FRESHWATER RESERVOIR EFFECT VARIABILITY IN NORTHERN GERMANY

Bente Philippsen[1] • Jan Heinemeier

AMS ^{14}C Dating Centre, Dept. of Physics and Astronomy, Aarhus University, Ny Munkegade 120, 8000 Aarhus C, Denmark.

ABSTRACT. The freshwater reservoir effect is a potential problem when radiocarbon dating fish bones, shells, human bones, or food crusts on pottery from sites near rivers or lakes. The reservoir age in hardwater rivers can be up to several thousand years and may be highly variable. Accurate ^{14}C dating of freshwater-based samples requires knowing the order of magnitude of the reservoir effect and its degree of variability. Measurements on modern riverine materials may not give a single reservoir age correction that can be applied to archaeological samples, but they show the order of magnitude and variability that can also be expected for the past. This knowledge will be applied to the dating of food crusts on pottery from the Mesolithic sites Kayhude at the Alster River and Schlamersdorf at the Trave River, both in Schleswig-Holstein, northern Germany.

INTRODUCTION

Reservoir effects can lead to erroneously large radiocarbon ages if the sample's carbon originates from marine or freshwater systems. These sample types include aquatic plants, shells, and fish bones, but also bones of omnivores such as humans, pigs, and dogs. Charred food remains on pottery, the so-called food crusts, also fall into this category.

The freshwater reservoir effect has been known for over 60 yr (Godwin 1951; Deevey et al. 1954). Since then, it has mainly been examined in modern aquatic plants and animals (Broecker and Walton 1959; MacDonald et al. 1987). The past few decades have seen growing recognition of its effect on archaeology (Lanting and van der Plicht 1995/1996; Cook et al. 2001; Shishlina et al. 2007; Olsen and Heinemeier 2009; Smits and van der Plicht 2009; Olsen et al. 2010), and also of its importance in pottery dating (Fischer and Heinemeier 2003; Boudin et al. 2009; Philippsen 2010; Philippsen et al. 2010).

For a characterization of the reservoir effect in a certain freshwater system, modern samples of water, aquatic plants, and fish are often dated. In early studies, limited sample numbers led to simplified conclusions (Deevey et al. 1954; Oana and Deevey 1960). However, research has indicated a large degree of variability of the freshwater reservoir effect (Olsson et al. 1969; Stuiver 1975; Philippsen 2012). This study examines the short-term variability of the freshwater reservoir age Rf and variations between different species of aquatic plants and animals. The sample types we analyze follow the food chain, from water dissolved inorganic carbon (DIC) over aquatic plants to fish and shellfish, in the Alster and Trave rivers in northern Germany.

The archaeological purpose of this study is to date the region's earliest pottery, which belongs to the Late Mesolithic Ertebølle culture. The oldest dates for pottery of this hunter-fisher-gatherer culture have been obtained from the sites Kayhude at the Alster River and Schlamersdorf at the Trave River. Frequent inundations of the rivers caused an unclear stratigraphy. Therefore, it is very difficult to find terrestrial samples clearly associated with the potsherds and the pottery has to be dated directly. Because of the high age of the pottery, up to 1000 yr older than the same type of pottery from coastal sites in Schleswig-Holstein, a freshwater reservoir effect had been suspected.

[1]Corresponding author. Email: bphilipp@phys.au.dk.

© 2013 by the Arizona Board of Regents on behalf of the University of Arizona
Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 1085–1101

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

LOCATION

Figure 1 shows a map with the rivers and archaeological sites that are examined in this study: Kayhude at the Alster River and Schlamersdorf at the Trave River. The Alster discharges into the Elbe in Hamburg, the Trave into the Baltic Sea at Lübeck/Travemünde. The rivers run through a morainal landscape from the last 2 glaciations (Stewig 1982).

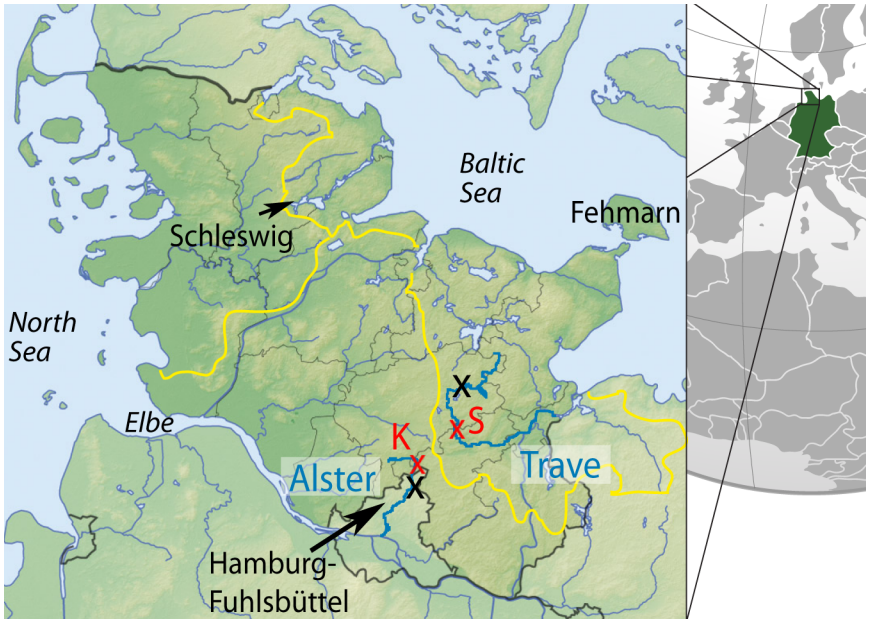


Figure 1 Map of the Alster and Trave rivers, the archaeological sites Kayhude/Alster (red X, marked K) and Schlamersdorf/Trave (S), locations for cation measurements (black X) and 3 locations for precipitation measurements (Schleswig, Fehmarn, and Hamburg-Fuhlsbüttel). Main watersheds are indicated by yellow lines (after http://www.erneuerbare-energien.de/files/bilder/allgemein/image/gif/flussgebietseinheiten.gif, Umweltbundesamt, 2004). Map of Schleswig-Holstein by Wikimedia user NordNord-West, relief by Wikimedia user Lencer, globe by Wikimedia user TheEmirr.

The Alster passes upper and lower moraines (the former from the Weichselian glaciation, the latter from the Saale glaciation). The pedogenic bedrock in the upper moraines is glacial till, Geschiebemergel, with about 20% calcium carbonate. The glacial sand in the lower moraines, Geschiebesand, only contains 0–5% calcium carbonate (Stewig 1982 and references therein).

The site Kayhude is situated in a narrow floodplain (~50 m wide) with geest ridges on both sides of the Alster. Two fens, the Wakendorfer Moor to the north of the site, to the south the Niendorfer Moor, are likely to be former lakes. Pollen analysis indicated shallow-water slow sedimentation. The Alster at that time was ~50 m wide and often changed its riverbed (Clausen 2007; I Clausen, personal communication, 2007).

The Trave runs through a morainal landscape originating from the Weichselian glaciation, the upper moraines of which contain about 20% calcium carbonate (Stewig 1982 and references therein). The Trave, a lake/river system in the Mesolithic, has been straightened in historical times. On one of these occasions in the 1930s, stone artifacts were found 3 km northwest of Schlamersdorf and provided a first indication for the presence of an archaeological site (Hartz 1997).

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

During the Atlantic period, there was a large body of water in the Trave Valley with a slow current. Probably, the Trave ran through this lake system already during the Boreal (Cimiotti 1983). In the Atlantic, a strong aggradation of the lake basin started the formation of a lowland with fens through which the Trave River was flowing, surrounded by wetlands. Through the dry phase of the Sub-Boreal, the water level sank and forests spread along the river, resulting in the formation of peat (Bruchwaldtorf) but were drowned again during the cool and humid Sub-Atlantic, leading to fens and the formation of fen peat. Today, the Trave Valley would still be dominated by fens if there had not been changes of the landscape through straightening of the river and drainage (Cimiotti 1983). The present-day Trave flows through a lake, Wardersee, which has an average depth of 3.7 m and consists of 2 parts that are only connected via a 5-m-wide, shallow ditch (Nixdorf et al. 2003). In spite of the straightenings, the Trave Valley is called "one of the best-preserved examples of subglacial meltwater tunnel valleys" with an almost undisturbed landscape (Ministerium für Umwelt, Naturschutz und Landwirtschaft des Landes Schleswig-Holstein 2003).

MATERIALS AND METHODS

In this section, we describe the sampling, cleaning, CO_2 preparation, and measurement for the modern and archaeological samples analyzed in this study.

