also suggested a different environment in the steppe compared to the forest-steppe, with increasing percentage of arboreal taxa in the forest-steppe associated with increasing precipitation.

Concerning the difference between eastern and western Eurasia, the pollen data showed an eastern predominance of steppe vegetation; specifically, during the Atlantic period, temperate deciduous forests dominated the North-Pontic region, while cool steppe was typical of the Kazakhstan environment. The later "warm and dry" Subboreal period was apparently more continental and severe in eastern Eurasian steppe (Kremenetski, 2003). In contrast, as already mentioned, the Ukrainian environment displays more varied vegetation than Kazakhstan, reflecting a more temperate climate. Therefore, an environmental diversity between prehistoric eastern and western Eurasia is testified by several pollen analysis, both during the Eneolithic and the Early Bronze Age.

The bulk carbon isotope analysis and the compound-specific stable carbon isotope analysis generally offered additional information about vegetation and indirectly about climate. The forest-steppe were characterized by a predominance of C3 plants compared to the steppe where the hypothesis is that a small proportion of C4 plants was present. Also, the carbon isotope analysis offered an interesting seasonal distinction; the increasing $\delta^{13}C$ values of the ruminant dairy fats might suggest a further increasing of C4 plants. Others hypotheses have been outlined, including the possibility that the increased $\delta^{13}C$ values are connected to (i) greater aridity, so it might derive from water-stressed C3 plants (Evershed et al., 2008b), or (ii) seasonal pastoralism so the possibility that

these horses might have grazed on other lands, characterized by a higher abundance of C4 plants, during the seasonal transhumance.

Finally, the compound-specific stable hydrogen analysis of the fats with an equine fat origin did not contribute to the environmental reconstruction of the overall North-Pontic steppe climate; very likely other external factors influenced the deuterium values, including the possibility that the horses in the North-Pontic region came from other areas, perhaps due to migration of the horse herds.

CHAPTER 9

OVERVIEW, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

9.1 Subsistence economy in the North-Pontic region

As stated in the first Chapter of this thesis, numerous archaeological investigations have considered the cultures that lived in the North Black Sea area during the 3800-2200 BC because of the occurrence of some intriguing events that appeared in this region, notably: (i) horse domestication; (ii) metallurgical technology; (iii) Indo-European languages, likely connected to cultural migrations and interactions in the vast Eurasian steppe (Kuzmina, 2003; Sherratt, 2003).

Unfortunately, a number of factors, such as the isolation of Eastern Europe and Central Asia during the twentieth century and much literature remaining unpublished, means Eurasian prehistory is poorly understood; in addition, evidence of several aspects of human lifestyles and subsistence economy is exceptionally scarce during this period of time therefore an interdisciplinary approach is required in order to elucidate important aspects related with the subsistence economic strategies.

The transition to food production in North-Pontic region was mainly based on stock-breeding, differently to the European Neolithic and Bronze Age which was indeed called "the agricultural revolution" (Renfrew, 2002). Therefore, animal husbandry was an established and widespread way of life, becoming especially evident from the Early Bronze Age onward (ca. 3000/2800-2200/2000 BC), when the so-called Yamnaya culture appeared in the steppe region (Rassamakin, 1999). According to some studies (Bunyatyan, 2003; Kotova, 2003), domesticated ruminants appeared in the North-Pontic region at around the 6th millennium BC, however other evidence, such as faunal remains and previous isotopic analysis, suggested that the degree of animal exploitation was mainly influenced by local

environmental conditions and specific needs (e.g. Bunyatyan, 2003; Gerling, 2014; Kaiser, 2010; Kuzmina, 2003; Lillie, 2000; Lillie et al., 2011; Rassamakin, 1994, 2006, 2002, 1999, 1996). Furthermore, despite scarce, the archaeological and archaeobotanical evidence from sites across the North Black Sea might suggest that the gathering and processing of wild and domesticated plants might have been a significant component of local subsistence strategies (Bendrey et al., 2013; Bibikova, 1969; Levine et al., 1999; Pashkevich, 2003; Pashkevych, 2012; Velichko et al., 2009).

To date, there are no reports of organic residues in pottery from the Ukrainian archaeological literature. Thus, this research provides the first interdisciplinary investigation of diet and subsistence strategies of the human groups that lived in the North-Pontic region during the transitional periods of the Eneolithic and Early Bronze Age (see also Mileto et al., 2017b). This research aimed specifically to clarify the extent of the exploitation of domesticates and subsistence economic strategies in two distinct regions: (1) the forest-steppe area in the modern Cherkasy oblast, and (2) the steppe region in the modern Dnepropetrovsk and Zaporizhia oblasts.

The following discussion provides a summary of the main findings of this thesis. The information obtained from existing evidence (Chapter 5) and from molecular and stable isotope analysis (Chapter 6 and 7) will be integrated in order to provide a comprehensive picture of prehistoric animal and plant exploitation in the North-Pontic region from the Eneolithic to the Early Bronze Age.

9.2 **Summary of main findings of this thesis**

A total of 216 sherds (including six potsherds analysed in a previous pilot; Whelton and Evershed 2012) were analysed from two distinct regions in the North-Pontic area, to attempt to identify the extent of the exploitation of domesticates for their dairy and carcass products, and also further elucidate diet and subsistence practices. The ceramic sherds came from archaeological sites of Dereivka, Molyukhov Bugor, Mikhailovka, Nizhniy Rogachik and Generalka. The number of potsherds analysed, recovery rates and mean lipid concentrations are shown in Table 9.1. Lipid preservation was excellent with a total of 75% of potsherds (n=163) yielding appreciable lipid concentrations (>5 $\mu g\ g^{-1}$).

Most significantly the results obtained from molecular and compound-specific stable carbon analysis of the lipid residues in pottery, largely reflect the existing zooarchaeological records, confirming a changing pattern of subsistence economy in North-Pontic region and specifically the existence of two regionally distinct dietary habits (separately discussed in Sections 9.2.1. and 9.2.2.), based on the balance between equine and ruminant consumption. Examination of Figure 9.1 clearly highlights this distinction; the pie charts display the proportions of animal products detected within

pottery vessels, revealing that the ceramic vessels recovered from the two forest-steppe sites of Dereivka and Molyukhov Bugor were mainly used to process horse products (black slice), in contrast the three steppe sites (Mikhailovka, Nizhniy Rogachik and Generalka) reveal that the great majority of vessels were used to process ruminant products (greys slices). A summary of the specific findings and conclusions is given in the subsequent Sections.

Table 9.1. Number of potsherds analysed from each archaeological site in this thesis, percentage of lipid recovery and mean lipid concentration μg g^{-1}.

Archaeological site	Location	N° of vessels analysed	% lipid recovery	Mean lipid concentration (μg g^{-1})
Dereivka	Forest-steppe	40	67	18.8
Molyukhov Bugor	Forest-steppe	25	60	18.7
Mikhailovka I	Steppe	36	94	621.7
Nizhnyi Rogachik	Steppe	30	77	127.1
Mikhailovka II	Steppe	21	90	53,9
Mikhailovka III	Steppe	23	70	130,1
Generalka	Steppe	41	65	43.9

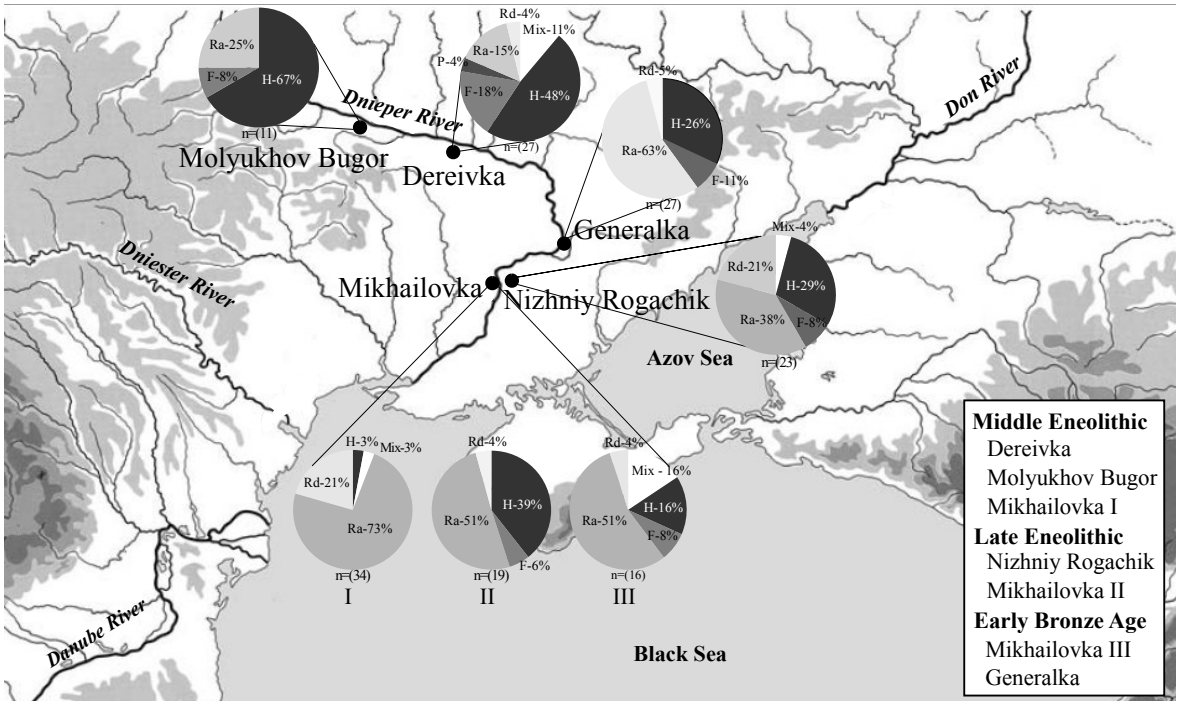


Figure 9.1. Pie charts showing the proportions of animal products detected within pottery vessels from the Eneolithic settlement of Dereivka (n=27); Molyukhov Bugor (n=11); Mikhailovka I (n=34); Nizhniy Rogachik (n=24) and Mikhailovka II (n = 19); and from the Early Bronze Age settlements of Mikhailovka III (n=16) and Generalka (n=27). Only those lipid residues that have been assigned by compound-specific stable isotope analysis are included (i.e. sherds containing plant lipids are not included, nor are sherds that did not yield any lipid). Total number of lipid extracts are given at the base of the pie charts. Abbreviations: Horses (H); Fresh water fish (F); Ruminant adipose fat (Ra); Ruminant dairy fat (Rd); Porcine/Pigs (P).

9.2.1 *Diet and subsistence Economy in Eneolithic forest-steppe of the North-Pontic region*

In Chapter 4 (Sections 4.2 and 4.3) an introduction to Dereivka and Molyukhov Bugor sites was given. These were two middle Eneolithic settlements of a same culture (Dereivka culture) located on the left bank of the Dnieper River in the forest-steppe region of Ukraine.

Chapter 6 displayed the results of the molecular and isotope analysis showing a common trend of the two forest-steppe sites: the near absence of pottery vessels showing ruminant dairy products (only one ceramic sherd out of 55 suggests a weak dairy fat contribution). The latter indicates that the Eneolithic forest-steppe populations did not commonly exploit secondary products, and perhaps that the practise of animal domestication was in a development phase (Rassamakin, 1999).

Overall, the subsistence economy of the Dereivka community was based on horse exploitation as equine products prevailed in 48% of the extracts (Figure 9.1). The latter result reflects the faunal assemblage, of which horses dominated (60% NISP; Figure 9.2). Additionally, according to the faunal records, ruminant hunting was a widely practiced activity, as deer and elk comprised 75% the total wild animal assemblage (Kaiser, 2010); domesticated ruminants (mainly cattle; 15.3%) were also exploited. Ruminant products exploitation is confirmed by the carbon isotope results, which revealed that 19% of the investigated pots were used to process ruminant fats. Finally, fishing was practiced as evidenced by both faunal records (3% NISP) and the carbon isotope results (18% of the total extracts might have a freshwater fish origin). However, the detection of C_{20} and C_{22} APAAs as biomarkers for unsaturated fats, would have further confirmed the processing of aquatic resources in pots (Cramp et al., 2014). Nevertheless, the latter suggestion is also supported by the other researches (e.g. Lillie et al., 2011). From these data it appears that Dereivka subsistence economy was mainly based on horse exploitation associated with complementary activities including ruminant hunting, fishing and cattle breeding.

The subsistence economy of the neighbouring site of Molyukhov Bugor was more challenging to reconstruct. Interestingly, the compound-specific stable carbon values of the fatty acids in the pottery from Molyukhov Bugor were dominated by equine products (67%); however, the faunal records revealed a lower percentage of equine bones (ca. 14%). The latter mismatch can be explained as follow: (i) the mixture of materials due to the peculiar type of soil (*Chernozem*) might have altered the faunal assemblage, or (ii) equine products were preferentially processed in vessels while other animal products were processed in other ways (e.g. using a spit over an open fire). According to the faunal records hunting was a widespread activity as the 37% of the faunal assemblage comprised wild animals. In addition, the 44% were attributed to domesticated ruminants (including cattle, sheep and goats) suggesting that ruminant breeding was a significant complementary practise, also supported by the fatty acid carbon isotope values that suggest 25% of the lipid residues in pottery to have a ruminant origin.

