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Organic analysis of «food crusts» from sites in the Schelde valley, Belgium: a preliminary evaluation

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Abstract

Charred food residues adhering to archaeological pottery are an attractive substrate for radiocarbon dating due to their association with a cultural artefact. Carbon present in the food crusts may be unsuitable for this purpose if it is derived from marine/ freshwater sources or from the post-depositional environment. Here we examine the evidence for freshwater fish processing in a number of pots from the Schelde Valley in Belgium. Organic components of the food crusts were extracted and analysed using GCMS, GC-C-IRMS and the results were compared with IRMS of the entire sample. Lipid biomarkers for fish were identified in several samples. Elevated $\delta^{15}N$ values were also observed in some of the food crusts. We suggest that radiocarbon dates on these samples could well be inaccurate.

Keywords: food crust, prehistoric pottery, freshwater fish, radiocarbon dates, reservoir effect.

Résumé

Le résidu organique adhérant à des fragments de céramique se révèle un matériau idéal pour une datation radiocarbone vu l'association directe avec l'artéfact culturel. Toutefois, l'échantillon pourrait être moins propice dans le cas où le carbone présent dans le résidu est originaire de sources marines et/ou d'eau douce, voire même d'origine post-dépositionnelle. Dans cette étude, nous avons examiné l'hypothèse d'une préparation de poissons de rivières dans plusieurs récipients céramiques préhistoriques provenant de la vallée de l'Escaut en Belgique. Des éléments organiques ont été extraits des résidus et analysés en chromatographie en phase gazeuse couplée à la spectrométrie de masse (CPG/SM) ainsi que par couplage chromatographie en phase gazeuse/combustion/spectrométrie de masse isotopique du carbone (CG/C/SMI). Les résultats obtenus ont alors été comparés aux résultats d'analyses SMI d'échantillons complets. Dans plusieurs échantillons ont été trouvés des indices de lipides appartenant aux poissons. Certains résidus ont également donné des valeurs en $\delta^{15}N$ assez élevées. Par conséquent, il se pourrait que certaines dates radiocarbones obtenues pour les sites Swifterbant et Michelsberg de la vallée de l'Escaut soient trop vieux puisqu'elles sont affectées par l'effet de réservoir.

Mots-clés : résidu organique, céramique préhistorique, poissons d'eau douce, dates radiocarbones, effet réservoir.

1. Introduction

Charred residues encrusted on the interior of archaeological ceramic vessels are interesting phenomena and can provide valuable information concerning pottery use (Andersen, Malmeros, 1984; Odermans & Boon, 1991; Koch, 1998; Morton & Schwarcz, 2004). They are also often used as substrates for radiocarbon dating. Whilst generally considered reliable for this purpose, Fischer and Heinemeier (2003) have recently noted that several dates from this source are too old with respect to their depositional context. They suggest that various amounts of «old» carbon are introduced into the food residue through the processing of marine and freshwater organisms in vessels. Worse still, they suggest that unlike with bone collagen, the magnitude of the 'reservoir effect' cannot be accounted for due to the heterogeneous nature of charred residues.

A number of food crusts from sites in the Schelde valley dating to the Late/Final Mesolithic and Early/Middle Neolithic were dated. As recent excavations at several of these sites (Doel-*Deurganckdok* Sector B, Oudenaarde-*Donk* sector Neo. 1) revealed extensive accumulations of freshwater fish remains, the accuracy of these dates is questionable. No macroscopic remains of fish could be identified in the food crusts, although protracted heating during the formation of food chars may have destroyed this evidence. Organic analysis of lipids preserved in the food crusts offers an alternative method to identify the original contents (see Heron, Everhsed, 1993; Mottram *et alii,* 1999 for overview). In this investigation, lipids were extracted from a number of food crusts and analysed using gas chromatography and mass spectrometry. This analysis was supported by isotopic measurements of individual fatty acid components extracted from the residue and bulk carbon and nitrogen isotope analysis of the entire sample.

The principal objectives were:
- to examine whether any molecular evidence could be found to support the processing of freshwater fish,
- to identify the remains of other food products in the residues.

2. Sample selection

The analysed samples were selected from four prehistoric sites situated in the floodplain area of the Schelde River in the north-western part of Belgium. On all sites the archaeological remains were found within, mostly bioturbated, sandy deposits covered by peat and/or alluvial sediments.