Water

On 21 August 2007, 25 September 2008, 18 February 2009, and 6 July 2010, water samples were collected in 0.5L bottles and preserved with $HgCl_2$. The samples were kept dark and cool until analysis. The water was acidified with 100% H_3PO_4, which converted all DIC into CO_2. N_2 was bubbled through the water and the CO_2 was trapped cryogenically.

Modern Plants and Animals

Aquatic macrophytes and animals were collected at the same sites as the water samples. They were freeze-dried prior to analysis. No visible carbonate encrustations were found on the aquatic plants. HCl pretreatment was therefore not considered necessary. Local fishermen provided fish from the rivers. Collagen was extracted from some recent fish bones, as this is the material used for analyses of archaeological bones. A modified Longin procedure with ultrafiltration was used (Longin 1971; Brown et al. 1988; Jørkov et al. 2007).

Archaeological Samples

Archaeological charcoal samples were pretreated with 1M HCl at 80 °C for 1 hr, 1M NaOH at 80 °C for at least 3 hr, and 1M HCl at 20 °C overnight. Archaeological food crusts were pretreated like charcoal, but at 20 °C, and with 0.5 or 0.2M NaOH. The samples were converted to CO_2 by combustion in sealed evacuated quartz tubes containing CuO.

Shells

Shells were cleaned with ultrasound in demineralized water. Depending on size, the outer 10–25% of the shell was dissolved with 1M HCl. Possible organic remains were removed with $KMnO_4$ at 80 °C. Some 13–14 mg of pretreated shell was dissolved in 100% H_3PO_4 at 25 °C, to produce CO_2 for ^{14}C dating and measurement of $\delta^{13}C_{shell}$ and $\delta^{18}O_{shell}$.

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

Graphitization and Radiocarbon Dating

For ^{14}C dating, the CO_2 was converted to graphite with the H_2 reduction method (Vogel et al. 1984). The samples were measured at the AMS ^{14}C Dating Centre at Aarhus University (lab code AAR-). The dating results are reported according to international convention (Stuiver and Polach 1977) as conventional ^{14}C age BP.

Marine reservoir ages are commonly denoted *R* (Stuiver et al. 1986). Accordingly, we call freshwater reservoir ages Rf, measured in ^{14}C yr. Rf have been estimated from the measured age BP and the ^{14}C-concentration of the atmosphere during the preceding growing season. Rf of water samples has been estimated by comparing the measured age BP with the ^{14}C level of the atmosphere at the time of sampling (rather than averaging over the entire growing season). The atmospheric data used for these calculations is shown in Table 1.

Table 1 Atmospheric ^{14}C levels, measured on atmospheric CO_2, expressed as pMC and ^{14}C age, which were used for estimating reservoir ages. Measurements from the Black Forest station Schauinsland are used (Levin et al. 2010; I Levin, personal communication, 2012). In spite of the high altitude, they are assumed to be a better estimate than the available data from a low-altitude station, Heidelberg, in the heavily polluted Rhein-Neckar area, which is affected both by additional ^{14}C from a nearby nuclear power plant and ^{14}C-free CO_2 from industry, heating, and transport (Levin et al. 2008).

Month	Mean pMC	Mean ^{14}C age (BP)
August 2007	105.80	–453
September 2008	105.44	–425
February 2009	104.47	–352
July 2010	104.83	–379
Growing season up to	Mean pMC	Mean ^{14}C age (BP)
August 2007	105.64	–440
September 2008	105.39	–421
February 2009	105.39	–421
July 2010	104.52	–355

Monthly means are given for the months in which water samples had been collected, and averages of the growing seasons before the sampling of aquatic plants and animals (data from Levin et al. 2010; I Levin, personal communication, 2012). Errors are insignificant compared to the measurements on water DIC, plants, and animals, and thus not given in this table.

Stable Isotope Measurements

$\delta^{13}C$ and $\delta^{15}N$ analyses on organic samples were performed by combustion in a EuroVector elemental analyzer coupled to an IsoPrime stable isotope ratio mass spectrometer at the Aarhus AMS Centre. $\delta^{13}C$ values are reported as ‰ VPDB (Coplen 1994), $\delta^{15}N$ values as ‰ AIR (Mariotti 1983). The C/N ratios were derived from total organic carbon (TOC) and total nitrogen (TN) measurements and are presented as atomic ratios.

$\delta^{13}C$ of water DIC, shell carbonate, and many organics was measured on a CO_2 aliquot from the ^{14}C preparation using a dual-inlet IsoPrime stable isotope mass spectrometer at the Aarhus AMS Centre. Measurements were performed relative to the internal standard material Carrara $CaCO_3$ and reported as ‰ VPDB. $\delta^{13}C$ values obtained using the elemental analyzer are marked (EA), those using the dual inlet are marked (DI).

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

Additional Methods

In 2007, 2008, and 2010, the bicarbonate concentration was measured immediately after sample collection with test strips (Merckoquant Carbonate Hardness Test 1.10648.0001). Measurements of the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} were obtained from "Landesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig–Holstein," formerly "Landesamt für Natur und Umwelt." Both survey stations, Wulksfelde/Alster and Warderbrück/Trave, downriver of the lake Wardersee, are marked with a black X on Figure 1.

RESULTS AND DISCUSSION

Water Samples

The ^{14}C and $\delta^{13}C$ results on water DIC are presented in Table 2 and Figure 2. All water samples have ^{14}C ages >1000 BP (1170–2620 BP), instead of the –400 BP expected in case of equilibrium with the atmosphere. The ^{14}C age of Alster DIC is greater than that of Trave DIC for every sampling date (Table 2). On average, the estimated reservoir age of Alster DIC is Rf = 2490 ± 490, and for the Trave Rf = 2050 ± 560. $\delta^{13}C$ values range between –15 and –9‰. $\delta^{13}C$ values in the Alster are, with the exception of September 2008, between 1.37 and 5.91‰ lower than in the Trave.

Table 2 Measurements on water DIC. The carbonate hardness in °dH was measured with an aquarium test-kit. The calcium and magnesium concentrations had been measured south of the Wardersee (Trave) and at the gauge Wulksfelde (Alster). They are given in mg/L as well as converted to °dH. The measurement uncertainty of the calcium and magnesium concentrations is estimated to be ~10 mg/L, which certainly overestimates the actual measurement uncertainty, but is the typical variation from one month to another. At the Alster, Ca and Mg were only measured from 1997 to 2006 and in 2011. Here, the average of the period 1997–2006 is used for 2007 and 2008; for water samples from 2009 and 2010, the average value of 2011 is used (Landesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig-Holstein, personal communication, 2012).

Date	AAR-	River	Carbonate hardness (°dH)	Ca + Mg (mg/L)	Ca + Mg (°dH)	DIC $\delta^{13}C$ (‰ VPDB)	DIC pMC	DIC ^{14}C age	Reservoir age estimate
Aug 2007	11779	Alster	10.5	66.71 ± 9.58	9.3 ± 1.3	–14.96 ± 0.05	78.30 ± 0.30	1967 ± 33	2418 ± 44
Sep 2008	12881	Alster	10	66.71 ± 9.58	9.3 ± 1.3	–10.92 ± 0.05	72.18 ± 0.43	2619 ± 48	3044 ± 57
Feb 2009	13612	Alster		63.09 ± 9.18	8.8 ± 1.3	–14.85 ± 0.05	82.75 ± 0.36	1521 ± 35	1873 ± 47
July 2010	14332	Alster	11	63.09 ± 9.18	8.8 ± 1.3	–14.27 ± 0.05	75.49 ± 0.24	2259 ± 26	2638 ± 40
Aug 2007	11780	Trave	13	90.64 ± 10	12.7 ± 1.4	–13.59 ± 0.05	86.45 ± 0.57	1170 ± 55	1622 ± 62
Sep 2008	12882	Trave	12	76.94 ± 10	10.8 ± 1.4	–11.30 ± 0.05	78.04 ± 0.42	1992 ± 44	2417 ± 53
Feb 2009	13611	Trave		130.46 ± 10	18.3 ± 1.4	–8.94 ± 0.05	86.38 ± 0.35	1176 ± 33	1528 ± 45
July 2010	14333	Trave	10	81.87 ± 10	11.5 ± 1.4	–11.86 ± 0.05	75.52 ± 0.25	2255 ± 27	2634 ± 41

$\delta^{13}C$ and the ^{14}C age (Figure 2) are strongly correlated in the Alster ($r = 0.82$, $R^2 = 0.67$), but not in the Trave ($r = 0.11$, $R^2 = 0.01$). Without the samples from February 2009, though, the correlation coefficients are $r = 0.95$, $R^2 = 0.91$ for the Alster and $r = 0.89$, $R^2 = 0.79$ for the Trave, as the removal of the February values reduces most of the seasonal spread. This agrees with our expectation that higher $\delta^{13}C$ values indicate a higher proportion of fossil, ^{14}C-free carbonates (which have $\delta^{13}C \approx 0$). The ^{14}C age of Alster DIC is greater than that of Trave DIC for every sampling date (Table 2), although the $\delta^{13}C$ values are lower. If the only source for large ^{14}C ages was dissolved carbonate minerals, and the only source for small ^{14}C ages soil CO_2, then the low $\delta^{13}C$ values of the Alster would be inconsistent with the large ^{14}C ages. A possible explanation is mineralization of old organic matter, such as peat, in the catchment of the Alster. Another possible explanation is the fact that the Trave flows through the shallow lake Wardersee (Nixdorf et al. 2003). This leads to a comparatively long residence time of the water and facilitates exchange with atmospheric CO_2.