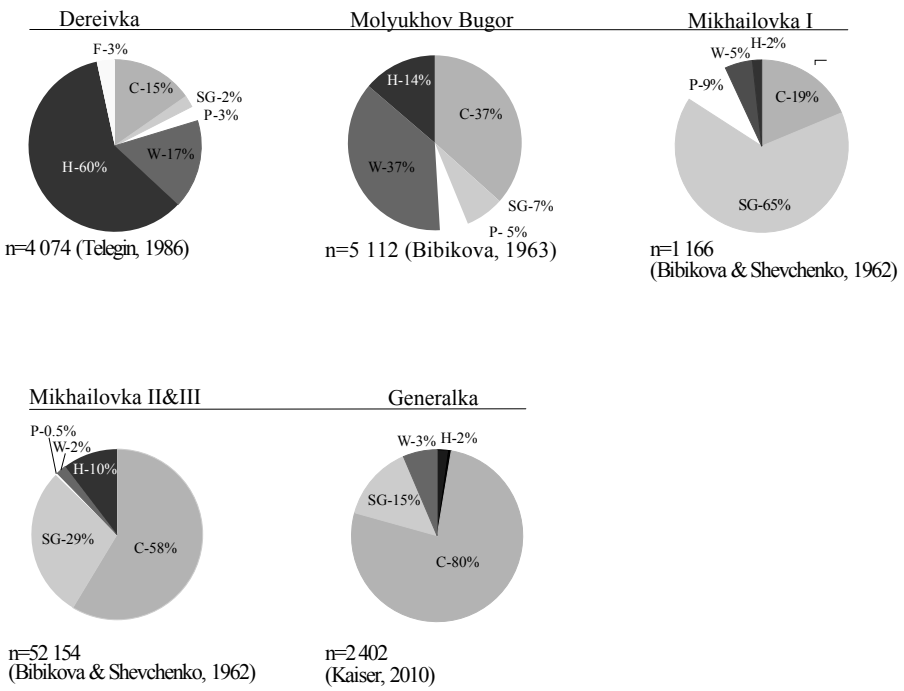


Figure 9.2. Pie charts of the percentage of bone finds (NISP%) recognized as being horses, cattle, sheep/goats, pigs, wild animals and fish are illustrated. Total number of bone finds are given at the base of the pie charts. Abbreviations: Horses (H); Fresh water fish (F); Porcine/Pigs (P); Wild animals (W); Cattle (C); Sheep and Goat (SG).

Furthermore, both forest-steppe sites display cereal seed impressions in pots (which reliability is discussed by Motuzaite-Matuzeviciute, 2012, 2014); together with a number of finds of agricultural tools (Chapter 5, Section 5.8) suggesting that plant exploitation might have been a complementary activity; a hypothesis supported by several archaeologists (e.g. Rassamakin, 1999). Possible plant biomarkers (discussed in Chapter 6) including long-chain fatty acids and *n*-alkanols were also recognized in four sherds from Molyukhov Bugor. They might be ascribed to a plant origin (Tulloch, 1976), however the very low concentration or absence of long–chain *n*-alkanes precludes unambiguous identification of plant waxes in pots.

9.2.1.1 Horse domestication?

Commonly, the exploitation of secondary products, e.g. dairy fats, suggests a full pastoral economy of prehistoric communities. Therefore, the absence of ruminant dairy product residues from the Dereivka and Molyukhov Bugor pottery may suggest a relatively unsophisticated knowledge of ruminant domestication. The latter evidence might imply the occurrence of wild rather than domesticated horses. In fact, taming a horse is considered extremely complicated (Levine, 1999b) and possession of a high level of experience in animal husbandry and herding techniques is considered a prerequisite in order to domesticate a wild horse (Kuzmina, 2003). However, the latter might be countered by the finding of equine dairy fats in Botai pots (Outram et al., 2009), a site essentially devoid of domestic ruminants (Olsen et al., 2006). Indeed, the faunal records of Botai site revealed that 99.9% of the total assemblage was ascribed to equine bones; therefore, these species are unknown

in the faunal records of Botai and were not prevalent in northern Kazakhstan until the Bronze Age (Olsen et al., 2006). Hence, the near absence of ruminant bones from the Botai faunal records indicates an exceptional level of horse specialisation by the Botai people from which it could be inferred that they developed a profound knowledge of the equine biology (Kuzmina, 2003, *ref.* Zaibert, 1993). According to Zaibert, such a knowledge led the Botai people to attempt domestication of a few horses as an aid to driving the herds (Kuzmina, 2003, p. 212). Therefore, the knowledge of horse domestication could have been acquired by communities with no obvious knowledge of ruminant milking (Kuzmina, 2003). However, in Dereivka case, the scarce indirect archaeological evidence for horse domestication in the North-Pontic region generally point to horses at Dereivka site being wild (as discussed in Chapter 5, Section 5.7) such that many archaeologists (Kuzmina, 2003; Levine, 1999a, 1998, 1990; Levine and Rassamakin, 1996; Rassamakin, 1999) believe that the communities of the Eneolithic North-Pontic region did not commonly domesticate horses. Therefore, the absence of ruminant dairy products in the pots from the forest-steppe sites further support the hypothesis that horses from Dereivka and Molyukhov Bugor communities were likely wild (Anthony, 2007; Kuzmina, 2003; Levine, 2005; Rassamakin, 1999).

9.2.2 *Diet and subsistence Economy in the Eneolithic and Early Bronze Age Steppe of the North-Pontic Region*

The introduction to the steppe sites of Mikhailovka, Nizhniy Rogachik and Generalka was given in Chapter 4, Sections 4.4, 4.5 and 4.6. The three sites cover a broad period, from the Middle Eneolithic to Early Bronze Age. The information obtained from existing archaeozoological and botanical records (Chapter 5, Sections 5.5 and 5.6) and from molecular and stable isotope analysis (Chapter 7) suggests a completely different pattern compared with the two forest-steppe sites. Interestingly, according to both faunal records (Chapter 5; Kaiser, 2010; Rassamakin, 1999; Telegin et al., 1986) and isotope results (Chapter 7), the steppe dietary habit was ruminant-based.

Ruminant dairy products were widely exploited from the steppe communities (19 out of 119 residues have a clearly dairy origin, exhibiting $\Delta^{13}C$ values ranging from -5 to -2.5‰). However, Generalka departs from this trend producing only one residue has a dairy fat origin and four residues might have a weak dairy fat contribution ($\Delta^{13}C$=-2.6‰). Interestingly, the predominance of cows over bulls in the faunal records and the high number of bones attributed to animal in slaughter age (36-48 months), suggest an economy mainly based on meat and dairy production (Chapter 5, Section 5.6; Tuboltsev, 2015 in prep.), possibly indicating that the selection of the ceramic fragments may have biased interpretations. Notwithstanding this, the occurrence of dairy products in pottery correlates with the widespread evidence of domestic ruminants in steppe sites and the identification of ovines and bovids in the faunal assemblage, reinforcing the idea of a full pastoral economy of the steppe communities.

The exploitation of horses appears to be secondary but still relevant as few TLEs (23 out of 119 extracts displayed equine fat origin) were attributable to equine products, again reflecting trends in the faunal records. Perhaps the horses of the steppe were mainly used for their secondary products rather than for their meat. Furthermore, based on compound-specific carbon isotope analysis of fatty acids, the non-ruminant residues recovered from the steppe potsherds, were attributed to: (i) freshwater fish oils, suggesting that the steppe populations also practised fishing as a secondary activity, and (ii) mixing of commodities was also observed suggesting non-specialised use of vessels. However, despite the attempt to identify biomarkers for fish including the C_{20} and C_{22} APAAs as biomarkers for unsaturated fats, the absence of these biomarkers in the extracts, do not allow confirmation of the presence of freshwater fish oil.

Finally, both faunal records and stable carbon isotope analysis of fatty acids support the absence of porcine species from the steppe subsistence economy; only one lipid residue from Nizhniy Rogachik (NR18) displays carbon isotopic values closer to the porcine fat range (showing $\delta^{13}C_{16:0}$ value = -29.7‰, mean $\delta^{13}C_{18:0}$ value = -28.3‰ and $\Delta^{13}C$ value = 1,4‰). However, carbon isotopic values of porcine products are typically more enriched (Copley et al., 2003; Evershed et al., 1997a), therefore, the residue could derive from a mixture of commodities, possibly freshwater fish and porcine products as the $\Delta^{13}C$ values plot well within the non-ruminant fat area of the graph.

Furthermore, several seed imprints, including millet, in ceramic vessels confirm the agricultural activities at the steppe communities (Chapter 5, Section 5.8; Pashkevich, 2003). Unfortunately, plant biomarkers in pots were absent; only one extract from Nizhniy Rogachik (Late Eneolithic site) showed possible presence of plant biomarkers (discussed in Chapter 7, Section 7.2.1.3).

9.2.2.1 Cattle versus small ruminant carcasses: an unusual proportion

High level consumption of ruminant products among the steppe people is suggested by the fatty acid carbon isotopic data. However, Mikhailovka faunal records exhibit an important difference in the type of the exploited ruminants: an overall predominance of cattle in Mikhailovka II and III (Late Eneolithic and Early Bronze Age periods), and a predominance of sheep and goats bones in the earlier Mikhailovka I (Telegin, 1986; Rassamakin, 1999; Kaiser, 2010). The shift to cattle was not detected until the Yamnaya culture (3100 BC onwards) that also corresponds to the climate change occurred at around the 3rd millennium BC, from a more humid environment (set in the Late Atlantic epoch) to a more arid one.

The latter occurrence is quite difficult to explain; cattle husbandry increased in a period where higher mobility and higher aridity are believed to occur (Anthony, 2007), however cattle are usually more exploited from sedentary communities and, in addition, are challenging to be bred during arid periods as they require higher quantity of water; sheep on the contrary are more arid-resistant animals and are usually more common in mobile communities. What made the communities of the North-Pontic region to exploit cattle in a period more suitable for sheep and goats breeding? Possibly the

North-Pontic steppe societies were autonomous adopting a unique subsistence economy, influenced neither by climate, environment nor external influences. Therefore, the latter may have been based on cultural belief or economic drivers. The last assumption strongly reflects the fact that the following periods (Middle and Late Bronze Age) were characterized by a subsistence economy mainly based on cattle exploitation (Kaiser, 2010). Since, the results presented herein cannot provide a definitive answer to the latter question, resolution will have to await future investigations.

9.3 **Environment and climate**

Chapter 8 offered the description of the available environmental evidence in the North-Pontic region. As already mentioned, the latter are very scarce which means that many doubts and questions are associated to this region in relation to climate, vegetation and their impacts on the lives of the people lived in this area and during this period of time.

The evidence reported in the current thesis and discussed in Chapter 8 are:

1) Pollen analyses (Bostonalieva, 2015; Kremenetski, 2003, 1995; Kremenetski et al., 1999);
2) Bulk isotope analysis of human bones (Gerling, 2014; Lillie et al., 2011);
3) And the compound-specific stable carbon analysis of residues carried out during the current research project (as $\delta^{13}C_{16:0}$ also carries environmental information).

Figure 9.3 summarizes the evidence: the two analysed periods (Late Atlantic; LA and Subboreal; S) are divided into two seasons; winter (WLA and WS) and summers (SLA and SS).