The sites of Doel-*Deurganckdok* sector B (Crombé *et alii,* 2000; 2002) and sector J/L (Bats *et alii,* 2003) yielded pottery of Swifterbant/Ertebølle tradition mixed with Late/Final Mesolithic flint artefacts (trapezes and Montbani blades). In sector B these were associated with numerous burnt bones and carbonised plant remains (hazelnuts, ivy, wild apples, sloe plums, acorns, hawthorn berries). Both sites are radiocarbon dated roughly between ca. 6000 and 5800 uncal. BP on several samples of food crust from potsherds (table 1). Sector B was also dated on charcoal and carbonised seeds/hazelnuts retrieved from presumed surface-hearths or dumps of surface-hearths. These dates, however, are on average 200-400 BP-years younger than the potsherd dates. Not one single date seems to be compatible with the food crust dates. The question arises if this discrepancy is due to repeated (spatially overlapping) visits or rather results from a freshwater reservoir effect.

The sites of Doel-*Deurganckdok* sector C (Crombé *et alii,* 2000, 2002) and Oudenaarde-*Donk* sector Neo. 1 (Parent *et alii,* 1987) yielded archaeological material which presents strong affinities with the Michelsberg culture of the Belgian Middle Neolithic. At the former site only ceramics and flint artefacts were collected. One radiocarbon date on food crust situates the occupation around 5110 uncal. BP. The Michelsberg site of Oudenaarde-*Donk* apparently was better preserved, as excavations yielded also large numbers of non-carbonised organic remains, such as bones from fish, mammals (wild game as well as domesticates),

Sample code	*Lab. Ref.*	*BP date*	*Dating material*
Doel-*Deurganckdok* sector B (Swifterbant culture)			
W24/Z2(4)	KIA-20232	6015±30	food crust on potsherd
109	KIA-12260	5980±35	food crust on potsherd
742	KIA-14339	5835±35	food crust on potsherd
W16/Z7(1)	KIA-17995	5635±30	*Sorbus* charcoal
W19/Z1(4)h	KIA-17996	5595±35	*Quercus* charcoal
W20/Z2(1)	KIA-17994	5575±35	*Cornus* charcoal
W6/Z6(3)	KIA-17987	5570±30	carbonised seeds
W19/Z1(4)	KIA-17997	5550±35	carbonised *Hedera helix* seeds
W6/Z18(4)	KIA-17986	5400±30	carbonised *Prunus spinosa* pip
R069	NZA-12076	5220±55	charred hazelnut shell
Doel-*Deurganckdok* sector J/L (Swifterbant culture)			
46	KIA-20207	5900±45	food crust on potsherd
62	KIA-20233	5915±45	food crust on potsherd
Doel-*Deurganckdok* sector C (Michelsberg culture)			
989	KIA-14334	5110±35	food crust on potsherd
Oudenaarde-*Donk* sector Neo. 1 (Michelsberg culture)			
OD85/144-6 doos C	KIA-20230	5250±30	food crust on potsherd
OD85-190/32-27	KIA-20231	5180±30	food crust on potsherd
	IRPA-743	5240±70	food crust on potsherd
	IRPA-744	5050±70	outer ring of wooden post
	IRPA-667	4990±70	wood
	IRPA-745	4670±70	wood (small branch)

Table 1. — List of radiocarbon dates from the four analysed sites in the Schelde valley (Van Strydonck, Crombé in press; Parent *et alii,* 1987).

birds, etc., plant remains and even bone and antler tools. This site has been dated on wood as well as on food crusts (table 1). Again both series of dates deviate with the food crust dates being approximately 200-250 BP-years older than the dates on wood samples.

3. Materials and methods

Samples of food crusts that had been radiocarbon dated were obtained from pottery from three sites from the Schelde valley and are summarised in table 2. Analytical methods are described in the appendix. Three samples of modern freshwater fish (*Esox lucius, Carassius carassius, Perca fluviatilis*) were also analysed.

4. Results and discussion

4.1. Mass spectrometry of lipid extracts

Lipids were extracted and quantified using gas chromatography (GC), the total amounts of lipids present are shown in table 2. Immediately obvious is that much higher concentrations of lipid could be recovered from the food crust from the Oudenaarde-*Donk* site. Also noticeable were differences in the quality of the lipids extracted from the different sherds, this was further investigated by combined gas chromatography mass spectrometry (GCMS). A selection of chromatograms is shown in figure 1 which illustrates the main differences observed in the samples and these data are further summarised in table 2.