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

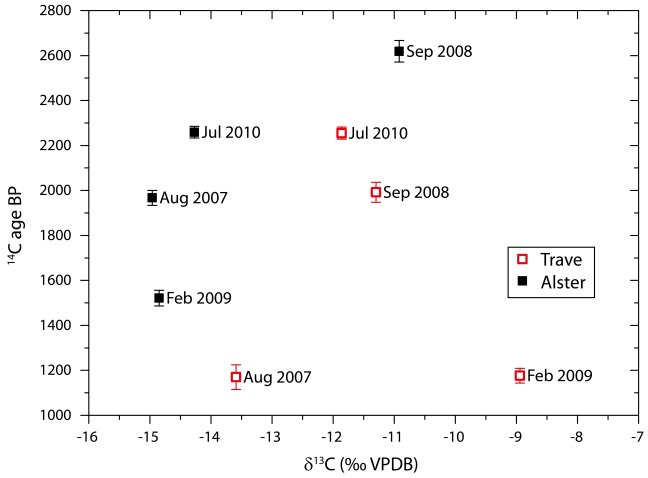


Figure 2 Measurements on water DIC: ^{14}C age and δ^{13}C

The water hardness measured with test strips and the water hardness derived from Ca and Mg measurements agree within the large error margins and vary between 9 and 13 °dH. The exception is the Ca and Mg measurement of the Trave in February 2009, which corresponds to 18 °dH.

Daily sums (in mm) of precipitation were obtained from the German Weather Service for the 3 stations Schleswig, Fehmarn, and Hamburg-Fuhlsbüttel (see Figure 1; Deutscher Wetterdienst 2007–2010). The amount of precipitation in the week and in the month before sample collection was calculated and is presented in Table 3.

Table 3 Sum precipitation of the 7-day period before sampling and of the 30-day period before sampling is given for 3 measurement stations: Hamburg-Fuhlsbüttel, Schleswig, and Fehmarn (see Figure 1). Data from Deutscher Wetterdienst (2007–2010).

Date	Precipitation (mm/week) Fuhlsbüttel	Precipitation (mm/month) Fuhlsbüttel	Precipitation (mm/week) Schleswig	Precipitation (mm/month) Schleswig	Precipitation (mm/week) Fehmarn	Precipitation (mm/month) Fehmarn
Aug 2007	10	134.9	19.3	116.8	10.1	103.8
Sep 2008	1.3	14	2.4	33.9	0.6	19.2
Feb 2009	6.7	27.1	11.1	34.4	5.8	24.1
July 2010	7.1	26.8	0.2	36.1	0.6	28.7

pH measurements for the rivers were not available, but in the Wardersee the pH value is relatively stable around 8.4 (Nixdorf et al. 2003). At this pH, most of the DIC occurs in the form of bicarbonate (Olsson and Kaup 2001). The carbonate hardness (Table 2) should thus be a good indicator of DIC concentration. Carbonate hardness is also expected to indicate the DIC age, as larger amounts of dissolved ^{14}C-free carbonates lead to greater ^{14}C ages. However, the Alster water has greater ^{14}C ages but lower Ca concentrations. None of the rivers show a correlation between DIC ^{14}C ages and water hardness.

For both rivers, it was checked whether the amount of precipitation correlated with the ^{14}C age or the δ^{13}C values. In all cases, the correlations of ^{14}C or δ^{13}C with precipitation data are negative; maximum values are given in the list below. Thus, the more rain in the period before sampling,

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

1. The smaller the ^{14}C age (more "modern" carbon, relatively less $CaCO_3$; e.g. $r = –0.65$ for the ^{14}C age of Alster DIC and weekly precipitation sum from Fehmarn and $r = –0.92$ for the ^{14}C age of Trave DIC and weekly precipitation sum from Schleswig);
2. The lower the $\delta^{13}C$ values (more terrestrial material; e.g. $r = –0.94$ for $\delta^{13}C$ values of Alster DIC and weekly precipitation sum from HH-Fuhlsbüttel and $r = –0.76$ for $\delta^{13}C$ values of Trave DIC and monthly precipitation sums from Schleswig and Fehmarn).

In almost all cases, the correlation of the precipitation of the week before sample collection and the ^{14}C age is stronger than the correlation between monthly precipitation and ^{14}C age. Short-term precipitation fluctuations thus appear to have a considerable influence on ^{14}C age and $\delta^{13}C$ values. This could explain the large short-term variability of the values. The fact that the greatest correlation of Trave DIC $\delta^{13}C$ values occurs with monthly precipitation sums indicates a larger water residence time in this river system. However, more data would be needed to draw any firm conclusions.

Aquatic Plants

The aquatic plants have ^{14}C ages between –74 and 2273 BP (Table 4). Comparison with the average ^{14}C level of the atmosphere during the preceding growing season (Table 1) yielded estimated reservoir ages (Rf) from 347 to 2700 ^{14}C yr. ^{14}C ages do not differ systematically between submerged and floating leaves. The ^{14}C age range of the plants overlaps with that of the water (which has ^{14}C ages between 1170 and 2620 BP), but is shifted towards lower values. The most striking result of the analysis of aquatic plants is the fact that floating leaves do not have younger ^{14}C ages than submerged plants. A submerged plant with an estimated Rf of only 350 ^{14}C yr contrasts with a floating plant, collected on the same day at the same part of the river, with a much higher Rf of 1300 ^{14}C yr (Table 4).

Two leaves of the yellow water lily *Nuphar lutea*, one from Alster and one from Trave, have been subsampled twice, at the bottom of the petiole (stem) and at the tip of the leaf. In both cases, the tip of the leaf is slightly older than the end of the petiole, and both subsamples show a substantial reservoir effect. The estimated reservoir age of the *N. lutea* from the Trave is Rf = 600–640 ^{14}C yr, from the Alster, Rf = 2300–2500 ^{14}C yr. *N. lutea* is proven to assimilate CO_2 (Birks 2001). This CO_2 can derive from different sources, including the atmosphere, water, and sediment. Furthermore, the petiole of *N. lutea* uses nutrients from the rhizome (root stock) that were stored during the previous growing season (Osmond et al. 1981). These different carbon sources have potentially very different ^{14}C ages. Sediment organic matter, for example, can be several decades old and thus heavily affected by bomb carbon (Olsson and Kaup 2001).

"Internal winds" in *N. lutea* transport atmospheric air from the younger leaves through petioles and rhizome to the older leaves, where most of the CO_2 from this transport is photosynthesized (Dacey 1980). This continuous air transport is most likely the reason for petioles and leaves having the same ^{14}C ages. The high ages of the water lilies (Table 4) indicate a surprisingly large contribution from water CO_2 for photosynthesis.

Our results disagree with previous studies where emergent plants and floating leaves of *N. lutea* were found to have ^{14}C contents in equilibrium with the atmosphere (Deevey et al. 1954; Olsson and Kaup 2001). In a study by Törnqvist et al. (1992), however, *N. lutea* showed a full hardwater effect of about Rf = 500 yr, while the white water lily *Nymphaea alba* had a terrestrial ^{14}C age. Differences in ^{14}C levels for aquatic plants from the same region, as well as high and variable reservoir ages without differences in floating and submerged plants have previously been found (Olsson et al. 1969; Srdoč et al. 1980).

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

Table 4 Modern aquatic plants and animals.

