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The freshwater reservoir effect in radiocarbon dating

Bente Philippsen

Abstract

The freshwater reservoir effect can result in anomalously old radiocarbon ages of samples from lakes and rivers. This includes the bones of people whose subsistence was based on freshwater fish, and pottery in which fish was cooked. Water rich in dissolved ancient calcium carbonates, commonly known as hard water, is the most common reason for the freshwater reservoir effect. It is therefore also called hardwater effect. Although it has been known for more than 60 years, it is still less well-recognized by archaeologists than the marine reservoir effect. The aim of this study is to examine the order of magnitude and degree of variability of the freshwater reservoir effect over short and long timescales. Radiocarbon dating of recent water samples, aquatic plants, and animals, shows that age differences of up to 2000 ^{14}C years can occur within one river. The freshwater reservoir effect has also implications for radiocarbon dating of Mesolithic pottery from inland sites of the Ertebølle culture in Northern Germany. The surprisingly old ages of the earliest pottery most probably are caused by a freshwater reservoir effect. In a sediment core from the Limfjord, northern Denmark, the impact of the freshwater reservoir effect on radiocarbon dating in an estuarine environment is examined. Here, freshwater influence causes reservoir ages to vary between 250 and 700 ^{14}C years during the period 5400 BC - AD 700. The examples in this study show clearly that the freshwater reservoir effect can seriously corrupt radiocarbon dating at inland sites. Reservoir effects should therefore be considered whenever food remains on pottery or the bones of omnivores are radiocarbon dated - irrespective of the site's distance to the coast.

Introduction

Throughout the entire history of radiocarbon dating, new sources of error have appeared, have been examined, and corrections have been found. Of particular interest and complexity are the so-called reservoir effects, which result in apparent ages that are too old.

One of the basic assumptions in radiocarbon dating is that a sample incorporates carbon in equilibrium with the atmosphere. This can be directly, e.g. in a plant via photosynthesis, or indirectly, e.g. when an animal feeds on plants. This type of sample is called *terrestrial*. If a sample obtains its carbon from another reservoir with a lower ^{14}C level than the atmosphere, the basic assumption is no longer valid. The measured ages can be too old. This is typically the case for *aquatic* samples, originating in the sea (*marine* samples) or in freshwater systems such as lakes and rivers. This is of particular concern to archaeologists, as aquatic resources were an important contribution to human nutrition in Northern Europe, from Mesolithic hunter-gatherer-fishers to medieval Christians.

The marine reservoir effect is well-acknowledged among archaeologists, although the knee-jerk subtraction of 400 years from radiocarbon dates of marine samples might be too simplistic in some cases.

At least theoretically, the freshwater reservoir effect (FRE) has been known for a longer time than the marine reservoir effect. The most common cause of high apparent ages in freshwater systems is the presence of dissolved ancient carbonates, leading to the so-called hardwater effect. Under closed system conditions, calcite dissolution by carbonic acid leads to a 50% dilution of the ^{14}C concentration [1,2], causing a maximum FRE of one half-life of ^{14}C, about 5,370 years. Under open system conditions, water DIC is continuously exchanging with the infinite reservoir of ^{14}C-active soil CO_2, causing no reservoir offset. In reality, freshwater systems have intermediate conditions, and a FRE between 0 and almost 6,000 years is possible [1].

Correspondence: bphilipp@phys.au.dk
AMS ^{14}C Dating Centre, Department of Physics and Astronomy, University of Aarhus, Ny Munkegade 120, 8000 Aarhus C, Denmark

The hardwater effect was already predicted by J. Iversen in a private communication to E. S. Deevey, October 5, 1949 [3]. The effect was considered by Godwin in 1951 [4] when discussing radiocarbon dates from the British Isles, and measured for the first time in 1954 on aquatic plants [5]. The marine reservoir effect was observed and discussed slightly later in the 1950s [6-8].

However, it took several decades before the FRE was measured and discussed in archaeologically relevant sample types, such as human bones [9-14] or food crusts on pottery [15-18]. In these cases, the consumption or preparation of large amounts of freshwater fish lead to spurious apparent ages of the bones and pottery.