The two food crusts from Oudenaarde-*Donk* contain high amounts of solvent soluble lipids (ca. 1-4 % wt./wt.). The lipid profiles from each food crust are almost identical (sample OD85/144-6 doos C shown in fig. 1a) and are dominated by saturated fatty acids, notably palmitic acid (16:0) and stearic acid (18:0) with lesser amounts of monounsaturated fatty acids (16:1, 18:1; 20:1). Interpreting these chromatograms is complicated as the lipids most likely derive from more than one source. For example sterols originating from both animal and plant sources were identified, i.e. cholesterol and β-sitosterol respectively (fig. 1a). The most abundant lipids, palmitic and stearic acid, are found in a range of plant and animal foodstuffs, however large relative amounts of stearic acid, as observed here, are more typical of terrestrial animal fats (Enser, 1991)[1]. Lipids commonly, although not specifically, found in fish and plants are monounsaturated fatty acids and these were observed in both of the food crusts from Oudenaarde-*Donk*. Notably the presence of eicosenoic

[1]The ratio of palmitic to stearic acid in the two samples from Oudenaarde «Donk» is ca. 1.0, wheras in plant tissues it is usually >3.0 and the equivalent ratio in the three species of freshwater fish that were analysed ranged between 3.0 - 3.4. The absolute ratio of C16:0 to C18:0 can however be distorted by post-depositional preferential dissolution, by percolating groundwater, of the lighter C16:0 component (Bell 1973).

Site	*Sample code*	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	*BP date*	*Lab. Ref.*	*Total Lipd Extract (mg g^{-1} sample)*	*Lipids detected and inference*
Oudenaarde -*Donk*	OD85/144-6 doos C	-27.3	+9.1	5250±30	KIA-20230	9.7	Saturated and unsaturated fatty acids, cholesterol, β-sitosterol. Mixed animal, plant products and fish.
Oudenaarde -*Donk*	OD85-190/32-27	-26.5	+7.0	5180±30	KIA-20231	35.8	Saturated and unsaturated fatty acids, cholesterol, β-sitosterol. Mixed animal, plant products and fish.
Doel -*Deurganckdok* Sector B	W24/Z2 (4)	-27.2	+8.2	6015±30	KIA-20232	0.1	Low concentrations of polyaromatic hydrocarbons (PAH). No detectable residue.
Doel -*Deurganckdok* Sector J/L	Do-62	-28.3	+8.8	5915±45	KIA-20233	2.2	Cholesteol, β-sitosterol, trace amounts of fatty acids. Principally animal products
Doel -*Deurganckdok* Sector J/L	Do-46	-27.3	+7.7	5900±45	KIA-20207	0.4	β-sitosterol, trace amounts of fatty, PAHs. Plant products.

Table 2 — Summary of analysis of ^{14}C dated food crusts.

acid (22:1) is only present at high concentration in marine and freshwater fish.

Lipid biomarkers specifically for fish oils, such as polyunsaturated fatty acids, do not readily survive as they are easily oxidised in the burial environment. However, thermal products of these molecules (ω-(*o*-alkylphenyl)alkanoic acids), produced by protracted heating, have recently been demonstrated in archaeological pottery (Hansel *et al.*, 2004). Positional isomers of two of these compounds were detected at very low concentrations in both the food crusts from Oudenaarde-*Donk* by mass spectrometry (fig. 1a). The