River	Collection date	AAR-	Species	C fraction	N fraction	C/N ratio	$\delta^{13}C$ (‰ VPDB)	$\delta^{15}N_{AIR}$ (‰), $\delta^{18}O_{VPDB}$ (‰)[a]	pMC	^{14}C age (BP)	Res. age (^{14}C BP)
Alster	Sep 2008	12873	Submerged plant	0.221±0.132	0.025±0.018	7.54±0.56	–31.62±0.23[b]	12.63±0.58	75.36±0.38	2273±41	2694±41
Alster	July 2010	14334	*Nuphar lutea* (tip of leaf)	0.419±0.209	0.049±0.001	10.02±1.74	–31.50±0.05[c]	10.40±0.27	76.83±0.24	2117±25	2472±25
Alster	July 2010	14335	*Nuphar lutea* (end of petiole)	0.364±0.038	0.023±0.008	17.58±3.20	–31.24±0.05[c]	10.39±0.49	78.51±0.23	1944±24	2299±24
Trave	Sep 2008	12870	Submerged plant	0.263±0.022	0.022±0.007	10.36±0.68	–25.42±0.46[b]	9.89±0.52	100.93±0.44	–74±35	347±35
Trave	Sep 2008	12871	Floating plant	0.377±0.021	0.043±0.003	10.94±0.83	–28.09±0.73[b]	12.05±0.55	89.64±0.41	879±37	1300±37
Trave	Sep 2008	12872	Submerged plant	0.255±0.001	0.024±0.001	11.54±0.46	–17.45±1.88[b]	6.81±2.51	80.93±0.55	1700±55	2120±54
Trave	July 2010	14336	Submerged plant	0.319±0.004	0.032±0.001	11.58±0.86	–34.22±0.05[b]	12.82±0.15	78.80±0.24	1914±24	2269±23
Trave	July 2010	14337	Submerged/floating plant	0.427±0.006	0.063±0.002	7.51±0.79	–26.95±0.05[c]	–3.35±0.40	85.45±0.24	1263±23	1618±23
Trave	July 2010	14338	*Nuphar lutea* (tip of leaf)	0.415±0.017	0.061±0.010	10.18±1.40	–27.52±0.05[c]	7.86±0.23	96.48±0.24	288±20	643±20
Trave	July 2010	14339	*Nuphar lutea* (end of petiole)	0.350±0.007	0.020±0.001	20.51±0.49	–26.67±0.10[b]	5.35±0.12	97.04±0.30	241±25	596±25
Alster	Sep 2007	11460	Mussel shell (probably *Unio* sp.)				–13.22±0.05[c]	–7.21±0.06	85.98±0.37	1214±34	1654±35
Alster	Sep 2007	11461	Snail shell				–15.36±0.05[c]	–8.01±0.05	94.75±0.37	433±32	869±34
Alster	Sep 2007	11462	Roach, bone collagen	0.362±0.007	0.132±0.001	3.19±0.03	–25.46±0.05[c]	12.24±0.33	97.27±0.35	223±29	660±33
Trave	Sep 2007	11394	Roach, bone collagen	0.422±0.010	0.156±0.003	3.15±0.10	–25.91±0.05[c]	14.85±0.44	96.51±0.38	285±32	727±33
Trave	Sep 2007	11396	Roach, bone collagen (from cooked bone)	0.428±0.011	0.161±0.004	3.11±0.10	–24.24±0.05[c]	15.27±1.03	97.01±0.34	244±28	685±25
Trave	Sep 2008	12874	Mallard feather	0.498±0.024	0.161±0.004	3.74±0.28	–23.99±0.11[b]	4.81±0.24	104.77±0.41	–374±32	47±31
Trave	Sep 2008	12875	Spined loach	0.485±0.008	0.132±0.001	4.32±0.12	–27.24±0.09[b]	15.55±0.34	81.29±0.39	1664±39	2085±39
Trave	Sep 2008	12876	Crayfish	0.390±0.114	0.060±0.036	4.20±0.06	–27.89±0.46[b]	11.89±2.04	84.37±0.42	1365±40	1787±40
Trave	Sep 2008	12878	Roach, flesh	0.486±0.022	0.144±0.008	3.92±0.28	–22.30±0.10[b]	14.86±0.19	99.17±0.40	67±32	488±32

[a] $\delta^{18}O$ values are shaded gray; all other (unshaded) values are $\delta^{15}N$.

[b] Samples combusted in an elemental analyzer prior to measurement.

[c] Measurements on sample CO_2 from off-line combustion or acidification with the dual-inlet (DI) method.

In our case, the differences between the 2 rivers are larger than the differences between the 2 collection dates. The average Rf values of the, admittedly few, samples are 2490 ± 200 for the Alster and 1270 ± 770 for the Trave. The samples collected in September 2008 have an average Rf of 1620 ± 1020, while the samples collected in July 2010 on average have Rf = 1650 ± 850. The average values are given below:

	September 2008	**July 2010**
Alster	2690 ± 40 (1 sample)	2390 ± 120 (2 samples)
Trave	1260 ± 890 (3 samples)	1280 ± 810 (4 samples)

Also, the range of $\delta^{13}C$ values is large for the plants analyzed here and spans from –34.2 to –17.5‰ (Table 4). Eight out of the 10 plants have values between –31.6 and –25.4‰; the broad range is thus caused by 2 extreme values. No correlation of $\delta^{13}C$ values with growing location (submerged or floating) was seen. $\delta^{13}C$ values of aquatic plants are expected to reflect the isotopic composition of their source carbon, apart from an isotopic shift due to fractionation, usually 18–19‰ from bicarbonate to plant cell (Olsson and Kaup 2001). Regarding water DIC $\delta^{13}C$ values (Table 2), the water plants in this study are expected to have $\delta^{13}C$ values between –33 and –29‰; the measured values, however, were –34.2 to –17.5‰. The more enriched values are probably caused by reduced fractionation as a consequence of bicarbonate limitation. It has even been reported that water DIC and aquatic plants can have the same $\delta^{13}C$ values (Higham et al. 2010).

Many aquatic plants can utilize both DIC species, CO_2 and HCO_3^-, whereas others are specialized in only one of them (Osmond et al. 1981). CO_2 in equilibrium with HCO_3^- at 10 °C has ~9.5‰ lighter values than the HCO_3^- (Emrich et al. 1970; Romanek et al. 1992). The dominating DIC species in the rivers analyzed here is bicarbonate. Plants utilizing CO_2 experience thus a limited carbon pool and discriminate less against ^{13}C than plants utilizing bicarbonate. The suitability of $\delta^{13}C$ values of aquatic plants for identifying CO_2 or HCO_3^- assimilation is therefore limited, as low $\delta^{13}C$ values can be caused by the assimilation of HCO_3^- involving large fractionation or by the assimilation of CO_2 without fractionation.

C/N ratios span a large range from 7.5 to 20.5, which corresponds to a range from typical values of algae to those of terrestrial matter (Meyers and Teranes 2001). Six out of 10 of the aquatic plants analyzed here, however, fall into a narrower range of C/N ratios between 10 and 11.5 (Table 4). Floating leaves tend to have higher carbon fractions than submerged plants or parts of plants. On average, floating leaves have a carbon fraction of 0.410 ± 0.022, and submerged plants and parts of plants, 0.295 ± 0.057. No other measured parameter distinguishes between submerged and floating plants.

Studies of reservoir ages and $\delta^{13}C$ values of aquatic plants are highly important. Especially the carbon source of floating leaves should be explored. *Nymphaea alba*, for example, has been used for constructing an age model, just as terrestrial samples (Hammarlund et al. 2003). Furthermore, the rhizomes of both *Nuphar* and *Nymphaea* have been widely used as human food (Hutchinson 1975 and references therein). Freshwater reservoir effects in water lilies could thus introduce reservoir effects into age models and human nutrition.

Aquatic Animals

The average Rf of the animals from Alster and Trave is 1120 ± 620 ^{14}C yr (excluding the mallard feather). For the Alster alone, the average Rf is 1060 ± 520, and for the Trave, Rf = 1150 ± 730. The large variability of ^{14}C ages for fish and other freshwater animals (Table 4) is not surprising, regarding the large variability on the basis of the food web, including water DIC and aquatic plants. How-

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

ever, the average Rf of the animals does not differ between Alster and Trave, while the average Rf of aquatic plants from the 2 rivers differed substantially (see above). Organic samples (fish bone collagen, flesh, and whole animals) have $\delta^{13}C$ values between –22 and –28‰.

The bone collagen of *R. rutilus* collected in 2007 had $\delta^{13}C$ values around –25‰, and experimental food crusts made of flesh from these fish had $\delta^{13}C$ values between –27 and –29‰. The raw flesh was not measured but is expected to have approximately the same $\delta^{13}C$ values as the food crust. The difference between flesh and bone collagen as measured here corresponds thus to the collagen-flesh differences in previous studies (Katzenberg et al. 1995; Lanting and van der Plicht 1998). However, the flesh of a *R. rutilus* collected in 2008 had a $\delta^{13}C$ value of –22.3‰. Unfortunately, bone collagen from this fish was not measured. However, if the same flesh-bone collagen fractionation applies to this fish as well, its bone collagen would have $\delta^{13}C$ values between –20 and –18‰. The large difference between the fish from 2008 and those from 2007 cannot be explained with our current knowledge but is most probably a result of different food sources of the individual fish.