Also aquatic plants which are incapable of assimilating carbonates, and rely on CO_2, such as aquatic mosses, can show a substantial FRE [19]. High apparent ages can also be measured in carbonate-free groundwater and surface water [20], and apparent ages of up to 20,000 BP were reported from an Icelandic geothermal area [21].

In softwater lakes, the FRE can be caused by slow CO_2 exchange between the atmosphere and the lake water due to a large depth-to-surface ratio, good wind protection or extended periods of lake ice cover [22,23]. Other causes for a soft-water FRE are the inflow of old groundwater [22], the oxidisation of old organic matter [24], the inflow of water from a glacier containing old CO_2, or old CO_2 from volcanic activity [23].

Freshwater reservoir effects can vary significantly within one lake or river [18,25,26], even when only regarding submerged plants [26], or a single fish species from one lake [27]. Furthermore, the FRE influences radiocarbon dating in fjords and estuaries and can lead to site and time specific reservoir ages [28-30].

However, little attention has been paid to the *temporal* variability of the freshwater reservoir effect, and rivers have been underrepresented in studies of the FRE, with most studies focusing on lakes.

This study was designed to address some of these topics: the FRE in rivers; the short-term variability of the FRE; and the impact of the FRE on radiocarbon dating in estuarine environments. Therefore, modern river samples, archaeological samples from riparian sites, and samples from a fjord sediment core were radiocarbon dated. These radiocarbon dates were obtained as part of different studies from the author's PhD project, all employing a variety of methods. See [17,18,31-33] for details on the individual sub-projects. For this paper, the radiocarbon dating results of the different sub-projects are extracted and discussed in the context of other authors' studies on the FRE. This will provide an overview of use to archaeologists who consider dating materials which may be affected by a FRE. The author hopes that this paper can serve as a useful introduction to the FRE for researchers who are not familiar with this topic.

Location

The locations examined in this study are mapped in Figure 1. Two main regions are in the focus of this paper, both located on the Jutland peninsula.

The first region this paper deals with is the southern part of the Jutland peninsula, the northernmost federal state of Germany, Schleswig-Holstein. Here, the short-term variability of the freshwater reservoir effect in the rivers Alster and Trave is measured. Both rivers run through a morainal landscape from the last two glaciations. The moraines have calcium carbonate contents of up to 20% ([35]; see [32] and [31] for details on the study area). In the same region, the impact of the freshwater reservoir effect on radiocarbon dating of pottery was studied. Mesolithic pottery, maybe the earliest in that region, was found at the sites Kayhude at the Alster and Schlamersdorf at the Trave. These sites are marked "K" and "S" on Figure 1.

The second region examined in this paper is the Limfjord, a sound through Northern Jutland. The study location Kilen is a former inlet of the Limfjord at 56°30.005'N, 08°34.089'E. Today, after the construction of a dam, Kilen is a brackish embayment. As Kilen was naturally protected from strong currents, storms and wave action in the past, a continuous sediment sequence has been preserved. It is therefore possible to study the influence of the freshwater reservoir effect on radiocarbon dates in the Limfjord over long time scales. Details on this study area are provided in [31,33,36,37].

Materials and methods

This section describes the sample collection, chemical preparation, and measurement techniques. Modern samples of water, aquatic plants, fish and shellfish from the rivers Alster and Trave have been collected. Archaeological samples were provided from the Late Mesolithic sites of Kayhude/Alster and Schlamersdorf/Trave. Samples for studying the Limfjord were obtained from a sediment core.