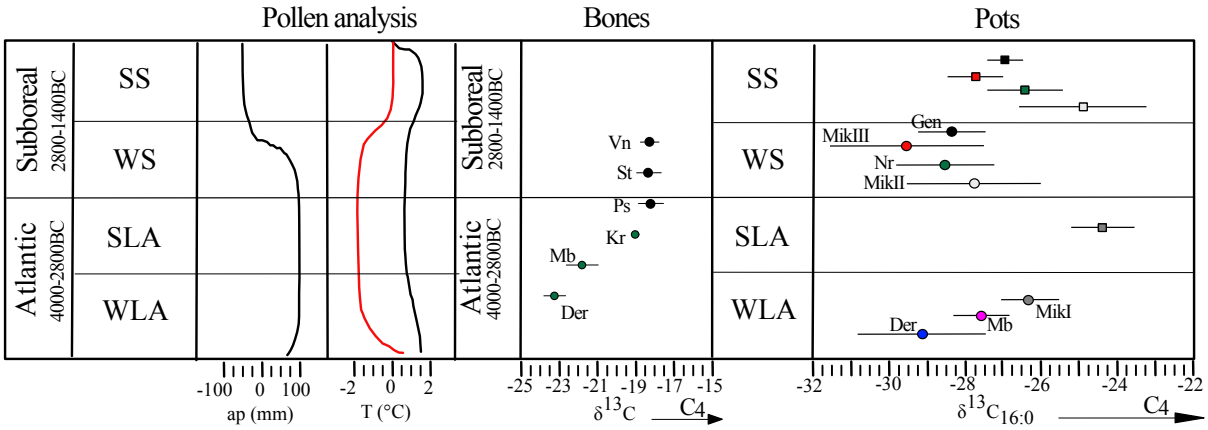


Figure 9.3.Summary of (i) the climate reconstruction made by Kremenetski (1995) based on the pollen analysis, showing the annual precipitation (ap mm) and the temperature (T°C) through the summers of the late Atlantic period (SLA), the winters of late Atlantic period (WLA), the summers of the Subboreal period (SS) and the winters of the Subboreal period (WS); (ii) the bulk carbon isotope analysis of bones from Dereivka (Der), Molyukhov Bugor (Mb) carried out by Lillie et. al, (2011) and from Kirovograd (Kr), Peshtchanka (Ps), Sh Stepnaya (St) and Vinogradnoe (Vn) carried out by Gerling (2014); and (iii) the compound-specific stable carbon analysis of residues from pots from Dereivka (Der), Molyukhov Bugor (Mb), Mikhailovka I (MikI), Mikhailovka II (MikII), Nizhnyi Rogachik (Nr), Mikhailovka III (MikIII) and Generalka (Gen) carried out over this research project. The fats have been grouped in adipose fats (dots) and ruminants dairy fats (squares) in order to make a more seasonal distinction.

The pollen analysis displayed a difference in arboreal taxa amount between forest-steppe and steppe. The forest-steppe is described as more green and humid compared to the steppe, however the steppe was never extremely arid (Kremenetski, 2003). According to the carbon isotope evidence, the two studied ecosystems contained a proportion of C4 plants or water-stressed C3 plants; in addition, the steppe were characterized by increasing $\delta^{13}C_{16:0}$ plants input especially during summers. Therefore either ruminants naturally grazed on wild C3/C4 plants, which ratio increased toward C4 during summer, or it may be assumed that the management of the herd was sophisticated and that the domesticated animals were possibly raised in a different way (e.g. cows were raised on a mixed C3/C4 plant diet). After all, the predominance of domesticated animals detected in both faunal and carbon isotope records, together with the detection of ruminant dairy products in the vessels from the North-Pontic steppe sites, is indicative of a high level of knowledge of domestication and exploitation of secondary animal products.

9.4 **Recommendations for the future work**

This work presents the results of the first study of absorbed organic residues recovered from archaeological ceramics in the North-Pontic region of Ukraine. As was to be expected with a preliminary study, this research has raised many questions and opened a number of avenues for further exploration. Indeed, there are several aspects of the work that need to be further developed. These are discussed below.

9.4.1 *Collection of Ukrainian modern reference fats*

The analysis of the modern reference materials collected from Ukraine did not provide the results expected: commercial diets altered the isotope values preventing the use the modern Ukrainian reference materials for the assessment of prehistoric fat residues (as discussed in Chapter 2). Therefore, a more appropriate collection of reference fats of modern Ukrainian plant and animal materials would aid better interpretation of plant lipid residues and animal products. Above all, it would make possible the identification of equine dairy products by allowing comparison of compound-specific stable hydrogen analysis of ancient and modern fats. As discussed in Chapter 6, Section 6.5, compound-specific stable hydrogen analysis of archaeological animal fatty acids (extracted from North-Pontic region ceramic fragments) revealed extensive overlap between fat groups, precluding the possibility of identifying equine dairy products. Very likely, the fundamental problem was the smaller seasonal difference in Ukrainian δD value compared to Kazakhstan.

9.4.2 *Extending the number of ceramic pottery and investigated sites*

The analysis of both lipid biomarkers and fatty acid carbon isotope provided very interesting and novel information. However, in some cases the results also raised questions. For instance, the analysis

of the pottery from Generalka did not produce a significant number of ruminant dairy product residues generating doubts about the knowledge of domestication in this society. However, considering the predominance of cattle in the faunal record and the fact that contemporaneous neighbouring sites revealed extensive dairy product evidence, it is possible that sampling bias in the selection of the sherds may have missed. Therefore, it would be interesting to verify this hypothesis by analysing a larger number of sherds from Generalka sites.

In addition, the investigations were restricted to five sites not ideally distributed along the Dnieper River and across the steppe and the forest-steppe environments. As mentioned in Chapter 1, the first sample set was chosen to focus mainly on a possible chronological transformation; and thus, in order to trace a possible dietary change; for this two sites were targeted from each archaeological period. However, when it was found that the subsistence economy was strictly connected with regional environments rather than chronological periods, an addition of thirty ceramic sherds from Mikhailovka I, a site located in the steppe and dated Middle Eneolithic, was selected to enable comparison between sites from same periods but different environments and to test the hypothesis of a diverse subsistence economy driven by specific environmental factors. The latter hypothesis has been confirmed: the earlier sites of Dereivka, Molyukhov Bugor and Mikhailovka I are characterized by a contrasting diet, horse-based in the communities of the forest-steppe and ruminant-based in the sites of the steppe. Therefore, in order to obtain a more reliable distinction between regional economies and to strengthen the hypothesis of a subsistence economy mainly based on local environment, the analysis of two later forest-steppe sites would be essential. The latter would also provide information whether milk use occurred at an earlier in the communities of the North- Pontic forest-steppe. Indeed, the virtual absence (n=2) of ruminant dairy fat from the two Eneolithic northern sites (Dereivka and Molyukhov Bugor) raised questions about the first exploitation of secondary animal products in the North-Pontic forest-steppe. Nevertheless, the analysis of later sites located in the same area, might be useful in identifying the period when these people began to extensively milk animals.

9.4.3 *Application of δD analysis of lipid in pottery as an environmental proxy*

The main goal of using compound-specific stable hydrogen analysis was to identify equine dairy products (results discussed in Chapter 6, Section 6.5). However, in the attempt to (i) possibly clarify some aspects of this isotopic application as environmental records and (ii) aid in the paleoclimatic reconstruction of the ancient Ukraine; the δD values of pottery-derived fatty acids were assessed as a possible environmental proxy. Unfortunately, a number of factors prevented the use of this proxy including: (i) the limited understanding of the rules governing the fractionation of the hydrogen isotopes from the meteoric water to animal tissue (Cormie et al., 1994; Chivall, 2008); (ii) the limited number of studies applying this approach to archaeological organic residues and hence, (iii) the

limited hydrogen isotope database, finally (iv) the possibility that changes in feeding and drinking behaviour of ancient animals might alter the archaeological δD values (Hobson, 1999).

Added to that, the impracticability, in the case of the current research, to compare modern and archaeological equine fats due to the lack of modern Ukrainian reference animal fats, has further limited the understanding of the use of this proxy as a palaeoenvironmental proxy, making application of this methodology to the current research ineffective. However, an extensive and more specific experimental application involving compound-specific stable hydrogen analysis of a number of modern equine adipose and dairy fats recovered from Ukraine would aim to achieve the above-mentioned understanding, would be a very worthwhile avenue of investigation.

9.4.4 *Direct radiocarbon dating of fatty acids*

Highly interesting would also be radiocarbon dating of lipids extracted from archaeological ceramics of the North-Pontic region. The appreciable concentrations of lipids present in the TLEs, suggests that there would be sufficient carbon present for AMS dating. This would solve many of the problems regarding dating (explained in Chapter 4), by providing an absolute chronology for the sherds and allow ^{14}C dates derived from bulk lipids to be directly linked to the commodities processed in the vessels during their use. Furthermore, once determined the $\delta^{13}C$ and δD values of absorbed lipids, could also be radiocarbon dated, thereby establishing temporal relationships between local climate, ecology, diet and subsistence practices.

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APPENDIX

CONTENTS

APPENDIX A

A total of 30 reference animal fats, including cows, sheep, goats, horses, fish and pigs, were collected from Ukraine and Moldova (Table 1) intended for use as reference materials for comparison with the archaeological fats. Unfortunately, the diet of many of the farm animals was mainly cereal-based formulations (bran), i.e. a mixture of wheat, maize and barley and potentially other unknown components or components that would never have been encountered in the region in prehistory, e.g. maize and potatoes. Therefore, the animals were not raised on a natural diets, which is known to fundamentally affects the resulting isotope compositions (e.g. Salque et al., 2017), often in unpredictable ways, and thus do not meet the criteria required for use in assigning prehistoric fats (Tables 2 and 3). The animals diet, sources and their stable isotope compositions are reported below.

Table 1. List of modern reference fats recovered from Ukraine (sample 1 to 23) and Moldova (samples 24 to 30).

N°	Specie	Region	Diet
1.	Fish (silver carp)	Uman' (Cherkasy region)	Natural
2.	Pork	Lehedzyne (Cherkasy region, Tal'ne district)	Wheat, maize, fodder beet, potatoes. The fodder was cultivated in the same region.
3.	Pork	Lehedzyne (Cherkasy region, Tal'ne district)	Wheat, maize, fodder beet, potatoes. The fodder was cultivated in the same region.
4.	Beef	Vil'shana Slobidka (Cherkasy region, Uman' district)	Hay, wheat, barley, maize.
5.	Sheepmeat	Sobkivka (Cherkasy region, Uman' district)	Hay, grass, wheat
6.	Sheepmeat	Sobkivka (Cherkasy region, Uman' district)	Hay, grass, wheat.
7.	Cow milk	Ladyzhynka (Cherkasy region, Uman' district)	Hay, beet pulp (sugar beet), wheat, maize.
8.	Cow milk	Dobrovody (Cherkasy region, Uman' district)	Fodder beet, beet pulp (from Ivan'ky, Man'kivka district, Cherkasy region), hay, grain, oil cake (sunflower).
9.	Beef	Hromy (Cherkasy region, Uman' district)	Hay, wheat, maize, barley.
10.	Pork	Polyanets'ke (Cherkasy region, Uman' district)	Bran (components not defined), fodder beet, potatoes.
11.	Pork	Polyanets'ke (Cherkasy region, Uman' district)	Bran (components not defined), fodder beet, potatoes.
12.	Cow milk	Rubanyi Mist (Cherkasy region, Uman' district)	Hay, fodder beet, bran (maize, wheat, barley), beet pulp.
13.	Cow milk	Stavyshche (Kyiv region, Stavyshche district)	Hay, fodder beet, bran (unknown components, but possibly wheat, shredded soya and oil cake).
14.	Cow milk	Stavyshche (Kyiv region, Stavyshche district)	Hay, fodder beet, bran (unknown components, but possibly wheat, shredded soya and oil cake).
15.	Beef	Salyvonky (Kyiv region, Vasyl'kiv district)	Hay, bran (unknown components, but contains in addition oat).
16.	Pork	Salyvonky (Kyiv region, Vasyl'kiv district)	Wheat, barley, maize.
17.	Fish (grass carp)	Kaniv (Kyiv region, Kaniv district).	Natural

18.	Goat milk	Hoholiv (Kyiv region, Brovary district)	Hay, fruits and vegetables, cabbage, carrots, bran (wheat and maize), fodder beet, beet pulp, sometimes banana and orange paring (not really from the region). This animal did not get salt.
19.	Horse milk	Dibrivka (Poltava region, Myrhorod district)	Hay, oat, wheat straw
20.	Horse milk	Dibrivka (Poltava region, Myrhorod district)	Hay, oat, wheat straw
21.	Goat milk	Yares'ky (Poltava region, Shyshaky district)	Hay, dry medicago, fodder beet, shredded maize, oil cake. This animal doesn't get salt.
22.	Goat milk	Yares'ky (Poltava region, Shyshaky district)	Hay, dry medicago, fodder beet, shredded maize, oil cake. This animal doesn't get salt.
23.	Goat fat	Yares'ky (Poltava region, Shyshaky district)	Hay, dry medicago, fodder beet, shredded maize, oil cake. This animal doesn't get salt.
24.	Sheepmeat	Tocuz (Causeni district) Moldova (steppe)	Mother's milk (who eats only grass).
25.	Sheepmeat	Căuşeni district, Moldova (steppe)	Mother's milk (who eats only grass).
26.	Pork	Tocuz (Căuşeni district), Moldova (steppe)	Wheat, maize, bread, fodder breed. The origin of both bread and wheat is unknown.
27.	Fish	Dnestr within the Ştefan Vodă district, Moldova (steppe)	Natural
28.	Cow milk	Zaim (Căuşeni district), Moldova (steppe)	Medicago, maize, hay, wheat, oil cake, beet pulp, fodder beet.
29.	Cow milk	Bălţi, Moldova (steppe)	Hay, pumpkin, maize haulms (but not the grains).
30.	Goat milk	Bălţi, Moldova (steppe)	Bean shells and haulms, maize haulms, hay, oil cake, fodder beet, Chelidonium.

Table 2. List of $\delta^{13}C$ values for the stearic and palmitic fatty acids of aquatic fats, equine dairy fat, ruminant dairy fats, ruminant adipose fats and porcine adipose fats from animals raised in Ukraine and Moldova.