$\delta^{13}C$ values and ^{14}C ages of *R. rutilus* bone collagen are of the same order of magnitude for both rivers, with $\delta^{13}C$ values around –25‰ and ^{14}C ages around 250 BP. This yields an estimated reservoir age between Rf = 660 and 730 ^{14}C yr. The flesh from a roach caught 1 yr later, however, had a $\delta^{13}C$ value of –22.3‰ and a ^{14}C age of 70 BP (Rf = 490 ^{14}C yr). The fish with the unusually high $\delta^{13}C$ value thus also had an unusually low ^{14}C age.

$\delta^{13}C$ values of inorganic samples (shells) are –13‰ and –15‰, while shell $\delta^{18}O$ values are –7.2 and –8.0‰. These $\delta^{13}C$ and $\delta^{18}O$ values of the shells from the Alster are comparable to values reported in the literature (e.g. Keith et al. 1964). The $\delta^{13}C$ values are furthermore comparable to water DIC $\delta^{13}C$ values from the same river and period (Table 2). The mallard feather has $\delta^{15}N = 4.8$, whereas the fish samples have $\delta^{15}N$ values between 12 and 16‰. The high $\delta^{15}N$ values of the fish agree with the high $\delta^{15}N$ values of the aquatic plants (see above and Figure 3).

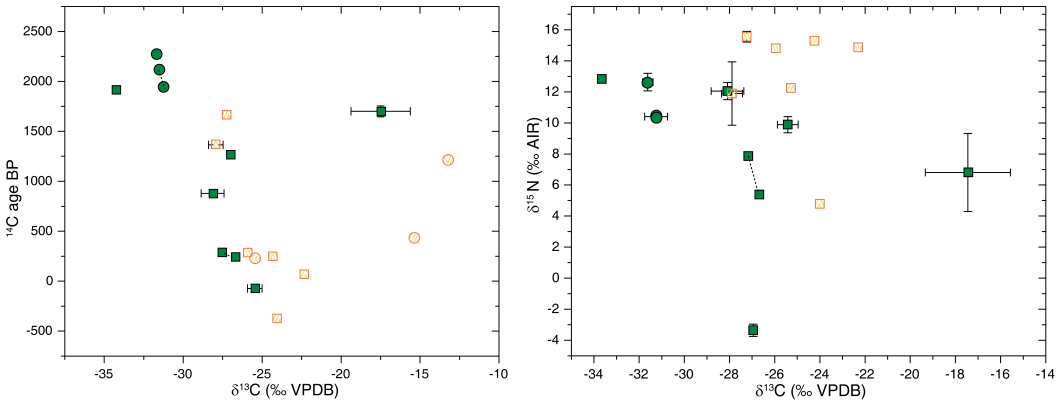


Figure 3 Measurements on modern aquatic plants and animals. Squares: Trave; Circles: Alster; Green solid: plants; Orange hatched: animals. Error bars in the left plot are of the same magnitude as symbols and therefore left out. Values in Table 4.

The $\delta^{13}C$ values and ^{14}C ages of modern aquatic organisms are correlated (cf. Figure 3). Without the 2 samples of shell carbonate, the Pearson correlation coefficient is $r = –0.52$ ($R^2 = 0.27$). When excluding on outlier value of an aquatic plant ($\delta^{13}C = –17.45$), the correlation coefficient is $r = –0.88$ ($R^2 = 0.79$). Interestingly, the correlation coefficients between $\delta^{13}C$ values and ^{14}C ages are positive for water DIC (see above and Figure 2).

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

Average Rf	Water DIC	Plants	Animals
Alster	2490 ± 490	2490 ± 200	1060 ± 520
Trave	2050 ± 560	1270 ± 770	1150 ± 730

Interestingly, the average reservoir ages Rf of water DIC and aquatic plants are equal in the Alster, while they differ substantially in the Trave. The animals from the Alster, however, have significantly lower Rf than the plants. In the Trave, on the other hand, aquatic plants and animals have similar average Rf values. We have not yet been able to find a satisfactorily explanation for these similarities and differences.

Archaeological Samples

Two terrestrial samples, 1 fish bone, and 4 food crusts on pottery from the archaeological site Kayhude at Alster River were dated. The results are presented in Table 5 and Figure 4. The samples from Kayhude are believed to be contemporaneous, as they were found embedded in a stone layer. Still, the 2 terrestrial samples have very different ^{14}C ages: 5450 and 9150 BP (Table 5, Figure 4). This bone must be an admixture from earlier layers, as it is not only older than the other terrestrial sample from Kayhude, but also older than the oldest finds of the entire Ertebølle culture. This exemplifies that the stone layer where we found our samples cannot be regarded as totally undisturbed. Direct ^{14}C dating of the pottery is thus necessary, as we cannot be sure which terrestrial samples are clearly associated with the pottery.

Table 5 Archaeological samples from the sites Schlamersdorf/Trave and Kayhude/Alster. FC = food crust. BC = bone collagen.

AAR-	Species/material	^{14}C age (uncal yr BP)	C/N ratio	$\delta^{13}C$ (‰ VPDB)	$\delta^{15}N$ (‰ AIR)
Kayhude, Alster					
11403	KAY8-432,01 FC pretreated	5695 ± 55	8.77 ± 0.38	–28.63 ± 0.05 (DI)	6.99 ± 0.43
11403	KAY8-432,01 FC not pretreated	—	8.93 ± 0.50	–29.01 ± 1.03 (EA)	6.76 ± 0.09
11403	KAY8-432,01 FC base-soluble	6740 ± 160	—	—	—
11404	KAY8-168,01 FC pretreated	6090 ± 55	8.28 ± 0.91	–28.90 ± 0.05 (DI)	12.54 ± 0.21
11404	KAY8-168,01 FC not pretreated	—	8.67 ± 0.43	–28.79 ± 0.17 (EA)	11.36 ± 0.21
11404	KAY8-168,01 FC base-soluble	6420 ± 65	—	—	—
11477	KAY8-815.0 BC terrestrial	9150 ± 110	—	—	—
11479	KAY8-412.01 FC pretreated	5350 ± 110	17.77 ± 0.32	–26.53 ± 0.13 (EA)	6.38 ± 0.34
11479	KAY8-412.01 FC not pretreated	—	17.41 ± 1.06	–26.55 ± 0.10 (EA)	7.44 ± 1.00
11479	KAY8-412.01 FC base soluble	6130 ± 60	—	—	—
11480	KAY8-176 Charcoal	5438 ± 41	—	–24.83 ± 0.05 (DI)	—
11695	Pike BC	8520 ± 80	—	–22.41 ± 0.05 (DI)	—
14212	KAY8-435 FC pretreated	5948 ± 35	15.46 ± 24.63	–26.72 ± 0.10 (EA)	—
Schlamersdorf, Trave					
11402	SLA5-10000 Wood	5638 ± 49	—	–26.49 ± 0.05 (DI)	—
11405	SLA5-10001 Wood	5762 ± 48	—	–27.25 ± 0.05 (DI)	—
11406	SLA5-10002 Wood	5818 ± 43	—	–28.78 ± 0.05 (DI)	—
11407	SLA5-10003 Wood	5750 ± 90	—	–27.03 ± 0.05 (DI)	—
11408	SLA5-10004 Wood	5642 ± 48	—	–27.47 ± 0.05 (DI)	—
11398	SL5-2784 BC Wild cat	5685 ± 60	3.25 ± 0.13	–19.27 ± 0.05 (DI)	6.49 ± 0.29
11399	SL5-2761 BC beaver	6480 ± 90	3.59 ± 0.11	–22.42 ± 0.05 (DI)	4.68 ± 0.89
11400	SL5-2883 BC wild boar	6035 ± 60	3.24 ± 0.01	–21.39 ± 0.05 (DI)	5.01 ± 0.13
11401	SL5-2913 BC fish; 5 vertebrae	—	3.27 ± 0.02	–21.40 ± 0.05 (EA)	4.75 ± 23
11401	SL5-2913 BC fish; rest of the bone fragments	—	3.25 ± 0.01	–26.91 ± 0.04 (EA)	7.91 ± 44

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

Table 5 Archaeological samples from the sites Schlamersdorf/Trave and Kayhude/Alster. FC = food crust. BC = bone collagen. *(Continued)*