Water

Dissolved inorganic carbon, DIC, is the carbon source for aquatic photosynthesis, and thus the material chosen for radiocarbon dating water samples. It comprises CO_2(aq), H_2CO_3(aq), HCO_3^-(aq) and CO_3^{2-}(aq). On 21 August 2007, 25 September 2008, 18 February 2009 and 6 July 2010, water samples were collected from the Northern German rivers Alster and Trave (Figure 1). They were sampled in 0.5L bottles and preserved with a few drops of a $HgCl_2$ solution. This prevented the growth of algae, which would have converted some of the DIC into organic

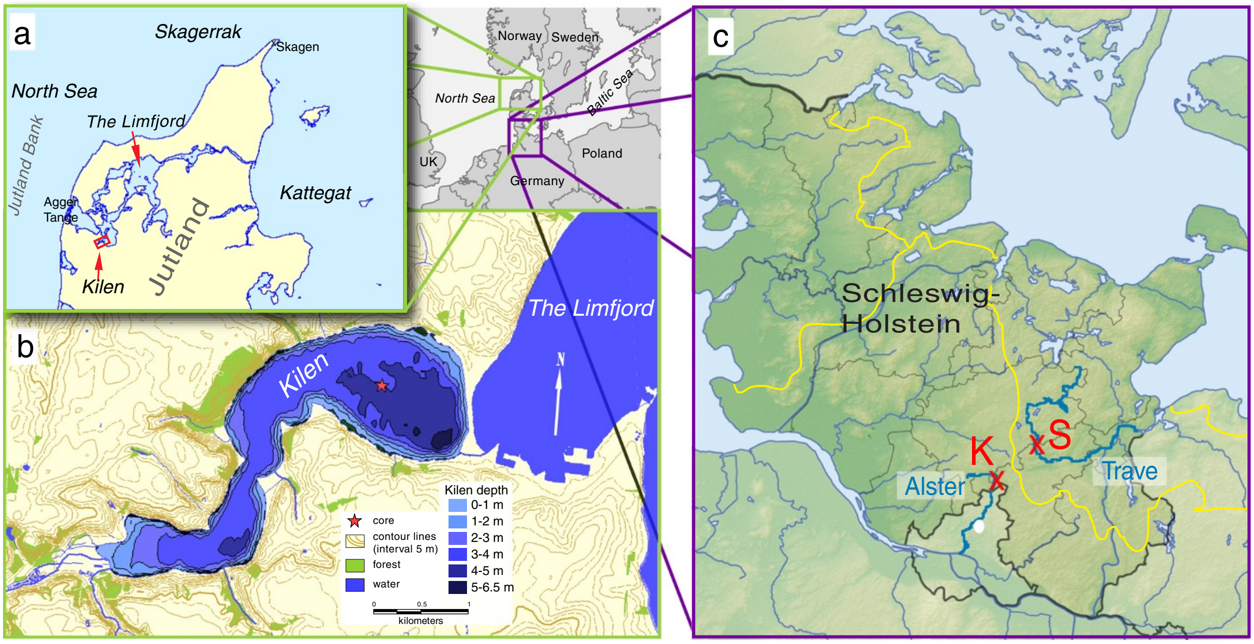

Figure 1 Map of the study area. Blank map of Europe by commons.wikimedia user Júlio Reis. **a)** The Limfjord region. Localities mentioned in the text are labelled. **b)** Detailed map of the Kilen core site. Own work, made with MapInfo Professional 7.8 using bathymetry data by Thorkild Høy, published in [34]. **c)** Map of the rivers Alster and Trave with the archaeological sites Kayhude/Alster (red cross, marked K) and Schlamersdorf/Trave (S). 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 commons.wikimedia user NordNord-West, relief by commons.wikimedia user Lencer.

carbon. 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 to free the CO_2, which 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 modern fishbones, as this is the material used for analyses of archaeological bones. A modified Longin-procedure with ultrafiltration was used [38-40]. The samples were converted to CO_2 by combustion in sealed evacuated quartz tubes containing CuO.

Sediment core from the Limfjord

In 2007, a 1560 cm long sediment sequence was obtained from Kilen, Limfjorden (Figure 1). The coring was made with a Russian peat sampler (chamber length 100 cm; [41]) in two parallel boreholes at a water depth of 390 cm below present sea level (bpsl). The sediments consist of homogenous grey-brown marine clay gyttja. This study focuses on the part between 467 and 1935 cm bpsl which was subsampled at 1–2 cm depth intervals. Material for AMS ^{14}C dating was retrieved by wet sieving. Other sample types and measurements from this core, e.g. stable isotope measurements, are described in detail in [33,36].