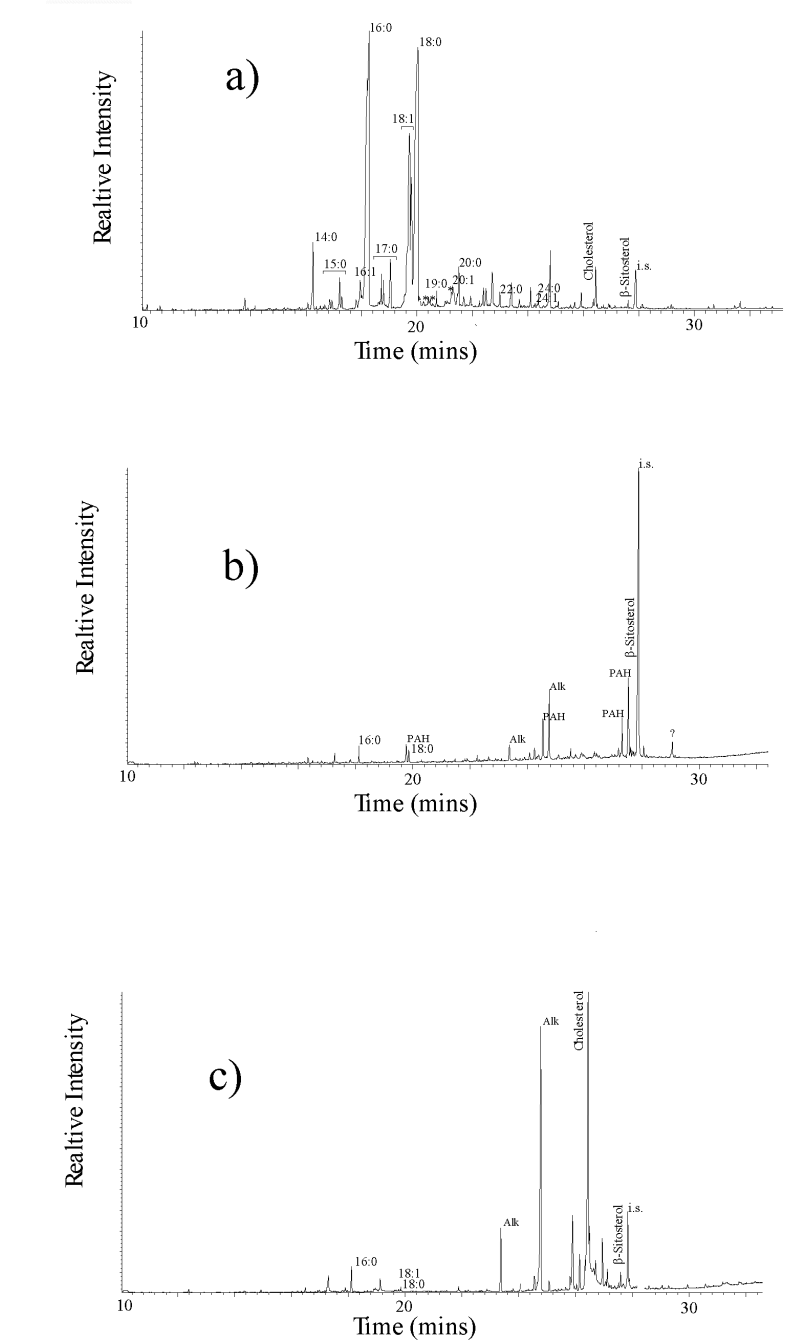

Fig. 1 — Partial gas chromatograms of total lipid extracts from food crusts. a) OD85/144-6 doos C; b) Do-46; c) Do-62. Peaks were identified by GC-MS. Numbers (X:Y) refer to chain lengths (X) and number of saturations (Y) in the TMS derivatives of the fatty acids. Alk = long chain alkane. PAH = polyaromatic hydrocarbons. i.s. = internal standard (20µg *n*-tetratriacontane). * = ω-(*o*-alkylphenyl)alkanoic acids identified as their TMS derivatives with principal fragment ions: m/z 105, m/z 91, $[M^+]$ 346 (18:3), $[M\text{-}15]^+$ 333 (18:3), $[M^+]$ 376 (20:3), $[M\text{-}15]^+$ 361 (20:3).

most likely source of these compounds is tri-unsaturated fatty acids (18:3, 20:3, fig. 1a). Whilst the 18:3 component is a common constituent of both vegetable oils and fish oils, the 20:3 component is only observed in the later (e.g. Passi *et alii,* 2002). The 18:3 and 20:3 fatty acids are also observed in the mass spectra of the modern fish samples (Koslova & Khotimchenko, 1993, 2000; Zenebe *et alii*, 1998). Taken together the lipid data provide good evidence for the processing of fish in these vessels. However, mixing of products in these pots cannot be ruled out, thus it is impossible to assess the contribution of fish to the whole food residue.