AAR-	Species/material	^{14}C age (uncal yr BP)	C/N ratio	δ^{13}C (‰ VPDB)	δ^{15}N (‰ AIR)
11475	SLA5-2869 BC cyprinid	7770 ± 100	—	—	—
11476	SLA5-2786 Tooth collagen, red deer (drilled out)	6275 ± 65	—	–23.63 ± 0.05 (DI)	—
11476	SLA5-2786 Tooth collagen, red deer (entire bone fragment)	6370 ± 65	—	–23.54 ± 0.05 (DI)	—
11481	SLA5-1713 FC	5190 ± 110	12.33 ± 2.04	–27.23 ± 0.45 (EA)	—
11481	SLA5-1713 FC not pretreated	—	15.96 ± 2.40	–27.66 ± 0.25 (EA)	3.95 ± 0.45
11481	SLA5-1713 Outer crust	6850 ± 120	16.29 ± 1.58	–28.01 ± 0.46 (EA)	3.39 ± 0.30
11482	SLA5-2707 FC pretreated	5590 ± 110	13.01 ± 1.36	–27.04 ± 0.22 (EA)	—
11482	SLA5-2707 FC not pretreated	—	19.36 ± 0.18	–27.68 ± 0.11 (EA)	2.86 ± 0.75
11483	SLA5-2742 FC pretreated	—	15.15 ± 0.25	–27.62 ± 0.05 (DI)	—
11483	SLA5-2742 FC not pretreated	—	19.55 ± 1.53	–27.42 ± 0.18 (EA)	3.09 ± 0.96
11483	SLA5-2742 plant rest from sherd	5985 ± 50	—	—	—
11484	SLA5-1802 FC pretreated	5950 ± 170	14.91 ± 2.57	–27.46 ± 0.39 (EA)	—
11484	SLA5-1802 FC not pretreated	—	16.39 ± 3.62	–27.65 ± 0.04 (EA)	1.88 ± 0.21
11842	SLA5-2912a BC	7640 ± 65	—	–26.78 ± 0.05 (DI)	—
11843	SLA5-2912b BC	—	5.36 ± 0.08	–27.58 ± 0.04 (EA)	9.40 ± 0.14
11844	SLA5-2906 BC	7620 ± 110	—	—	—
14211	SLA5-2683 FC	6871 ± 35	12.12 ± 0.84	–33.02 ± 0.05 (DI)	6.93 ± 0.15

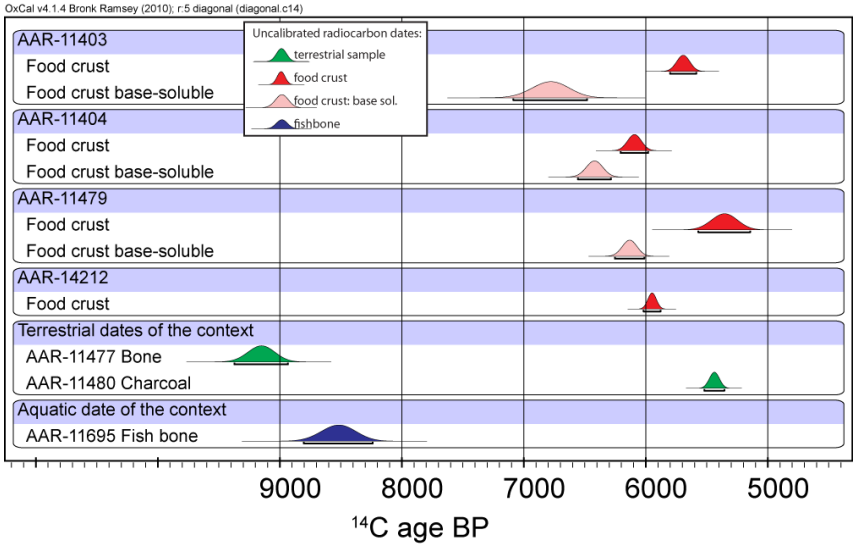


Figure 4 Archaeological samples from Kayhude/Alster. The plot was made with OxCal v 4.1 (Bronk Ramsey 2009), using a straight line x=y as "calibration curve"; 2σ-intervals are indicated below the probability distributions of the ^{14}C ages.

The pike bone collagen is ~3000 ^{14}C yr older than the charcoal sample. Food crusts on pottery have the same or slightly larger ^{14}C ages than the youngest terrestrial sample. None of the food crusts are as old as the fish bone. The base-soluble fraction of 3 food crusts has also been dated. It may consist of partly original material, e.g. fatty substances, but also partly of contamination from the soil such as humic acid. The base-soluble fraction is in all cases older than the food crusts (Figure 4), indicating contamination with an older soil substance.

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

If we assume that the charcoal AAR-11480 gives the correct age of the find layer, then the food crust AAR-11479 is not affected by reservoir effects. For the 3 other food crusts (AAR-11403, -11404, and -14212), reservoir ages of about Rf = 300–600 ^{14}C yr can be estimated. Compared to the average reservoir age of modern Alster animals, Rf = 1060 ± 520 ^{14}C yr, this would indicate 30% to 60% aquatic ingredients in the food crust.

If we assume that the fish bone AAR-11695 is contemporaneous with the charcoal and food crust samples, then the reservoir effect in the Mesolithic at Kayhude would be about Rf = 3000 ^{14}C yr. In this case, the reservoir ages of the food crusts AAR-11403, -11404, and -14212 would indicate only 10% to 20% aquatic ingredients.

From Schlamersdorf at the Trave River, 9 terrestrial samples, 3 fish bones, and 5 food crusts on pottery were dated (Table 5, Figure 5). The age range of terrestrial samples is very broad, ~1000 yr (Figure 5). The food crusts have the same age as the terrestrial samples or are slightly older, and the fish bone collagen is significantly older than the terrestrial samples.

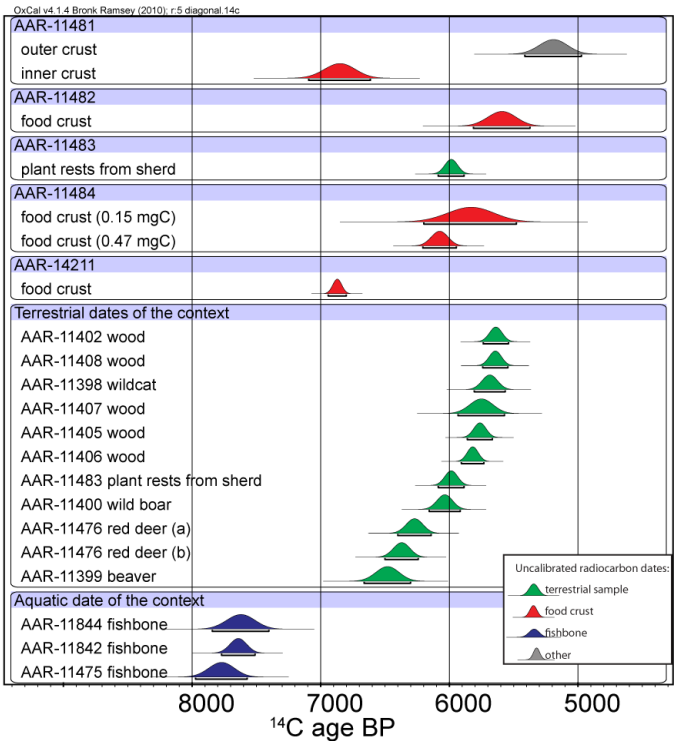


Figure 5 Archaeological samples from Schlamersdorf/Trave. The plot was made with OxCal v 4.1 (Bronk Ramsey 2009) using a straight line x=y as the "calibration curve"; 2σ-intervals are indicated below the probability distributions of the ^{14}C ages.

The terrestrial age range of Schlamersdorf complies with earlier charcoal datings from this site (Hartz 1993). The broad age range measured here (Figure 5) is unlikely to indicate an occupation period of 1000 yr. The site was probably occupied repeatedly for shorter periods, as archaeological analysis indicated that the site was a hunting or fishing station. The broad terrestrial age range reveals the necessity of direct pottery dating.

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

Three food crusts had previously been dated to ~5300 cal BC (Hartz 1996); their $\delta^{13}C$ values between –28.6 and –31.9‰ indicate freshwater ingredients and thus the possibility of a freshwater reservoir effect. Two of the 4 food crusts we ^{14}C dated from that site are from 5500–6000 BP (~4000–5000 cal BC), and 2 around 7000 BP (~5600–6000 cal BC; Figure 5). However, as the average Rf in modern Trave animals is 1150 ± 730, the large ages of the 2 oldest potsherds could have been caused by a reservoir effect. In case fish or other aquatic resources had been prepared in these pots, their reservoir age Rf could likely be ~1000 ^{14}C yr. It is thus probable that the true ages of all the food crusts from Schlamersdorf are about the same, and lie within an interval of ~4000–5000 cal BC.