Species	**Sample ID**	**Corrected $\delta^{13}C_{16:0}$ values (‰)**	**Corrected $\delta^{13}C_{18:0}$ values (‰)**	**$\Delta^{13}C$ (‰)**
Fish (grass carp)	Fish17	-35,4	-37,1	-1,6
Fish (silver carp)	Fish1	-22,4	-23,5	-1,1
Fish	Fish27	-34,2	-34,2	0,0
Sheepmeat	Sheep5	-27,4	-26,2	1,2
Sheepmeat	Sheep6	-27,2	-26,5	0,6
Beef	Beef9	-25,1	-24,9	0,2
Beef	Beef4	-27,5	-27,1	0,4
Beef	Beef15	-25,1	-27,3	-2,3
Goatmeat	Goat23	-25,4	-26,2	-0,8
Goat milk	GM30	-26,6	-31,1	-4,5
Cow Milk	CM 13	-23,8	-27,6	-3,7
Cow Milk	CM 12	-26,8	-29,3	-2,5

Cow Milk	CM 7	-23,1	-29,6	-6,4
Cow Milk	CM 8	-24,2	-26,7	-2,5
Cow Milk	CM14	-24,1	-27,5	-3,4
Goat milk	GM21	-20,2	-24,6	-4,4
Goat milk	GM22	-19,9	-23,3	-3,4
Horse milk	Hm19	-29,3	-30,5	-1,2
Horse milk	Hm20	-29,2	-30,5	-1,3
Pork	Pork10	-21,7	-21,1	0,6
Pork	Pork11	-20,3	-20,8	-0,5
Pork	Pork3	-25,7	-24,7	1,1
Pork	Pork16	-21,0	-21,1	-0,1
Pork	Pork2	-25,9	-25,3	0,6
Pork	Pork26	-21,1	-21,5	-0,4

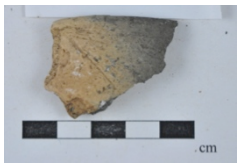
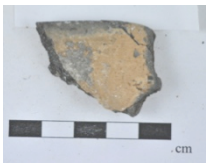
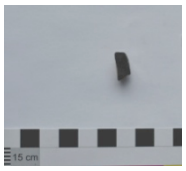
Table 3. List of δD values for the stearic and palmitic fatty acids of aquatic fats, equine dairy fat, ruminant dairy fats, ruminant adipose fats and porcine adipose fats from animals raised in Ukraine and Moldova.

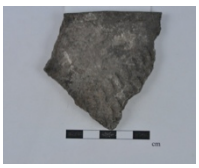
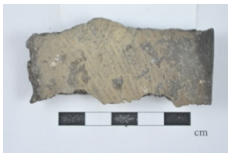
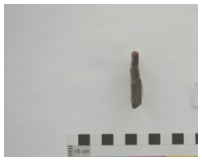
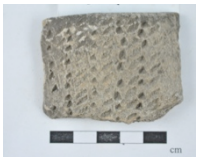
Specie	**Sample ID**	**Corrected $\delta D_{16:0}$ values (‰)**	**Corrected $\delta D_{18:0}$ values (‰)**	**$\Delta^{13}C$ (‰)**
Fish	Fish1	-262,5	-251,2	11,3
Fish	Fish17	-351,4	-339,9	11,6
Fish	Fish27	-261,8	-235,3	26,6
Pork	Pork26	-312,8	-322,5	-9,7
Pork	Pork11	-320,3	-298,0	22,4
Pork	Pork10	-332,7	-320,2	12,5
Pork	Pork3	-331,3	-324,5	6,8
Pork	Pork2	-315,7	-311,7	3,9
Pork	Pork16	-315,3	-294,9	20,4
Horse milk	HM19	-291,1	-268,1	22,9
Horse milk	HM20	-298,3	-265,3	33,1
Beef	Beef 9	-291,6	-273,8	17,8
Beef	Beef 15	-275,3	-277,6	-2,3
Beef	Beef 4	-250,7	-295,3	-44,6
Sheep	Sheep25	-246,7	-261,3	-14,6
Sheep	Sheep24	-286,5	-288,5	-2,0
Sheep	Sheep5	-279,6	-281,5	-1,9
Sheep	Sheep6	-276,5	-278,8	-2,3
Goat	Goat23	-275,4	-277,6	-2,2
Goat milk	GM30	-272,2	-218,7	53,5
Goat milk	GM22	-276,2	-238,5	37,7
Goat milk	GM21	-276,0	-243,2	32,8

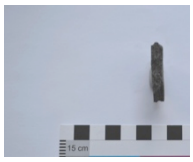
Goat milk	GM18	-261,9	-246,5	15,4
Cow milk	CM29	-251,4	-238,2	13,2
Cow milk	CM28	-259,0	-277,8	-18,8
Cow milk	CM12	-260,2	-245,4	14,8
Cow milk	CM8	-277,7	-243,7	34,1
Cow milk	CM7	-236,1	-249,5	-13,5
Cow milk	CM13	-268,1	-247,5	20,7
Cow milk	CM14	-267,9	-245,4	22,5

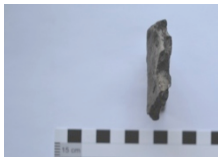
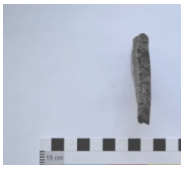
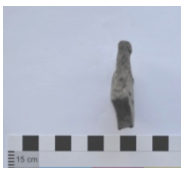
APPENDIX B

Table 1. Dereivka ceramic fragments (n=40).

Sample ID	Diameter (cm)	**Front**	**Retro**	**Rim**
DER1	Missing			
DER2	Too small			
DER3	Too small			
DER4	Missing			
DER5	>10			
DER6	15-20			
DER7	Too small			
DER8	Missing			
DER9	13-14			

DER10	Too small			
DER11	Too small			
DER12	>23			
DER13	Missing			
DER14	>15			
DER15	>20			
DER16	Missing.			
DER17	Too small.			
DER18	>25			
DER19	10-12			

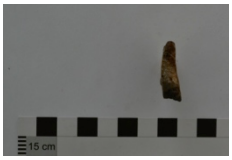
DER20	Too small.			
DER21	15-17			
DER22	22			
DER23	10			
DER24	20			
DER25	Missing			
DER26	10 - 12			
DER27	Missing			
DER 28	Missing			Too small after sampling.
DER29	14-17			
DER30	Missing			

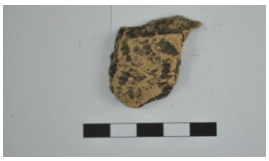
DER31	Missing			
DER32	30-35			
DER33	>20			
DER34	14-15			
DER35	Missing			
DER36	Missing			
DER37	30-35			
DER38	15-20			
DER39	>15			
DER40	Missing			

NB:The measurement of the diameters was taken after the first sampling so in many cases was not possible to collect this information as the rim was too small or missing.

Table 2. Molyukhov Bugor ceramic fragments (n=25).

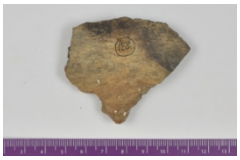
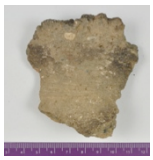
Sample ID	Rim Diameter (cm)	**Front**	**Retro**	**Rim**
MB1	Missing			Too small after sampling.
MB2	Too small			
MB3	25-35			
MB4	17-20			Too small after sampling.
MB5	Too small			
MB6	Too small			
MB7	<15			
MB8	20			
MB9	Missing			Too small after sampling.
MB10	Too small			

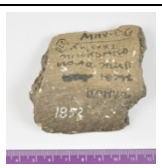
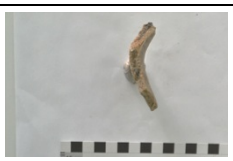
MB11	Missing			
MB12	Too small			
MB13	Too small			
MB14	Missing			
MB15	Too small			
MB16	Missing			
MB17	35			Too small after sampling.
MB18	20-25			
MB19	Missing			Too small after sampling.
MB20	Missing			Too small after sampling.
MB21	Too small			

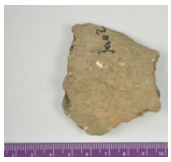
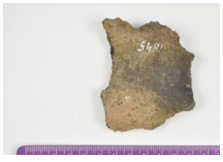
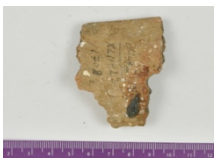
MB22	Missing			Too small after sampling.
MB23	Missing			Too small after sampling.
MB24	Missing			Too small after sampling.
MB25	Too small			Too small after sampling.

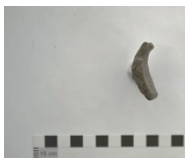
NB: The measurement of the diameters was taken after the first sampling so in many cases was not possible to collect this information, as the rim was too small or missing.

Table 3. Mikhailovka I ceramic fragments (n=36)

Sample ID	Diameter (cm)	**Front**	**Retro**	**Rim**
MIKI_50	Too small			
MIKI_52	20			
MIKI_53	<20			
MIKI_54	20-25			
MIKI_55	Missing			
MIKI_56	Missing			
MIKI_57	Missing			
MIKI_58	Missing			
MIKI_59	Missing			
MIKI_60	Missing			

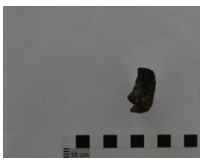
MIKI_61	Missing			
MIKI_62	Missing			
MIKI_63	35			
MIKI_64	Missing			
MIKI_65	Missing			
MIKI_66	Missing			
MIKI_67	Missing			
MIKI_68	Missing			
MIKI_69	15-20			
MIKI_70	Missing			
MIKI_71	Missing			

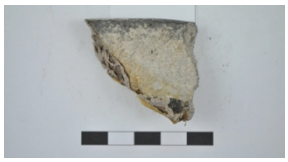
MIKI_72	Missing			
MIKI_73	Missing			
MIKI_74	<20			
MIKI_75	Too small			
MIKI_76	To small.			
MIKI_77	15-20			
MIKI_78	Missing			
MIKI_79	Too small.			
MIKI_80	Missing.			
MIKI_81	Missing.			
MIKI_82	Too small.			

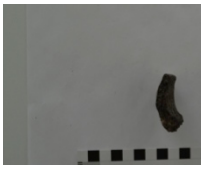
MIKI_83	Missing.			
MIKI_84	20-25			
MIKI_85	20-25			
MIKI_86	15-16			

NB: The measurement of the diameters was taken after the first sampling so in many cases was not possible to collect this information, as the rim was too small or missing.

Table 4. Mikhailovka II ceramic fragments (n=21).

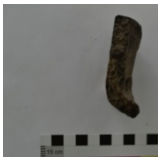
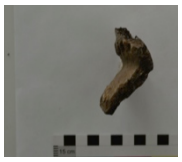
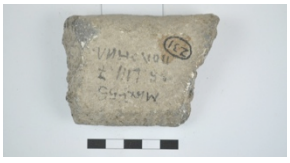
Sample ID	Diameter (cm)	**Front**	**Retro**	**Rim**
MIK II_4	Missing.			
MIK II_5	Too small.			
MIK II_6	20			
MIK II_7	30-35			
MIK II_8	>30			
MIK II_9	15-20			
MIK II_10	30-35			
MIK II_11	20-25			
MIK II_12	25-30			
MIK II_13	15-20			

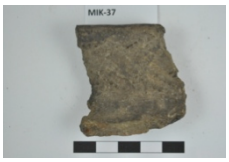
MIK II_14	Missing.			
MIK II_15	10-15			
MIK II_16	14-15			
MIK II_17	<20			
MIK II_18	Missing			
MIK II_19	17-20			
MIK II_20	10			
MIK II_21	Too small.			
MIK II_22	20-25			
MIK II_23	35			

MIK II_24	34-35			

NB: The measurement of the diameters was taken after the first sampling so in many cases was not possible to collect this information as the rim was too small or missing.

Table 5. Mikhailovka III ceramic fragments (n=23).

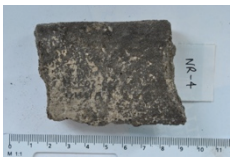
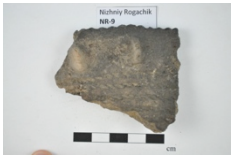
Sample ID	Diameter (cm)	**Front**	**Retro**	**Rim**
MIK III_25	20-25			
MIK III_26	22			
MIK III_27	<25			
MIK III_28	30-35			
MIK III_29	20-25			
MIK III_30	30-35			
MIK III_31	35			
MIK III_32	20-22			
MIK III_33	35			
MIK III_34	Too small.			

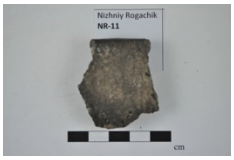
MIK III_35	Missing.			Too small after sampling.
MIK III_36	Missing.			
MIK III_37	30-35			
MIK III_38	13-15			
MIK III_39	25-35			
MIK III_40	30-35			
MIK III_41	Too small			
MIK III_42	Too small			
MIK III_43	Too small			
MIK III_44	Missing.			