Shells

Both modern shells, collected from the Northern German rivers, and shells from the sediment core in the Limfjord were pretreated with the following method: Shells were cleaned with ultrasound in demineralised 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. 13–14 mg of pretreated shell was dissolved in 100% H_3PO_4 at 25°C, to produce CO_2 for ^{14}C-dating.

Archaeological samples and terrestrial plant remains from the sediment core

Archaeological charcoal samples and plant remains from the sediment core were pre-treated with 1M HCl at 80°C for one hour, 1M NaOH at 80°C for at least three hours and 1M HCl at 20°C overnight. Archaeological food crusts can be used for dating the last usage of the pottery. They were pre-treated like charcoal, but at 20°C, and with only 0.5 or 0.2 M NaOH. Collagen was extracted from archaeological bones as described above for modern fish bones. The samples were converted to CO_2 by combustion in sealed evacuated quartz tubes containing CuO.

Radiocarbon dating

For radiocarbon dating, CO_2 from the combusted or acidified samples was converted to graphite with the H_2 reduction method [42]. It was measured at the AMS ^{14}C Dating Centre at Aarhus University (AAR-numbers) or at the ^{14}CHRONO Centre, Queen's University Belfast (UBA-numbers). The dating results are reported as conventional ^{14}C dates in ^{14}C yr BP [43]. Calibrated dates have been obtained using OxCal version 4 with IntCal09 [44,45] and are quoted as cal AD/BC.

For the sediment core, an age model was calculated based on 13 radiocarbon dates on macrofossils of unequivocally terrestrial origin. To account for changes in accumulation rate, boundaries are inserted at 447, 552, 1055 and 1748 cm, based on major changes in the $CaCO_3$ content (Figure 2). The age model was constructed using the P_sequence depositional model in OxCal 4.1 [44], with k values between 10 and 200. The final k value of 150 yielded an agreement index of 73.3%. The width of the green line in the age model, Figure 2, indicates the uncertainty of the age model.

Stable carbon isotope measurements

Measurements of the stable carbon isotope ratio, $^{13}C/^{12}C$, are essential for normalising ^{14}C-measurements. Furthermore, they provide information about the origin of a sample. They can for example distinguish between marine and terrestrial samples. Measurements were either performed on the pre-treated sample, using an elemental analyser, or on a CO_2 aliquot from combustion or acidification.

The analyses on pre-treated samples were performed by combustion in a EuroVector elemental analyser coupled to an IsoPrime stable isotope ratio mass spectrometer at the AMS ^{14}C Dating Centre at Aarhus University. Most samples yielded enough material for replicate measurements. $\delta^{13}C$ values are reported as ‰ VPDB. $\delta^{15}N$ values and C/N ratios were measured at the same time and are discussed in detail in other publications [31-33].

The analyses on a CO_2 aliquot from the radiocarbon preparation were performed using a Dual Inlet IsoPrime stable isotope mass spectrometer at the AMS ^{14} Dating Centre at Aarhus University. $\delta^{13}C$ values are reported as ‰ VPDB. The standard deviation of 0.05‰ was determined using internal laboratory standards.

Calculation of reservoir ages

The reservoir age R is the difference in ^{14}C age between an aquatic sample and a contemporaneous terrestrial sample. It is calculated by subtracting the ^{14}C age of a terrestrial sample $^{14}C_T$ from the ^{14}C age of the contemporaneous aquatic sample $^{14}C_A$:

$$R = {}^{14}C_A - {}^{14}C_T. \quad (1)$$

Finding the ^{14}C age of a contemporaneous terrestrial sample was challenging for all instances where reservoir ages were calculated: Modern samples are affected by bomb carbon [46,47], while not all ancient aquatic samples are clearly associated with terrestrial samples. Therefore, the following two sections will elaborate on how to calculate reservoir ages in these cases.