An interesting case is the potsherd AAR-11481 of which both the inner and outer crust have been dated. If one assumes that the outer crust is soot from the cooking fire, then it should give the date of cooking, or an older date in case old wood had been used. The reservoir effect would, in this case, be ~2000 yr. As this outer crust is younger than all the other terrestrial samples, it was suspected to be influenced by modern contamination. However, if it had been modern contamination from the burial environment, from the handling during the excavation, or later during storage in the archives, this contamination would be expected to have affected both sides of the sherd equally.

In one of the sherds, AAR-11483, we were lucky to find some plant remains that presumably had been incorporated into the clay during the forming of the pottery. The ^{14}C age of these plant remains is 6000 BP. The calibrated 2σ age range is 4999–4766 cal BC (92.7%) and 4756–4729 cal BC (2.7%), calibrated with OxCal v 4.1.2 (Bronk Ramsey 2009) and the IntCal04 atmospheric curve (Reimer et al. 2004). The probability for the pottery being older than 5000 cal BC is thus <5%. Unfortunately, the food crust sample of AAR-11483 was lost during dating. It would otherwise have helped to measure the reservoir effect in food crusts directly.

The hardwater effect at Schlamersdorf and Kayhude seems to be larger than the effect reported by Fischer and Heinemeier (2003), at least for the fish bones. In their study area, the Åmose in Zealand, Denmark, the fish was 100–500 ^{14}C yr older than the archaeological context, while the food crusts were up to 300 ^{14}C yr older.

CONCLUSION

The freshwater reservoir effect in the Alster and Trave rivers is large and very variable. In both rivers, ^{14}C age and $\delta^{13}C$ values of water DIC are correlated with each other and with the amount of precipitation in the week prior to sampling. After a period with small amounts of precipitation, the river water is dominated by hard groundwater with high $\delta^{13}C$ values and ^{14}C ages. Larger amounts of precipitation result in a larger contribution of terrestrial run-off, which takes up CO_2 with low $\delta^{13}C$ values and low ^{14}C ages from the root zone.

The high ages and large variability can also be found in aquatic plants. Short-term precipitation fluctuations are unlikely to be the reason, as the plants average ^{14}C levels over the entire growing season. Aquatic plants can utilize a multitude of carbon species for photosynthesis with ^{14}C ages varying between ancient (DIC from dissolved limestone), contemporaneous (atmospheric CO_2), and modern (organic material in the lake sediment that may be some decades old and thus contains bomb carbon). The large reservoir age of floating leaves clearly shows that the assimilation of atmospheric CO_2 is not the dominant carbon source for these specimens, despite the expectations. This result is certainly interesting for freshwater botanists. In the future, ^{14}C dating may be used for identifying carbon sources in photosynthesis of aquatic plants in their natural environment, as long as this is an aquatic system with high water DIC ages.

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

It is striking that almost all modern river samples have large ^{14}C ages. This indicates a substantial reservoir effect that would be even greater without the bomb effect. The ^{14}C age of the contemporaneous atmosphere is around –400 BP. As can be seen from Tables 2 and 4, the estimated reservoir ages Rf, calculated considering the atmospheric ^{14}C levels, are roughly 400 yr larger than the ^{14}C ages BP. Furthermore, the organic matter in the rivers and their catchments may have a "true age" of several years to decades and thus contain bomb carbon. When CO_2 from this decaying organic matter is incorporated into the plant, ^{14}C enrichment in the plants is the consequence. Due to the large variability, it is not possible to find a reservoir correction for any of the rivers.

In the archaeological material, the large spread of terrestrial ages emphasizes the importance of direct pottery dating. The age difference between terrestrial samples and fish bones indicates a substantial freshwater reservoir effect of >1000 yr in the Trave and >3000 yr in the Alster. Both for modern and archaeological samples, the reservoir age in the Alster is higher than in the Trave. Water hardness and cation ratios in the rivers would lead to the opposite expectation. This indicates that dissolved carbonate minerals are not the only source for the high reservoir ages. Mineralized organic matter or groundwater with high "real" ages could have increased the reservoir age of Alster water, while exchange with the atmosphere could have decreased the reservoir age in the Trave while it passed the shallow Wardersee.

In general, this study shows that the characterization of the reservoir effect in a freshwater system requires more than a few water, plant, or animal samples. It is shown that freshwater reservoir effects in rivers can be very high and strongly variable. Archaeologists should be made aware of this source of spurious ages when sending pottery or bones of omnivores like humans from inland sites for ^{14}C dating. The surprisingly large ages of northern German pottery are in all likelihood caused by the freshwater reservoir effect. There is no longer reason to believe that inland potters were hundreds of years ahead of their colleagues at the coast.

ACKNOWLEDGMENTS

We would like to thank the following people cordially for providing data and insights: Ingeborg Levin for unpublished atmospheric $^{14}CO_2$ measurements, Kathleen Giemsa from the "Landesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig–Holstein" for cation data of the Alster and Trave, Sönke Hartz and Ingo Clausen for archaeological samples, and Tom Vindbæk Madsen for explaining water lilies' photosynthesis and providing references. Claus von Carnap-Bornheim financed 30 of the ^{14}C datings, and the foundation "Prof. Werner Petersen-Stiftung" in Kiel, Germany, provided the funds.

REFERENCES

Birks HH. 2001. Plant macrofossils. In: Smol JP, Birks HJB, Last WM, editors. *Tracking Environmental Change Using Lake Sediments*. Dordrecht: Kluwer Academic Publishers. p 49–74.

Boudin M, Strydonck MV, Crombé P. 2009. Radiocarbon dating of pottery food crusts: reservoir effect or not? The case of Swifterbant pottery from Doel "Deurganckdok" (Belgium). In: Crombé P, Strydonck MV, Sergant J, Boudin M, Bats M, editors. *Chronology and Evolution in the Mesolithic of North-West Europe*. Newcastle upon Tyne: Cambridge Scholars Publishing. p 753–72.

Broecker WS, Walton A. 1959. The geochemistry of C^{14} in fresh-water systems. *Geochimica et Cosmochimica Acta* 16:15–38.

Bronk Ramsey C. 2009. Bayesian analysis of radiocarbon dates. *Radiocarbon* 51(1):337–60.

Brown TA, Nelson DE, Vogel JC, Southon JR. 1988. Improved collagen extraction by improved Longin method. *Radiocarbon* 30(2):171–7.

Cimiotti U. 1983. *Zur Landschaftsentwicklung des mittleren Trave-Tales zwischen Bad Oldesloe und Schwissel, Schleswig-Holstein*. Berliner Geographische Studien 13. Berlin: Technische Universität Berlin.

Clausen I. 2007. Steinzeitliches Alstervergnügen. *Archäologie in Deutschland* 2:54.

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

Cook GT, Bonsall C, Hedges REM, McSweeney K, Boroneant V, Pettitt BP. 2001. A freshwater diet-derived ^{14}C reservoir effect at the Stone Age sites in the Iron Gates Gorge. *Radiocarbon* 43(2A):453–60.

Coplen TB. 1994. Reporting of stable hydrogen, carbon and oxygen isotopic abundances. *Pure and Applied Chemistry* 66(2):273–6.

Dacey JWH. 1980. Internal winds in water lilies: an adaptation for life in anaerobic sediments. *Science* 210(4473):1017–9.

Dansgaard W. 1964. Stable isotopes in precipitation. *Tellus* 16(4):436–68.

Deevey ES, Gross MS, Hutchinson GE, Kraybill HL. 1954. The natural C^{14} contents of materials from hardwater lakes. *Proceedings of the National Academy of Sciences of the USA* 40(5):285–8.

Deutscher Wetterdienst. 2007–2010. Klimadaten für Messstationen in Deutschland. URL: www.dwd.de.

Emrich K, Ehhalt DH, Vogel JC. 1970. Carbon isotope fractionation during the precipitation of calcium carbonate. *Earth and Planetary Science Letters* 8:363–71.

Fischer A, Heinemeier J. 2003. Freshwater reservoir effect in ^{14}C dates of food residue on pottery. *Radiocarbon* 45(3):449–66.

Godwin H. 1951. Comments on radiocarbon dating samples from the British Isles. *American Journal of Science* 249:301–7.

Hammarlund D, Björck S, Buchardt B, Israelson C, Thomsen CT. 2003. Rapid hydrological changes during the Holocene revealed by stable isotope records of lacustrine carbonates from Lake Igelsjön, southern Sweden. *Quaternary Science Reviews* 22(2–4):353–70.