The 'food crust' samples from the other sites yielded much smaller quantities of lipids (table 2). The sample from Doel-*Deurganckdok* Sector B contained only very small amounts of polyaromatic hydrocarbons (PAHs; chromatogram not shown), sample 46 from Doel-*Deurganckdok* Sector J/L also yielded PAHs and additionally small quantities of fatty acids and β-sitosterol (fig. 1b). In contrast, a substantial amount of cholesterol was observed in sample 62 from this site (fig. 1c). Determining the origin of these food crusts is difficult due to the low amounts of extractable lipids. Only the sterols give some indication as to whether these residues are derived from animal or plant products. The polyaromatic hydrocarbons could be derived from wood smoke during vessels use or after deposition[2]. Alternatively they could have been formed through aromatisation of the food residues through prolonged or intense heating.

4.2. Carbon Stable Isotope analysis of individual fatty acids

Palmitic (16:0) and stearic acid (18:0) were observed in four of the samples (table 2). Recent methods have been developed to measure the stable isotopic composition of carbon in these compounds in order to determine their likely origin (Mottram *et alii,* 1999). Notably isotopic measurements have been made on fatty acids to distinguish different animal fats, i.e. ruminant fats, non-ruminant fats, dairy fats and mixtures of these (Dudd & Evershed, 1998; Copley *et ali,i* 2003). Identification of freshwater fish using this method is anticipated to be challenging as studies have shown high variability in the carbon (and nitrogen) isotopic composition within several species of lacustrine fish according to geographical location (Dufour *et alii,* 1999).

Nevertheless the isotope values of these fatty acids were compared with the modern fish samples and previously published standards (Dudd *et alii,* 1999) in figure 2. The four food crust samples plot together and apart from any of the published reference samples, including the freshwater fish. Whilst these results may indirectly reflect differences in local isotopic values for carbon derived from freshwater environments and assimilated into fatty acids by fish, the values are more in keeping with a terrestrial ruminant or even a dairy source. A mixture of these products is also plausible.

[2]Contamination with organic carbon in the burial environment is thought to be unlikely (Heron *et alii,* 1991) but see Bonsall *et alii* (2002) for discussion

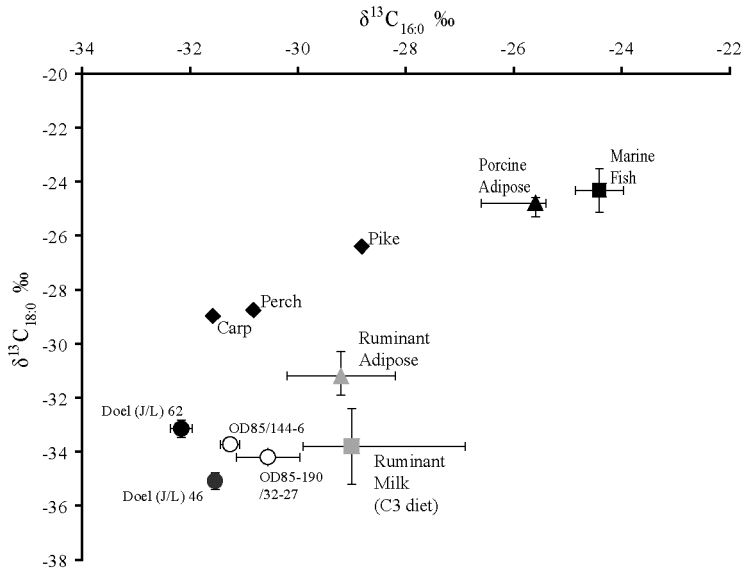

Fig. 2 — Plot of the $\delta^{13}C$ values of C18:0 and C16:0 fatty acids extracted from various foodcrusts and control samples. The later were obtained from Dudd *et al.* (1999: fig. 3) and from oils from marine and freshwater fish.

Notably, all the residues from this site produce similar $\delta^{13}C$ values indicating a similar origin for these lipids despite substantial qualitative differences observed in the total lipid distributions.

4.3. Carbon and Nitrogen isotope analysis of food crusts

It should be noted that only a very small proposition of the total residue is analysed using the methods described above, i.e. the soluble lipid fraction. By weight this fraction accounted for between 0.01% and 3.5 % of the total residue depending on the sample (table 2). Much greater quantities of non-extractable organic components must therefore be present within the matrix of the 'char'. These bound organic components could be derived from various foodstuffs processed in the vessel or from wood or peat smoke. Therefore analysis of lipid extracts only provides qualitative information on the vessel contents and cannot be used to quantify the various components that may affect the radiocarbon date. Indeed the two samples from Doel sector J/L and the one form sector B may have had a similar food input to the Oudenaarde samples but, due to differences in vessels use, the organic components became more highly charred and aromatised preventing extraction with organic solvents.