MIK III_45	Missing.			
MIK III_46	35			
MIK III_47	Too small			

NB: The measurement of the diameters was taken after the first sampling so in many cases was not possible to collect this information, as the rim was too small or missing.

Table 6. Nizhnyi Rogachik ceramic fragments (n=30)

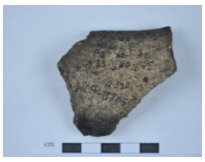
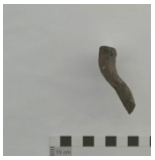
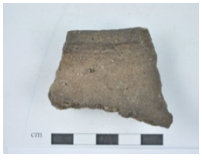
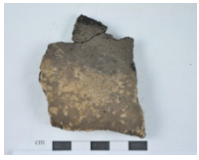
Sample ID	Diameter (cm)	**Front**	**Retro**	**Rim**
NR1	20			
NR2	>20			
NR3	Missing.			
NR4	25			
NR5	Missing.			
NR6	20			
NR7	20-25			
NR8	>15			
NR9	25-35			
NR10	>15			

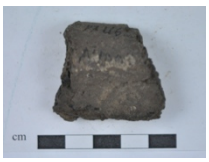
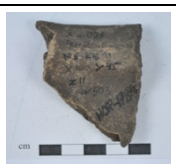
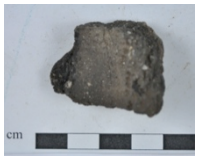
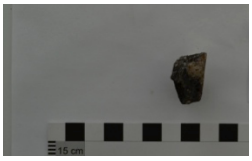
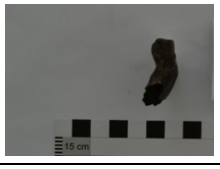
NR11	Too small.			
NR12	Missing.			
NR13	35			
NR14	25			Too small after sampling.
NR15	35			
NR16	13-15			
NR17	Missing-			
NR18	Missing.			
NR19	Missing.			
NR20	Missing.			
NR21	Missing.			Too small after sampling.

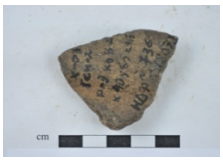
NR22	Missing.			Too small after sampling.
NR23	Missing.			
NR24	Too small.			Too small after sampling.
NR25	Missing.			
NR26	20			Too small after sampling.
NR27	Too small.			
NR28	Too small.			
NR29	15-20			
NR30	Missing.			

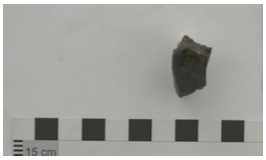
NB: The measurement of the diameters was taken after the first sampling so in many cases was not possible to collect this information, as the rim was too small or missing.

Table 7. Generalka ceramic fragments (n=35)

Sample ID	Diameter (cm)	**Front**	**Retro**	**Rim**
GEN1	17-20			
GEN2	Missing.			
GEN3	Missing.			
GEN4	17-20			
GEN5	Missing.			
GEN6	25			
GEN7	30			
GEN8	10-20			
GEN9	Missing.			
GEN10	Missing.			

GEN11	Missing.			
GEN12	Missing.			
GEN13	Missing.			
GEN14	16-20			
GEN15	20-23			
GEN16	17-20			
GEN17	Missing.			
GEN18	Missing.			
GEN19	Missing.			
GEN20	Missing.			
GEN21	Missing.			

GEN22	Missing.			
GEN23	Missing.			
GEN24	Missing.			
GEN25	Missing.			
GEN26	Too small			
GEN27	Missing.			
GEN28	15-17			
GEN29	Too small.			
GEN30	Missing.			
GEN31	10			

GEN32	Too small.			
GEN33	35			
GEN34	Missing.			
GEN35	Too small			

NB: The measurement of the diameters was taken after the first sampling so in many cases was not possible to collect this information, as the rim was too small or missing.

Table 8. Radiocarbon dates performed over the last decades. N=16 samples from Dereivka.

№	Site	Lab. №	Sample	Date (BP)	Date (BC) OxCal 3.10	Literature
1	Dereïvka - I	OxA-6577	Horse bone	1995±60	68.2% probability 86BC (1.8%) 80BC 55BC (66.4%) 75AD 95.4% probability 165BC (95.4%) 126AD	Anthony, Brown, 2003, 56
2		OxA-7185	Horse tooth	2295±60	68.2% probability 408BC (35.6%) 352BC 297BC (29.5%) 228BC 221BC (3.1%) 211BC 95.4% probability 536BC (0.4%) 528BC 522BC (95.0%) 196BC	
3		Ki-6962	Horse skull	2490±95	68.2% probability 776BC (68.2%) 514BC 95.4% probability 802BC (95.4%) 403BC	
4		Ki-5488	Horse skull	4330±120	68.2% probability 3321BC (10.1%) 3235BC 3170BC (0.7%) 3164BC 3114BC (52.5%) 2866BC 2804BC (4.9%) 2762BC 95.4% probability 3354BC (79.6%) 2831BC 2821BC (15.8%) 2631BC	
5		UCLA - 1671a*	Bone	4900±100	68.2% probability 3892BC (1.5%) 3884BC 3798BC (57.8%) 3630BC 3578BC (9.0%) 3534BC 95.4% probability 3952BC (93.9%) 3515BC 3422BC (0.2%) 3418BC 3410BC (0.4%) 3404BC 3398BC (1.0%) 3384BC3950 (93.1%) 3500 3450 (2.3%) 3350	
6		Ki-6965*	Bone	5210±70	68.2% probability 4224BC (5.2%) 4206BC 4162BC (9.2%) 4130BC 4072BC (53.8%) 3955BC 95.4% probability 4238BC (88.9%) 3931BC 3876BC (6.5%) 3806BC	
7		Ki-2197	Bone	5230±95	68.2% probability 4228BC (7.8%) 4199BC 4171BC (21.7%) 4088BC 4083BC (38.7%) 3962BC 95.4% probability 4322BC (2.5%) 4290BC 4267BC (85.7%) 3910BC 3878BC (7.2%) 3802BC	
8		Ki-6964*	Bone	5260±75	68.2% probability 4228BC (9.4%) 4200BC 4169BC (15.1%) 4126BC 4121BC (9.7%) 4091BC 4080BC (34.0%) 3986BC 95.4% probability 4321BC (2.3%) 4292BC	

					4266BC (93.1%) 3954BC	
9		Ki-6960*	Bone	5330±60	68.2% probability 4241BC (36.6%) 4146BC 4136BC (31.6%) 4054BC 95.4% probability 4327BC (8.9%) 4282BC 4272BC (84.3%) 4039BC 4016BC (2.3%) 4000BC	
10		Ki-6966*	Bone	5370±70	68.2% probability 4328BC (36.5%) 4224BC 4206BC (14.9%) 4162BC 4130BC (16.8%) 4072BC 95.4% probability 4346BC (95.1%) 4041BC 4009BC (0.3%) 4006BC	
11		Ki-2193	Shell	5400±100	68.2% probability 4344BC (40.7%) 4224BC 4206BC (12.6%) 4161BC 4130BC (15.0%) 4071BC 95.4% probability 4448BC (2.7%) 4416BC 4404BC (90.2%) 4036BC 4022BC (2.5%) 3994BC	
12		UCLA - 1466a*	Bone	5515±90	68.2% probability 4458BC (58.3%) 4318BC 4295BC (9.9%) 4264BC 95.4% probability 4548BC (90.0%) 4224BC 4206BC (2.8%) 4161BC 4130BC (2.6%) 4072BC	
13		Ki-2195	Shell	6240±100	68.2% probability 5314BC (35.9%) 5192BC 5182BC (32.3%) 5059BC 95.4% probability 5466BC (2.0%) 5436BC 5427BC (1.3%) 5405BC 5385BC (92.1%) 4948BC	
14	Dereivka-03	Poz-67463	Bone	4815±35	68.2% probability 3646BC (22.0%) 3631BC 3578BC (4.4%) 3573BC 3567BC (41.8%) 3536BC 95.4% probability 3660BC (29.8%) 3618BC 3610BC (65.6%) 3521BC	Topoi
15	Dereivka-04	Poz-67460	Bone	4830±35	68.2% probability 3655BC (35.1%) 3631BC 3578BC (2.6%) 3574BC 3565BC (30.6%) 3536BC 95.4% probability 3694BC (3.7%) 3678BC 3670BC (42.4%) 3625BC 3599BC (49.3%) 3525BC	Topoi
16	Dereivka-06	Poz-67461	Bone	5060±35	68.2% probability 3942BC (30.5%) 3894BC 3882BC (17.4%) 3855BC 3844BC (6.2%) 3834BC 3822BC (14.1%) 3800BC 95.4% probability 3958BC (95.4%) 3780BC	Topoi

Table 9. Radiocarbon dates performed over the last decades. N=5 samples from Molyukhov Bugor.

№	Site	Lab. №	Sample	Date (BP)	Date (BC) OxCal 3.10	Literature
1	Novoselitsa, Molyukhov Bugor-1994, pit 1, Qu. 3, level 4	Ki-7995	Bone	5425±80	68.2% probability 4356BC (55.9%) 4228BC 4201BC (8.4%) 4169BC 4126BC (1.3%) 4120BC 4092BC (2.6%) 4080BC 95.4% probability 4446BC (2.8%) 4418BC 4400BC (92.6%) 4048BC	Kotova, Videiko, 2004, Table 6
2	Molyukhov Bugor - 1995, pit 1, Qu . 2a, depth 0,4-0,5 m	Ki-7993	Bone	5330±80	68.2% probability 4250BC (68.2%) 4051BC 95.4% probability 4332BC (95.4%) 3991BC	Kotova, Videiko, 2004, Table 6
3	Molyukhov Bugor - 1995, pit 1, Qu. 2a, depth 0,4-0,5 m	Ki-7994	Bone	5270±80	68.2% probability 4229BC (10.7%) 4197BC 4173BC (46.6%) 4033BC 4026BC (10.9%) 3992BC 95.4% probability 4325BC (3.9%) 4286BC 4270BC (91.5%) 3956BC	Kotova, Videiko, 2004, Table 6
4	Molyukhov Bugor	Poz-22614	Horse bone	4875±35 2.3%N 8.6%C	68.2% probability 3694BC (21.7%) 3678BC 3670BC (46.5%) 3640BC 95.4% probability 3748BC (0.3%) 3744BC 3713BC (92.2%) 3632BC 3556BC (2.9%) 3538BC	Benecke et al.. 2009, 25; pers. inform. from Prof. N. Benecke
5	Molyukhov Bugor	Ki- ?	Animal bone	4760±60	68.2% probability 3638BC (63.4%) 3516BC 3397BC (4.8%) 3385BC 95.4% probability 3648BC (70.7%) 3494BC 3466BC (24.7%) 3375BC	Нераденко, 2009 (Звіт про...у 2009 році).

Table 10. Radiocarbon dates performed over the last decades. N=7 samples from Mikhailovka.

№	Site	Lab. №	Sample	Date (BP)	Date (BC) OxCal 3.10	Literature
1	Dwelling 1, depth 1,5-2,0 m	Bln-630	Charcoal	4330±100	68.2% probability 3308BC (1.2%) 3298BC 3283BC (0.8%) 3276BC 3265BC (3.4%) 3240BC 3105BC (60.3%) 2871BC 2801BC (2.4%) 2780BC 95.4% probability 3341BC (84.6%) 2840BC 2814BC (10.8%) 2676BC	Anthony, 2003; pp. 56

2	Dwelling 3	Ki-8182	Bone	4945±70	68.2% probability 3792BC (68.2%) 3651BC 95.4% probability 3944BC (15.7%) 3854BC 3848BC (79.7%) 3636BC	Kotova, Videiko, 2004, Table 6
3	Dwelling 3	Ki-8011	Bone	4890±80	68.2% probability 3779BC (63.6%) 3632BC 3556BC (4.6%) 3539BC 95.4% probability 3942BC (7.0%) 3856BC 3820BC (87.9%) 3516BC 3396BC (0.5%) 3386BC	
4		Pz-71116	Bone	4240±50	68.2% probability 2910BC (37.0%) 2861BC 2808BC (26.3%) 2757BC 2718BC (4.9%) 2706BC 95.4% probability 3002BC (0.6%) 2992BC 2930BC (45.3%) 2832BC 2820BC (48.6%) 2660BC 2650BC (1.0%) 2634BC	
5		Pz-71117	Bone	4220±35	68.2% probability 2896BC (31.6%) 2864BC 2806BC (34.7%) 2759BC 2716BC (1.9%) 2713BC 95.4% probability 2906BC (38.7%) 2848BC 2814BC (56.7%) 2678BC	
6		Pz-71118	Bone	4540±40	68.2% probability 3362BC (19.3%) 3323BC 3234BC (27.6%) 3172BC 3162BC (21.3%) 3116BC 95.4% probability 3368BC (35.8%) 3262BC 3252BC (59.6%) 3098BC	
7		Pz-71120	Bone	4320±35	68.2% probability 3010BC (18.4%) 2980BC 2939BC (49.8%) 2892BC 95.4% probability 3022BC (95.4%) 2886BC	

Table 11. Radiocarbon dates performed over the last decades. N=8 samples from Generalka.