Hartz S. 1993. Inland-Ertebølle in Schleswig-Holstein. Die Fundstelle Schlamersdorf LA5, Kr. Stormarn. Archäologie in Schleswig 1/1991 [Symposium Wohlde]. p 33–8.

Hartz S. 1996. Zehnter Arbeitsbericht des Archäologischen Landesamtes Schleswig-Holstein. Grabungsberichte der Jahre 1988–1993: Travenbrück (Altgemeinde Schlamersdorf), Kr. Stormarn, Steinzeitliche Wohnplätze Travenbrück, LA5 und LA15. *Offa* 53: 374–8.

Hartz S. 1997. Ertebøllekultur im Travetal. Ausgrabungen auf dem Fundplatz Travenbrück LA 5 (Gemarkung Schlamersdorf), Kreis Stormarn. Ein Vorbericht. In: Denkmalpflege im Kreis Stormarn III. *Stormarner Hefte* 20:171–86.

Higham T, Warren R, Belinskij A, Härke H, Wood R. 2010. Radiocarbon dating, stable isotope analysis, and diet-derived offsets in ^{14}C ages from the Klin-Yar site, Russian North Caucasus. *Radiocarbon* 52(2–3):653–70.

Hutchinson GE. 1975. *Limnological Botany*. New York: John Wiley.

Jørkov MLS, Heinemeier J, Lynnerup N. 2007. Evaluating bone collagen extraction methods for stable isotope analysis in dietary studies. *Journal of Archaeological Science* 34(11):1824–9.

Katzenberg MA, Schwarcz HP, Knyf M, Melbye FJ. 1995. Stable isotope evidence for maize horticulture and paleodiet in southern Ontario, Canada. *American Antiquity* 60(2):335–50.

Keith ML, Anderson GM, Eichler R. 1964. Carbon and oxygen isotopic composition of mollusk shells from marine and fresh-water environments. *Geochimica et Cosmochimica Acta* 28:1757–86.

Lanting JN, van der Plicht J. 1995/1996. Wat hebben Floris V, skelet swifterbant S2 en visotters gemeen? *Palaeohistoria* 37/38:491–519.

Lanting JN, van der Plicht J. 1998. Reservoir effects and apparent ^{14}C-ages. *The Journal of Irish Archaeology* 9:151–65.

Levin I, Hammer S, Kromer B, Meinhardt F. 2008. Radiocarbon observations in atmospheric CO_2: determining fossil fuel CO_2 over Europe using Jungfraujoch observations as background. *Science of the Total Environment* 391(2–3):211–6.

Levin I, Naegler T, Kromer B, Diehl M, Francey RJ, Gomez-Pelaez AJ, Steele LP, Wagenbach D, Weller R, Worthy DE. 2010. Observations and modelling of the global distribution and long-term trend of atmospheric $^{14}CO_2$. *Tellus B* 62(1):26–46.

Longin R. 1971. New method of collagen extraction for radiocarbon dating. *Nature* 230(5291):241–2.

MacDonald GM, Beukens RP, Kieser WE, Vitt DH. 1987. Comparative radiocarbon dating of terrestrial plant macrofossils and aquatic moss from the "ice-free corridor" of western Canada. *Geology* 15(9):837–40.

Mariotti A. 1983. Atmospheric nitrogen is a reliable standard for natural ^{15}N abundance measurements. *Nature* 303(5919):685–7.

Meyers PA, Teranes JL. 2001. Sediment organic matter. In: Last WM, Smol JP, editors. *Tracking Environmental Change Using Lake Sediments*. Dordrecht: Kluwer. p 239–69.

Ministerium für Umwelt, Naturschutz und Landwirtschaft des Landes Schleswig-Holstein. 2003. Landschaftsrahmenplan für den Planungsraum II - Kreis Ostholstein und Hansestadt Lübeck. Gesamtfortschreibung 2003.

Nixdorf B, Hemm M, Hoffmann A, Richter P. 2003. Dokumentation von Zustand und Entwicklung der wichtigsten Seen Deutschlands. Brandenburg University of Technology Cottbus. Report nr Berichtsnummer: UBA-FB. UFOPLAN-Nr 29924274. 1056 p.

Oana S, Deevey ES. 1960. Carbon 13 in lake waters and its possible bearing on paleolimnology. *American Journal of Science* 258(A):253–72.

Olsen J, Heinemeier J. 2009. AMS dating of human bone from the Ostorf cemetery in the light of new information on dietary habits and freshwater reservoir effects. In: Larsson L, Lüth F, Terberger T, editors. *Innovation and Continuity. Non-Megalithic Mortuary Practices in the Baltic*. Workshop Schwerin 24–25 April 2006.

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press

Olsen J, Heinemeier J, Lübke H, Lüth F, Terberger T. 2010. Dietary habits and freshwater reservoir effects in bones from a Neolithic northern German cemetery. *Radiocarbon* 52(2–3):635–44.

Olsson IU, Kaup E. 2001. The varying radiocarbon activity of some recent submerged Estonian plants grown in the early 1990s. *Radiocarbon* 43(2B):809–20.

Olsson IU, El GS, Goeksu Y. 1969. Uppsala natural radiocarbon measurements IX. *Radiocarbon* 11(2):515–44.

Osmond CB, Valaane N, Haslam SM, Uotila P, Roksandic Z. 1981. Comparisons of $\delta^{13}C$ values in leaves of aquatic macrophytes from different habitats in Britain and Finland; some implications for photosynthetic processes in aquatic plants. *Oecologia* 50(1):117–24.

Philippsen B. 2010. Terminal mesolithic diet and radiocarbon dating at inland sites in Schleswig-Holstein. In: *Landscapes and Human Development: The Contribution of European Archaeology.* Proceedings of the International Workshop "Socio-Environmental Dynamics over the Last 12,000 Years: The Creation of Landscapes (1–4 April 2009). Bonn: Dr. Rudolf Habelt GmbH. p 21–36.

Philippsen B. 2012. Variability of freshwater reservoir effects: implications for radiocarbon dating of prehistoric pottery and organisms from estuarine environments [PhD thesis]. Aarhus University.

Philippsen B, Kjeldsen H, Hartz S, Paulsen H, Clausen I, Heinemeier J. 2010. The hardwater effect in AMS ^{14}C dating of food crusts on pottery. *Nuclear Instruments and Methods in Physics Research B* 268(7–8):995–8.

Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck WJ, Bertrand C, Blackwell PG, Buck CE, Burr GS, Cutler KB, Damon PE, Edwards RL, Fairbanks RG, Friedrich M, Guilderson TP, Hughen KA, Kromer B, McCormac FG, Manning S, Bronk Ramsey C, Reimer RW, Remmele S, Southon JR, Stuiver M, Talamo S, Taylor FW, van der Plicht J, Weyhenmeyer CE. 2004. IntCal04 terrestrial radiocarbon age calibration, 0–26 cal kyr BP. *Radiocarbon* 46(3):1029–58.

Romanek CS, Grossman EL, Morse JW. 1992. Carbon isotope fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. *Geochimica et Cosmochimica Acta* 56:419–30.

Shishlina NI, van der Plicht J, Hedges REM, Zazovskaya EP, Sevastyanov VS, Chichagova OA. 2007. The Catacomb cultures of the North-West Caspian steppe: ^{14}C chronology, reservoir effect, and paleodiet. *Radiocarbon* 49(2):713–26.

Smits L, van der Plicht H. 2009. Mesolithic and Neolithic human remains in the Netherlands: physical anthropological and stable isotope investigations. *Journal of Archaeology in the Low Countries* 1(1):55–85.

Srdoč D, Obelic B, Horvatinčic N, Sliepčevic A. 1980. Radiocarbon dating of calcareous tufa: How reliable data can we expect? *Radiocarbon* 22(3):858–62.

Stewig R. 1982. *Landeskunde von Schleswig-Holstein*. Tietze W, Biays P, House J, Masatoshi Yoshino, editors. Berlin: Gebrüder Borntraeger.

Stuiver M. 1975. Climate versus changes in ^{13}C content of the organic component of lake sediments during the Late Quaternary. *Quaternary Research* 5(2):251–62.

Stuiver M, Polach HA. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Stuiver M, Pearson GW, Braziunas TF. 1986. Radiocarbon age calibration of marine samples back to 9000 cal yr BP. *Radiocarbon* 28(2B):980–1021.

Törnqvist TE, de Jong AFM, Oosterbaan WA, Van der Borg K. 1992. Accurate dating of organic deposits by AMS ^{14}C measurement of macrofossils. *Radiocarbon* 34(3):566–77.

Vogel JS, Southon JR, Nelson DE, Brown TA. 1984. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics Research B* 5(2):289–93.

https://doi.org/10.1017/S0033822200048001 Published online by Cambridge University Press