Bulk carbon and nitrogen isotope ratio mass spectrometry (IRMS) measures all the carbon and nitrogen in the sample and therefore provides more quantitative (but less qualitative) information on the composition of the food crust. IRMS measurements were obtained from the food crusts during the dating procedure (table 2) In addition a further eight samples from Doel B, two from Doel C were analysed (table 3). The results are plotted together in figure 3. $\delta^{13}C$ measurements (x-axis) of food crusts samples have been interpreted to reflect the amounts of C3 and C4 plants (Morton & Schwarcz, 2004) or marine and terrestrial products (Andersen & Malmeros, 1984; Fischer & Heinemeier, 2003) present in the residues. However, these values are also likely to be significant altered by the biochemical composition of the residue itself which may vary considerably as different foodstuffs contain various amounts of lipids, protein and carbohydrates and these will be variably preserved during burial. The problem arises as, for example, lipids are significantly depleted in ^{13}C compared to proteins from the same source (Galimov, 1985; Tieszen & Fagre, 1993; Jim *et alii*, 1999). I n this study, the extracted fatty acids were ca. 5-6 ‰ depleted compared to the bulk residue. Therefore without any knowledge of the composition of the residue $\delta^{13}C$ measurements are off little value in all but extreme cases, i.e. when very negative or very positive measurements are recorded.

The nitrogen stable isotope measurements are more useful, if it is assumed that any nitrogen present is only derived from a protein source. In this case, $\delta^{15}N$ measurements should broadly reflect the trophic level of the organism from which the food crust is derived. For several species of teleostean fish from various Eurasian lakes, Dufour (1999) observes $\delta^{15}N$ values between +7.0 ‰ to +15.0 ‰. $\delta^{15}N$ values for terrestrial animals and plants may be variable (Bocherens & Drucker, 2003) but for terrestrial herbivores from temperate Europe should not exceed +7 ‰ and terrestrial plants are around +3 ‰ (±1 ‰). Protein derived from omnivores (such as pigs) may be higher. Ideally isotope measurements on associated fauna are needed to more accurately ascertain these values. Several

Site	*Sample code*	*δ13C ‰*	*δ15N ‰*	*%C*	*%N*
Doel-*Deurganckdok* sector B					
	Do-266	-26.8	8.4	67.9	1.1
	Do-129	-27.6	7.2	74.8	0.9
	Do-102	-27.9	7.2	27.4	0.2
	Do-132	-26.0	9.8	53.7	0.2
	Do-248	-27.0	6.3	21.2	0.2
	Do-550	-27.0	9.6	71.3	0.8
	Do-86	-28.5	7.3	17.6	0.2
	Do-90	-26.8	6.4	36.1	0.2
Doel-*Deurganckdok* sector C					
	Do-1180	-27.2	3.9	65.7	0.4
	Do-1135	-27.3	3.3	6.0	0.1

Table 3 — Summary of stable isotope analysis of foodcrusts.