№	Site	Lab. №	Sample	Date (BP)	Date (BC) OxCal 3.10	Literature
1	Level of the ancient layer	OxA – 23080	Bone	4366±28	68.2% probability 3011BC (28.7%) 2977BC 2972BC (39.5%) 2921BC 95.4% probability 3086BC (6.6%) 3062BC 3030BC (88.8%) 2906BC	
2	Collar fragment K2-K3	Ki – 14867	N° 384	4070±80	68.2% probability 2852BC (10.5%) 2812BC 2744BC (3.9%) 2726BC	

	(piece2). Ditch n°1, level of the ancient layer.				2696BC (41.2%) 2550BC 2537BC (12.6%) 2490BC 95.4% probability 2882BC (95.4%) 2462BC	
3	Vessel piece D2-E2. Ditch n°1. Bottom of the ditch.	Ki – 14866	N°151	4160±80	68.2% probability 2878BC (14.0%) 2833BC 2818BC (50.2%) 2660BC 2649BC (4.0%) 2635BC 95.4% probability 2906BC (92.8%) 2565BC 2525BC (2.6%) 2496BC	
4	Collar fragment D2-D3. Ditch n°2. Level of the ancient layer.	Ki– 14865	N°689	3990±80	68.2% probability 2624BC (57.3%) 2430BC 2424BC (4.5%) 2401BC 2382BC (6.4%) 2348BC 95.4% probability 2862BC (5.2%) 2807BC 2758BC (2.5%) 2718BC 2706BC (87.0%) 2282BC 2248BC (0.7%) 2233BC	
5		Poz-0	Bone	>0 BP		
6		Poz-67457	Bone	4190±35	68.2% probability 2884BC (16.1%) 2857BC 2810BC (39.3%) 2750BC 2723BC (12.8%) 2700BC 95.4% probability 2892BC (24.3%) 2835BC 2817BC (71.1%) 2666BC	Kotova, Videiko, 2004, Table 6
7		Poz-67458	Bone	4340±35	68.2% probability 3010BC (25.8%) 2978BC 2966BC (8.6%) 2951BC 2942BC (33.8%) 2904BC 95.4% probability 3082BC (2.9%) 3068BC 3026BC (92.5%) 2893BC	
8		Poz-67459	Bone	3925±35	68.2% probability 2473BC (46.2%) 2400BC 2382BC (22.0%) 2348BC 95.4% probability 2558BC (2.8%) 2536BC 2491BC (92.6%) 2294BC	

APPENDIX C

Table 1. Dereivka faunal assemblage (Kaiser, 2010).

Broader typology	Species	MNI	NISP
	Cattle	18	618
	Sheep/Goat	16	88
	Pigs	9	114
	Dogs	5	33
	Horse	52	2412
Total Domesticated Animals		100 (Including Horses)	3265
Total Wild Animals		83	673
Total Birds		12	25
Total Fish		37	136
TOTAL (excluding dogs and birds)		**215**	**4074**

Table 2. Faunal assemblage recovered from Molyukhov Bugor settlement (Kaiser, 2010).

Broader typology	Species	MNI	NISP
	Cattle	8	1871
	Sheep/Goat	5	367
	Pigs	4	270
	Horse	10	704
Total Domesticated Animals		27 (Including Horses)	3212 (Including Horses)
Total Wild Animals		50	1900
TOTAL		**77**	**5112**

Table 3. Faunal assemblage recovered from Mikhailovka I horizon (Kaiser, 2010).

Broader typology	Species	MNI	NISP
	Cattle	9	217
	Sheep/Goats	36	760
	Pigs	4	104
	Horses	4	20
Total Domesticated animals		**53** (Including Horses)	**1101** (Including Horses)
Total Wild Animals		8	60
TOTAL		**61**	**1161**

Table 4. Faunal assemblage recovered from Mikhailovka II and III horizons (Kaiser, 2010).

Broader typology	Species	MNI	NISP
	Cattle	1627	30571
	Sheep/Goats	1202	14958
	Pigs	82	229
	Horses	656	5393
Total Domesticated animals		**3567** (Including Horses)	**51151** (Including Horses)
Total Wild Animals		265	1003
TOTAL		3567	52154

Table 5. Faunal assemblage recovered from Generalka settlement (Kaiser, 2010).

Broader typology	Species	NISP
	Cattle	1907
	Sheep/Goats	366
	Pigs	-
	Horses	54
Total Domesticated animals		**2327** (Including Horses)
Total Wild Animals		75
TOTAL		**2402**

APPENDIX D

Table 1. $\delta^{13}C$ values of the palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids originating from degraded animal products extracted from 27 archaeological ceramic sherds from Dereivka site (A); 11 archaeological ceramic sherds from Molyukhov Bugor site (B); 34 from Mikhailovka I (C); 24 from Nighty Rogachik (D); 19 from Mikhailovka II (E); 16 from Mikhailovka III (F) and 27 from Generalka (G).

(A)	ID sample	$\delta^{13}C_{16:0}$	$\delta^{13}C_{18:0}$	$\Delta^{13}C$	Fat origin
1	Der2	-29.9	-29.9	0.0	Equine products
2	Der7	-29.0	-29.8	-0.8	Equine products
3	Der10	-28.3	-28.6	-0.3	Equine products
4	Der13	-28.2	-28.2	-0.1	Equine products
5	Der16	-29.2	-29.6	-0.5	Equine products
6	Der25	-29.1	-29.8	-0.6	Equine products
7	Der30	-28.0	-28.7	-0.7	Equine products
8	Der32	-28.7	-28.1	0.6	Equine products
9	Der34	-29.2	-28.7	0.4	Equine products
10	Der36	-28.9	-29.7	-0.8	Equine products
11	Der39	-29.7	-29.5	0.2	Equine products
12	Der18	-27.7	-27.2	0.5	Equine products
13	Der28	-29.4	-28.9	0.5	Equine products
14	Der21	-32.0	-31.7	0.3	Freshwater fish products
15	Der4	-31.6	-30.9	0.7	Freshwater fish products
16	Der31	-31.0	-29.2	1.73	Freshwater fish products
17	Der33	-32.2	-31.4	0.9	Freshwater fish products
18	Der38	-31.4	-30.2	1.2	Freshwater fish products
19	Der37	-30.6	-31.0	-0.4	Mixed. Freshwater fish and Equine products
20	Der40	-31.1	-31.6	-0.5	Mixed. Freshwater fish and Equine products
21	Der1	-28.6	-27.3	1.2	Mixed. Porcine and Equine products
22	Der22	-26.7	-24.9	1.8	Porcine Products
23	Der9	-25.7	-26.9	-1.2	Ruminant adipose products
24	Der12	-27.4	-29.4	-2.0	Ruminant adipose products
25	Der14	-26.8	-28.1	-1.3	Ruminant adipose products
26	Der29	-29.5	-30.8	-1.3	Ruminant adipose products
27	Der35	-26.8	-30.0	-3.2	Ruminant adipose/dairy products
(B)	**ID sample**	$\delta^{13}C_{16:0}$	$\delta^{13}C_{18:0}$	$\Delta^{13}C$	**Fat origin**
1	MB7	-27.2	-28.0	-0.8	Equine products
2	MB10	-27.5	-27.3	0.2	Equine products
3	MB11	-27.1	-27.0	0.0	Equine products
4	MB12	-28.6	-29.5	-0.9	Equine products
5	MB14	-27.1	-27.1	0.0	Equine products
6	MB16	-29.1	-30.0	-0.9	Equine products
7	MB21	-27.6	-27.8	-0.2	Equine products
8	MB6	-26.5	-24.3	2.2	Porcine products

9	MB13	-28.1	-29.9	-1.8	Ruminant adipose products
10	MB15	-27.6	-29.8	-2.2	Ruminant adipose products
11	MB18	-27.6	-28.8	-1.1	Ruminant adipose products
(C)	**ID sample**	**$\delta^{13}C_{16:0}$**	**$\delta^{13}C_{18:0}$**	**$\Delta^{13}C$**	**Fat origin**
1	Mik53	-27.5	-28.0	-0.4	Equine products
2	Mik52	-28.4	-27.0	1.4	Mixed. Freshwater fish and Equine products
3	Mik74	-26.2	-27.3	-1.1	Ruminant adipose products
4	Mik78	-26.4	-27.6	-1.2	Ruminant adipose products
5	Mik82	-27.0	-28.2	-1.2	Ruminant adipose products
6	Mik56	-25.5	-27.5	-2.0	Ruminant adipose products
7	Mik57	-26.4	-28.0	-1.6	Ruminant adipose products
8	Mik58	-26.3	-27.8	-1.6	Ruminant adipose products
9	Mik59	-26.4	-28.1	-1.7	Ruminant adipose products
10	Mik60	-26.3	-28.6	-2.3	Ruminant adipose products
11	Mik61	-25.8	-27.6	-1.8	Ruminant adipose products
12	Mik62	-26.3	-28.0	-1.7	Ruminant adipose products
13	Mik63	-25.2	-27.1	-1.8	Ruminant adipose products
14	Mik65	-24.7	-26.6	-1.9	Ruminant adipose products
15	Mik67	-27.1	-28.8	-1.7	Ruminant adipose products
16	Mik71	-25.4	-27.7	-2.4	Ruminant adipose products
17	Mik76	-27.1	-28.8	-1.7	Ruminant adipose products
18	Mik77	-26.4	-28.0	-1.6	Ruminant adipose products
19	Mik79	-26.4	-28.3	-1.9	Ruminant adipose products
20	Mik84	-26.2	-28.4	-2.2	Ruminant adipose products
21	Mik85	-26.2	-28.2	-2.0	Ruminant adipose products
22	Mik51	-26.3	-28.0	-1.7	Ruminant adipose products
23	Mik68	-26.5	-27.9	-1.4	Ruminant adipose products
24	Mik73	-26.8	-28.3	-1.5	Ruminant adipose products
25	Mik75	-26.8	-28.3	-1.5	Ruminant adipose products
26	Mik80	-26.7	-28.2	-1.5	Ruminant adipose products
27	Mik69	-25.2	-27.7	-2.5	Ruminant adipose products
28	Mik54	-24.2	-27.9	-3.7	Ruminant dairy products
29	Mik55	-23.6	-28.6	-5.0	Ruminant dairy products
30	Mik66	-24.3	-29.1	-4.8	Ruminant dairy products
31	Mik72	-23.8	-27.9	-4.2	Ruminant dairy products
32	Mik81	-25.2	-28.3	-3.2	Ruminant dairy products
33	Mik83	-23.7	-28.1	-4.4	Ruminant dairy products
34	Mik86	-25.8	-28.7	-2.8	Ruminant dairy products
(D)	**ID sample**	**$\delta^{13}C_{16:0}$**	**$\delta^{13}C_{18:0}$**	**$\Delta^{13}C$**	**Fat origin**
1	NR16	-29.3	-30.3	-1.0	Equine products
2	NR9	-28.4	-29.5	-1.1	Equine products
3	NR10	-28.4	-29.0	-0.7	Equine products
4	NR19	-29.8	-30.3	-0.5	Equine products
5	NR3	-28.8	-29.0	-0.3	Equine products

6	NR8	-29.6	-29.9	-0.4	Equine products
7	NR18	-29.7	-28.3	1.4	Mixed. Freshwater fish and Porcine products
8	NR4	-31.1	-29.9	1.2	Freshwater fish products
19	NR6	-30.7	-29.9	0.7	Freshwater fish products
10	NR29	-28.6	-29.7	-1.1	Ruminant adipose products
11	NR2	-28.7	-30.1	-1.4	Ruminant adipose products
12	NR28	-27.7	-29.2	-1.4	Ruminant adipose products
13	NR11	-26.4	-28.9	-2.5	Ruminant adipose products
14	NR13	-27.5	-29.5	-2.0	Ruminant adipose products
15	NR17	-26.9	-29.3	-2.4	Ruminant adipose products
16	NR20	-26.9	-28.9	-2.0	Ruminant adipose products
17	NR27	-27.9	-29.8	-1.9	Ruminant adipose products
18	NR7	-27.9	-30.4	-2.5	Ruminant adipose products
19	NR12	-27.2	-30.2	-3.0	Ruminant dairy products
20	NR15	-25.3	-28.9	-3.6	Ruminant dairy products
21	NR23	-26.3	-29.8	-3.5	Ruminant dairy products
22	NR25	-25.6	-29.0	-3.4	Ruminant dairy products
23	NR30	-27.7	-30.5	-2.8	Ruminant dairy products