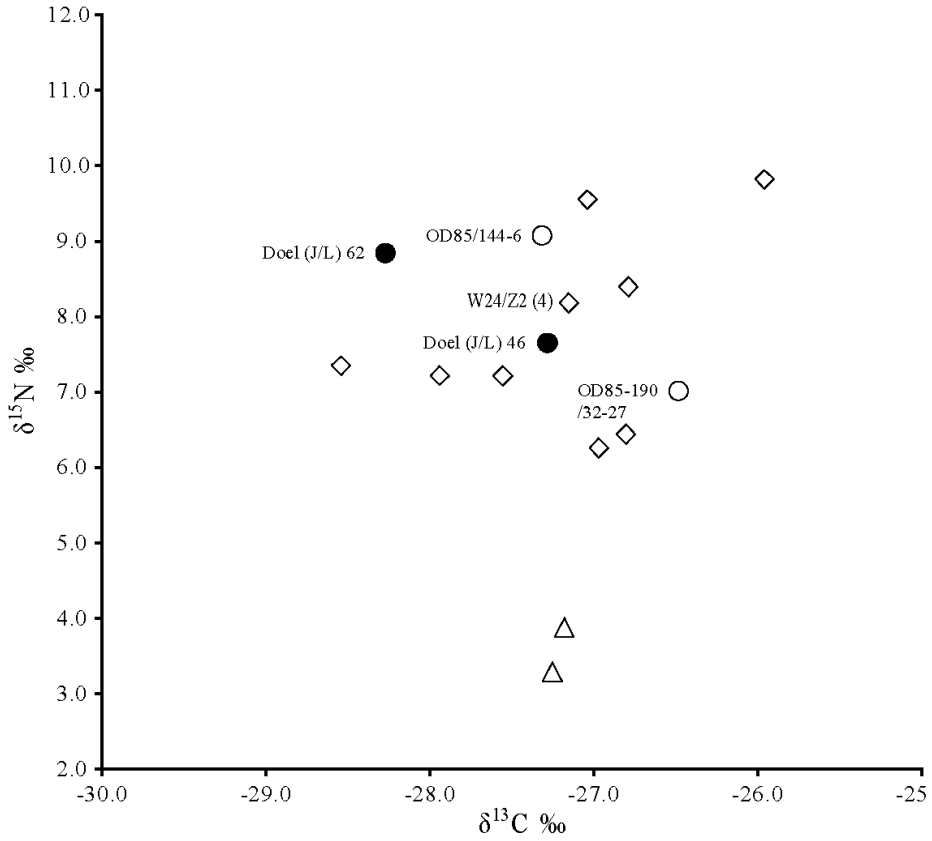

Fig. 3 — Plot of the $\delta^{13}C$ against the $\delta^{15}N$ values obtained from various foodcrusts. Open diamonds ~ Doel-*Deurganckdok* sector B, Solid circles ~ Doel-*Deurganckdok* sector J/L, Closed circles ~ Oudenaarde-*Donk*, Open triangles ~ Doel-*Deurganckdok* sector C

food crusts have $\delta^{15}N$ values between +8.5 ‰ and 10 ‰ (fig. 3, *y*-axis) including two of the dated samples. A likely source for nitrogen in these food crusts is from fish. Fish lipids were also identified in one of these samples (OD85/144-6 doos C). Therefore the dates made on these samples may indeed be too old due to the presence of carbon derived from freshwater sources.

The majority of other $\delta^{15}N$ values are between +6 ‰ and +8 ‰ which are consistent with protein from terrestrial herbivores, although the presence of fish cannot be ruled out. Indeed fish lipids were identified in one of these samples (table 2). Furthermore, a food crust taken from a Danish Early Neolithic funnel beaker, with clear evidence of freshwater fish bone and scales, had a $\delta^{15}N$ value of +6.5‰ (Craig *et alii,* forthcoming). However, it is likely that although present, carbon from freshwater fish is not the dominant constituent of these residues. The two residues from Doel-*Deurganckdok* sector C, with low $\delta^{15}N$, can only be derived from plant or terrestrial herbivores and thus are the only samples that would be expected to produce reliable dates.

5. Conclusions

The combined use of bulk stable isotope analysis and mass spectrometry analysis is a useful tool for identifying fish in archaeological food residues. However, the two techniques provide different 'types' of information and neither is ideally suited to accurately quantifying the proportion of carbon derived from freshwater or marine sources. The results indicate that the samples of food crusts analysed from sites in the Schelde valley are derived from a mixture of foodstuffs, including freshwater fish and meat or milk from terrestrial herbivores. Hence the radiocarbon dates obtained on these potsherd samples might be affected by a freshwater reservoir effect. The exceptions are two food crusts from Doel-*Deurganckdok* sector C which are depleted in ^{15}N and derived from terrestrial sources. Lipids from these samples are currently being investigated to corroborate this conclusion. It is suggested that food crusts with low $\delta^{15}N$ values (<+5 ‰) would make more reliable substrates for radiocarbon dating. Furthermore this can be easily and cheaply assessed using bulk IRMS prior to dating.

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Appendix

Summary of Methods

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Lipid analysis by Gas chromatography (GC) & Gas chromatography/Mass spectrometry

Lipids were extracted from the food crusts and analysed using standard laboratory protocols (Charters *et alii,* 1997; Dudd *et alii,* 1999). Briefly the samples were ground to a fine powder and lipids were ultrasonically extracted with mixture of chloroform and methanol (2:1 v:v; 3 x 10 ml). Samples of flesh from freshwater fish (*Essox lucius, Carassius carassiusm, Perca fluviatilis*) were obtained from lake Windermere, UK and lipid were extracted using the method of Floch *et alii* (1957).

A portion of each of these solvent extracts were treated with 20µl of *N,O*-bis(timethylsilyl) tetrafluroacetamide containing 1 % v/v chlorotrimethylsilane at 65°C for 30 minutes to produce trimethylsilyl derivatives which were then dried under nitrogen. These derivatised extracts were dissolved in hexane and analysed by GC and GCMS. Another portion was saponified with NaOH (5 % wt/vol in methanol; 70°C; 1 h) to release free fatty acids. The solution was acidified free fatty acids were methylated with 2ml of boron trifluoride-methanol complex (14 % wt/vol; 70°C; 1h; BDH, Poole, UK). The resulting fatty acid methyl esters (FAMEs) were extracted with diethyl ether prior to analysis by GC-C-IRMS.

Solvent extracts were analysed by gas chromatography on a Hewlett Packard 6890 gas chromatograph, fitted with a DB-1ht (J & Scientific) coated (0.1µm) fused silica column (14 m x 0.32 mm ID). The GC was equipped with a flame ionisation detector (FID) and split/splitless injector. Helium was the carrier gas with a head pressure of 25 psi at room temperature and a constant flow rate of 0.5 ml/min. The injector and FID were maintained at 300°C and 340°C respectively. The initial temperature of the oven was 50°C and then programmed to increase 10°C/min until it reached 220°C, then 5°C/min until it reached to 340°C, which was finally maintained for 12 minutes. Where the GC elution order was insufficient to identify all the compounds gas chromatography mass spectrometry was carried out using a Hewlett Packard 5890 series II GC connected to a HP 5972 series mass selective detector. Helium was the carrier gas, with a constant head pressure of 1 psi and a flow rate of 1ml/min at 50°C. The injector and interface were maintained at 330°C and 340°C respectively. The initial temperature of the oven was 50°C and then programmed to increase 10°C/min until it reached 220°C, then 5°C/min until it reached to 340°C, which was finally maintained for 12 minutes. The column was directly inserted into the ion source. Electron impact (EI) spectra were obtained at 70eV with full scan from 50 to 700 *m/z*.

Analysis of fatty acids by Gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS)

Ceramic samples which contained detectable amounts of 18:0 (stearic) and 16:0 (palmitic) fatty acids were chosen for GC-C-IRMS analysis (see table 1). These compounds were methylated, as described above, to produce FAMEs and were analysed using a Hewlett Packard 5890 gas chromatograph attached to a isotope ratio mass spectrometer (PDZ Europa Ltd Geo; Crewe, UK) via a Orchid II combustion interface (PDZ Europa Ltd; Crewe, UK). Analysis was performed using a 30 m x 0.32 mm I.D. fused-silica column coated with BPX70 stationary phase (immobilised 70 % cyanopropyl equivalent polysilphenylene-siloxane; 0.25µm film thickness; SGE, Milton Keynes, UK). The temperature program was as follows: 130°C (2 min); 130°-190°C at 4°C/min; 190°C (2 min). Helium was used as the carrier gas at a head pressure of 9.6 p.s.i. The combustion furnace was maintained at 860°C and the mass spectrometer source pressure was 7.6^{-6} Torr. The values were corrected for the derivitisation process by comparing with measurements obtained by isotope ratio mass spectrometry on purified preparations of a number of individual *n*-alkanoic acids (Sigma; UK). Carbon isotopes were expressed relative to the PDB standard (Belemnitella Americana), $\delta^{13}C = 1000\ [(R_{sample}/R_{standard} - 1]$, where R is $^{13}C/^{12}C$ in per mil (‰). Extracts from all samples were run at least in triplicate. All the modern samples were corrected for the effects of fossil fuel burning (Fredli *et al,* 1986).

Bulk Isotope Ratio Mass Spectrometry (IRMS)

Samples were removed from the inside of ceramic vessels with a sterile scalpel and ground to a fine powder with a mortar and pestle. Each sample was weighed (ca. 500μg) in duplicate into tin capsules which were analysed using ANCA-SL elemental analyser linked to a PDZ Europa 20/20 mass spectrometer (PDZ Europa Ltd, Crewe, UK). $\delta^{13}C$ measurements were made in relation to the VPDB standard and the $\delta^{15}N$ measurements in relation to the AIR standard. Analytical precision was estimated to be less than 0.2‰ in both cases.