(E)	**ID sample**	**$\delta^{13}C_{16:0}$**	**$\delta^{13}C_{18:0}$**	**$\Delta^{13}C$**	**Fat origin**
1	MIK5	-26.9	-28.0	-1.1	Equine products
2	MIK10	-30.0	-29.6	0.4	Equine products
3	MIK15	-27.8	-28.6	-0.8	Equine products
4	MIK16	-27.8	-28.5	-0.6	Equine products
5	MIK20	-29.3	-29.2	0.1	Equine products
6	MIK8	-30.3	-30.2	0.0	Equine products
7	Mik22	-27.0	-27.9	-0.9	Equine products
8	MIK7	-31.2	-30.2	1.0	Freshwater fish products
9	MIK13	-26.2	-28.0	-1.9	Ruminant adipose products
10	MIK17	-24.8	-26.1	-1.4	Ruminant adipose products
11	MIK18	-28.5	-30.2	-1.7	Ruminant adipose products
12	MIK21	-27.1	-29.5	-2.4	Ruminant adipose products
13	MIK23	-25.4	-27.7	-2.3	Ruminant adipose products
14	MIK24	-27.3	-29.4	-2.1	Ruminant adipose products
15	MIK9	-26.0	-27.9	-1.9	Ruminant adipose products
16	MIK6	-28.3	-29.4	-1.2	Ruminant adipose products
17	MIK19	-28.9	-30.1	-1.2	Ruminant adipose products
18	MIK12	-23.7	-27.9	-4.3	Ruminant dairy products
19	MIK14	-26.1	-29.5	-3.4	Ruminant dairy products

(F)	**ID sample**	**$\delta^{13}C_{16:0}$**	**$\delta^{13}C_{18:0}$**	**$\Delta^{13}C$**	**Fat origin**
1	MIK32	-30.0	-30.5	-0.5	Equine products
2	MIK34	-29.9	-30.1	-0.2	Equine products
3	MIK37	-31.6	-31.5	0.1	Mixed. Freshwater fish and Equine products
4	MIK46	-31.2	-31.7	-0.5	Mixed. Freshwater fish and Equine products

5	MIK44	-33.1	-31.6	1.5	Freshwater fish products
6	MIK26	-28.2	-29.8	-1.6	Ruminant adipose products
7	MIK27	-28.6	-30.1	-1.5	Ruminant adipose products
8	MIK28	-26.7	-29.4	-2.7	Ruminant adipose products
9	MIK30	-26.8	-28.5	-1.7	Ruminant adipose products
10	MIK31	-27.3	-29.3	-2.0	Ruminant adipose products
11	MIK36	-30.4	-31.8	-1.4	Ruminant adipose products
12	MIK42	-30.7	-33.0	-2.3	Ruminant adipose products
13	MIK29	-28.6	-31.6	-3.0	Ruminant adipose and dairy products
14	MIK33	-27.9	-31.5	-3.6	Ruminant dairy products
15	MIK35	-26.8	-30.7	-3.8	Ruminant dairy products
16	MIK41	-27.6	-31.2	-3.5	Ruminant dairy products
(G)	**ID sample**	**$\delta^{13}C_{16:0}$**	**$\delta^{13}C_{18:0}$**	**$\Delta^{13}C$**	**Fat origin**
1	Gen16	-28.2	-28.6	-0.4	Equine products
2	Gen15	-29.9	-30.6	-0.7	Equine products
3	Gen19	-30.1	-30.3	-0.2	Equine products
4	Gen29	-28.3	-28.9	-0.6	Equine products
5	Gen34	-30.0	-30.5	-0.5	Equine products
6	Gen4	-27.5	-28.4	-0.9	Equine products
7	Gen37*	-28.4	-29.5	-1.1	Equine products
8	Gen13	-31.5	-30.7	0.8	Freshwater fish products
9	Gen26	-31.2	-30.7	0.5	Freshwater fish products
10	Gen40*	-27.0	-32.9	-6.0	Ruminant dairy products
11	Gen1	-27.5	-30.2	-2.7	Ruminant adipose and dairy products
12	Gen7	-27.3	-29.8	-2.5	Ruminant adipose and dairy products
13	Gen31	-26.3	-28.9	-2.6	Ruminant adipose and dairy products
14	Gen18	-26.7	-29.4	-2.7	Ruminant adipose and dairy products
15	Gen3	-28.9	-30.3	-1.4	Ruminant adipose products
16	Gen8	-28.2	-29.5	-1.3	Ruminant adipose products
17	Gen6	-27.5	-29.1	-1.6	Ruminant adipose products
18	Gen21	-29.0	-30.7	-1.7	Ruminant adipose products
19	Gen30	-26.3	-28.3	-2.0	Ruminant adipose products
20	Gen9	-28.0	-30.4	-2.4	Ruminant adipose products
21	Gen10	-27.5	-29.5	-2.0	Ruminant adipose products
22	Gen11	-27.7	-29.4	-1.8	Ruminant adipose products
23	Gen36*	-27.0	-29.2	-2.2	Ruminant adipose products
24	Gen38*	-27.3	-28.9	-1.7	Ruminant adipose products
25	Gen39*	-26.8	-28.8	-1.9	Ruminant adipose products
26	Gen42*	-27.2	-29.1	-1.9	Ruminant adipose products
27	Gen12	-29.2	-30.9	-1.7	Ruminant adipose products

The * in Table1G are the residues integrated from the pilot study (Whelton & Evershed, 2012)

Table 2. δD values of the palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids originating from degraded animal products extracted from 56 archaeological ceramic sherds from four Ukrainian sites: Dereivka; Nizhnyi Rogachik; Mikhailovka III; and Generalka. Attributions of the fat origin have been made by compound-specific stable carbon isotope analysis.

Dereivka	**Corrected values**			
Sample ID	**$\delta D_{C16:0}$**	**$\delta D_{C18:0}$**	**ΔD**	**Animal origin**
Der 10	-273,7	-207,8	65,9	Equine products
Der 13	-257,5	-226,7	30,7	Equine products
Der 16	-269	-236,2	32,8	Equine products
Der 2	-269,6	-237,1	32,5	Equine products
Der 25	-302,7	-246,5	56,2	Equine products
Der 7	-269	-220	49	Equine products
Der 21	-291,1	-247,2	43,9	Freshwater fish products
Der 4	-272,4	-232,3	40,1	Freshwater fish products
Der 12	-271,9	-240,5	31,3	Ruminant adipose products
Der 14	-247,8	-206,5	41,3	Ruminant adipose products
Der 9	-261,4	-216,6	44,8	Ruminant adipose products
Nizhniy Rogachik	**Corrected values**			
Sample ID	**$\delta D_{C16:0}$**	**$\delta D_{C18:0}$**	**ΔD**	**Animal origin**
NR10	-247,4	-203,4	44	Equine products
NR16	-274,8	-232	42,7	Equine products
NR19	-233	-222,1	10,9	Equine products
NR3	-245,5	-234,2	11,3	Equine products
NR5	-296,6	-238,8	57,8	Equine products
NR8	-278,1	-231,3	46,8	Equine products
NR9	-234,1	-217,8	16,3	Equine products
NR4	-286,2	-227,8	58,4	Freshwater fish products
NR6	-281,2	-226,2	55	Freshwater fish products
NR11	-246	-227,5	18,5	Ruminant adipose products
NR17	-235,5	-220,7	14,8	Ruminant adipose products
NR20	-241,3	-236,6	4,6	Ruminant adipose products
NR27	-268,7	-241,4	27,3	Ruminant adipose products
NR28	-227,4	-226,9	0,5	Ruminant adipose products
NR29	-265,6	-228,3	37,3	Ruminant adipose products
NR7	-262	-240,8	21,2	Ruminant adipose products
NR12	-250,3	-249,6	0,7	Ruminant dairy products
NR23	-232,3	-224,1	8,2	Ruminant dairy products
NR25	-228,9	-221,7	7,2	Ruminant dairy products
NR30	-249	-228,2	20,8	Ruminant dairy products
Mikhailovka II	**Corrected values**			
Sample ID	**$\delta D_{C16:0}$**	**$\delta D_{C18:0}$**	**ΔD**	**Animal origin**
Mik10	-244,3	-222,4	21,9	Equine products

Mik15	-244,1	-229,9	14,3	Equine products
Mik16	-251,9	-233,5	18,4	Equine products
Mik20	-268,3	-229,3	39	Equine products
Mik5	-243,3	-218,9	24,4	Equine products
Mik8	-267,2	-246,7	20,5	Equine products
Mik7	-276	-218,5	57,5	Freshwater fish products
Mik13	-213,5	-198,6	15	Ruminant adipose products
Mik17	-252,7	-214,6	38,1	Ruminant adipose products
Mik18	-173,7	-201,5	-27,8	Ruminant adipose products
Mik23	-242,3	-240	2,4	Ruminant adipose products
Mik6	-217,1	-207,6	9,5	Ruminant adipose products
Mik9	-247,5	-227,6	19,9	Ruminant adipose products
Mik12	-219,7	-212	7,7	Ruminant dairy products
Mik14	-210,5	-199,4	11,1	Ruminant dairy products
Generalka	**Corrected values**			
Sample ID	**$\delta D_{C16:0}$**	**$\delta D_{C18:0}$**	**ΔD**	**Animal origin**
Gen15	-278,1	-225,4	52,7	Equine products
Gen16	-283,7	-244,9	38,8	Equine products
Gen19	-259	-221,9	37,1	Equine products
Gen29	-247,9	-230,6	17,2	Equine products
Gen34	-232,8	-225,5	7,4	Equine products
Gen11	-244,7	-217,5	27,1	Ruminant adipose products
Gen12	-229,1	-225,6	3,5	Ruminant adipose products
Gen21	-231,6	-239,4	-7,8	Ruminant adipose products
Gen6	-264,4	-233,8	30,6	Ruminant adipose products
Gen8	-244,8	-216,9	27,9	Ruminant adipose products

Figure 1. Mass spectra of the main fatty acids (FAs): palmitic ($C_{16:0}$), heptadecanoic ($C_{17:0;}$ $C_{17:0}$br), and stearic acids ($C_{18:0}$).

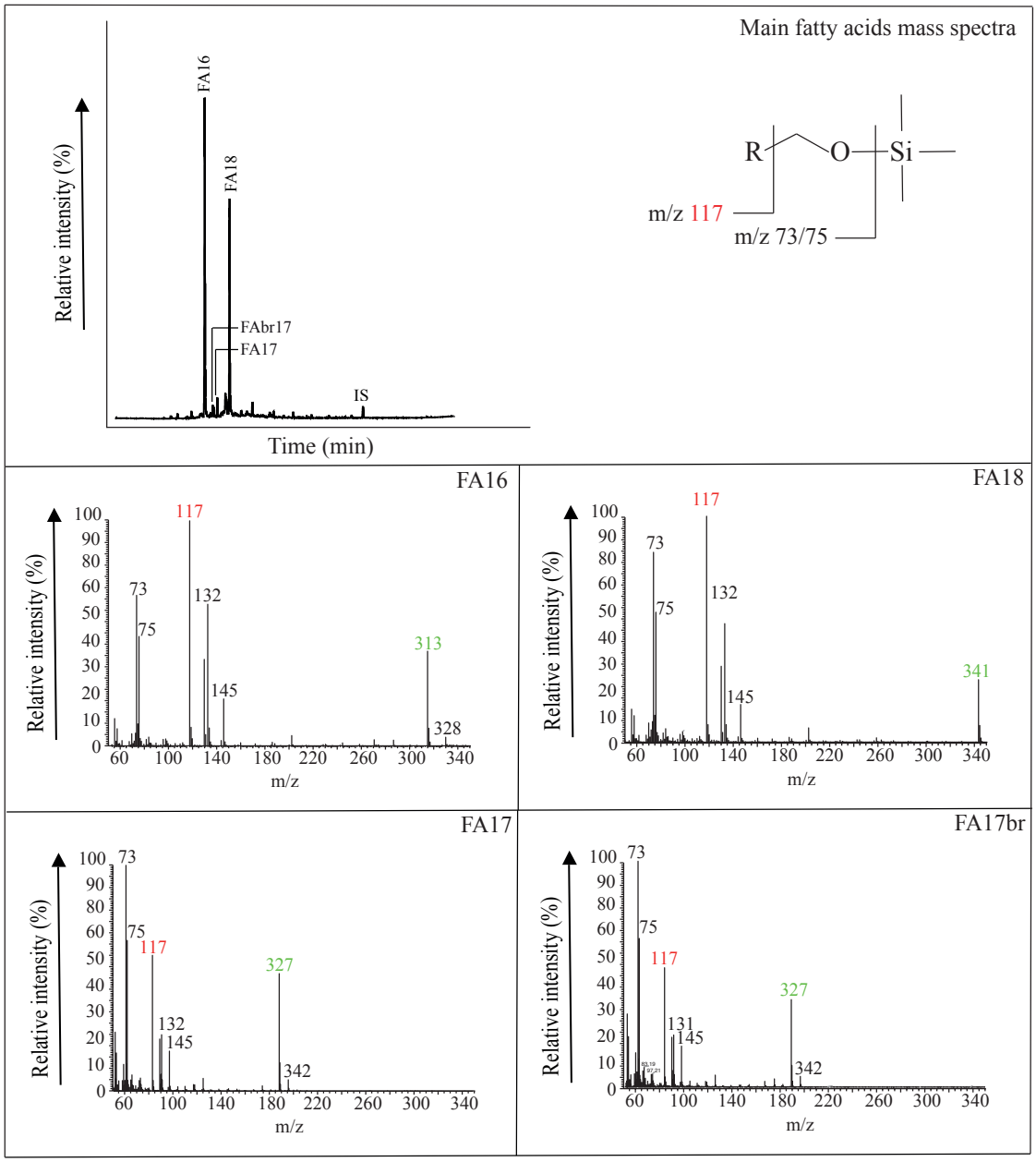


Figure 2. Mass spectra of the *n*- alkanols distribution (C_{24}, C_{25}, C_{26}, C_{27}, C_{28}, C_{29} and C_{30}).

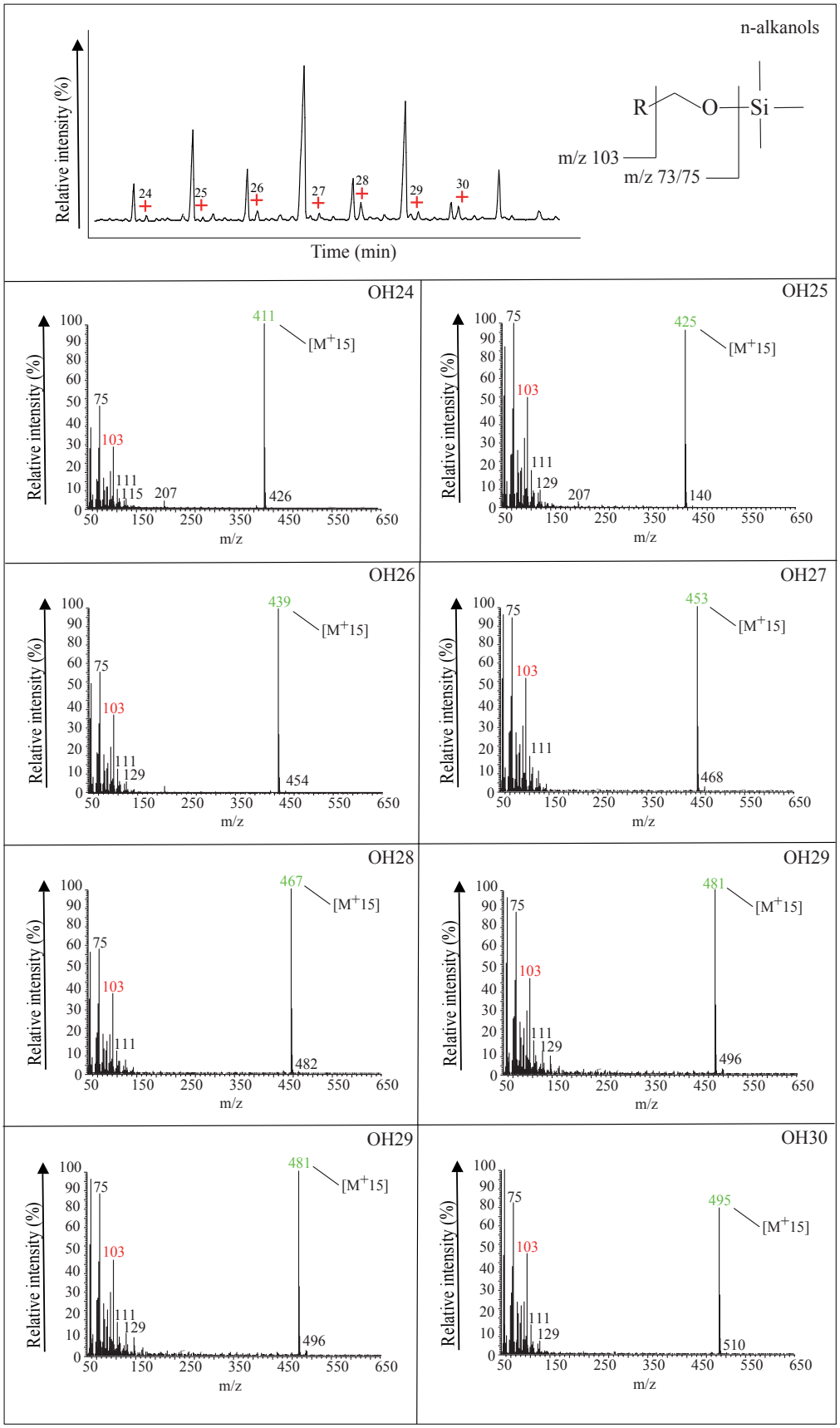
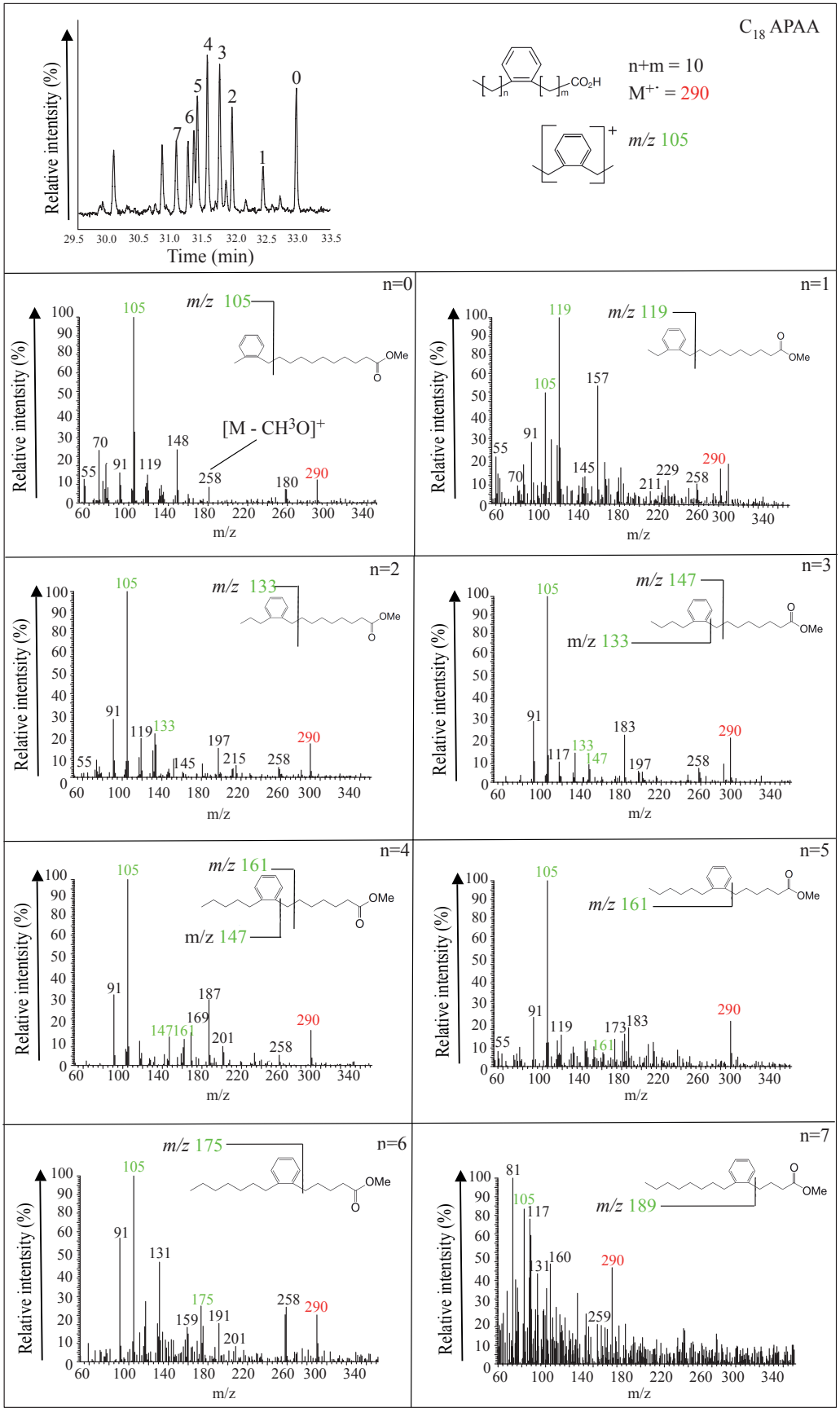


Figure 3. Mass spectra of C_{18} and C_{20} APAAs.



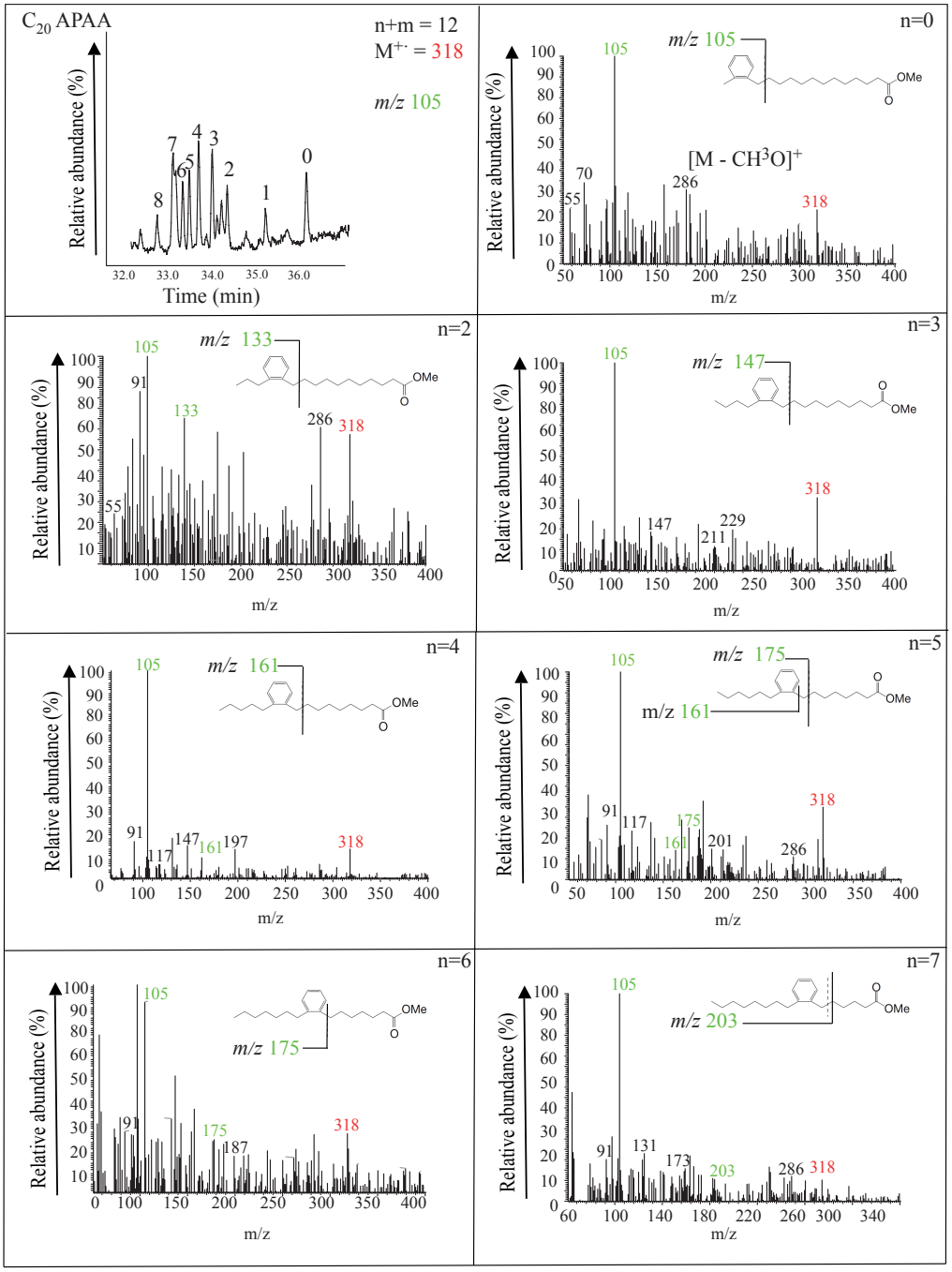

C20 APAA
n+m = 12
M+· = 318
m/z 105
Relative abundance (%)
Time (min)
n=0
m/z 105
[M - CH3O]+
n=2
m/z 133
n=3
m/z 147
n=4
m/z 161
n=5
m/z 175
m/z 161
n=6
m/z 175
n=7
m/z 203
m/z

Figure 4. Mass spectrum of 4,8,12-TMTD.