Calculation of reservoir ages of modern samples

As post-bomb terrestrial ^{14}C ages are negative, the ^{14}C age measured on an aquatic sample would underestimate

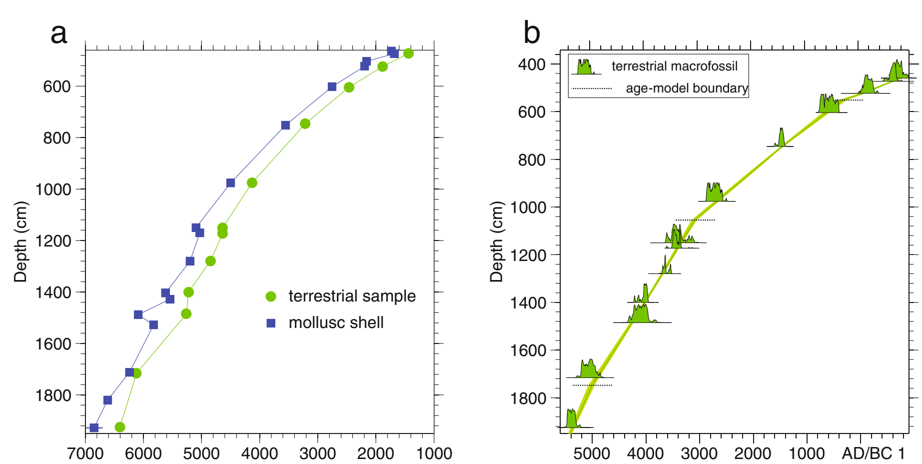

Figure 2 Radiocarbon ages of molluscs and terrestrial samples. a) Radiocarbon ages of terrestrial samples and mollusc shells from a sediment core from Kilen, Limfjorden, Denmark. **b)** Age-to-depth model for the sediment core. See [33] for details on calculations. The calibrated ages are given as calibrated ages AD/BC.

the reservoir effect. Therefore, both the aquatic sample and a modern terrestrial sample are dated. Measurements on atmospheric $^{14}CO_2$ (e.g. [48]) provide a convenient record of terrestrial references. The reservoir age R in ^{14}C years is calculated from the difference in ^{14}C ratios, which are given as percent modern carbon, pmC (pmC_A for the aquatic, pmC_T for the terrestrial sample; see [43] for details on notation and reporting of radiocarbon data):

$$R = 8033 \cdot \ln \frac{pmC_T}{pmC_A}, \tag{2}$$

where 8033 is the conventional "Libby" mean life of ^{14}C. The uncertainty of the calculated reservoir age R, $s(R)$, is calculated by propagation of uncertainty from the measurement uncertainties ΔpmC:

$$s(R) = 8033 \cdot \sqrt{\left(\frac{\Delta pmC_A}{pmC_A}\right)^2 + \left(\frac{\Delta pmC_T}{pmC_T}\right)^2}. \tag{3}$$

For the ^{14}C content of the contemporaneous atmosphere at the time of sample formation, pmC_T, measurements from the Black Forest station Schauinsland are used ([48] and pers. comm. I. Levin 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 [49].

Water DIC ^{14}C-concentrations measured in this study will be compared with those of the atmosphere in the month of sampling, and aquatic plant ^{14}C-concentrations with the average atmospheric concentrations of the entire growing season during which the plant grew (April-September, or April-July/August in case of sampling in summer). The average atmospheric ^{14}C levels used for these calculations are presented in Table 1. For calculations of the uncertainty of the reservoir age of water DIC, the uncertainty of $\pm 2‰$ of the atmospheric measurements was used [49]. In the case of aquatic flora and fauna, the standard deviation of the average atmospheric measurements throughout the growing season was used.

Calculation of reservoir ages for samples from a sediment core

In the case of mollusc samples from a sediment core, we need an independent control of the true age of the molluscs to calculate their reservoir ages. In some cases, shell and terrestrial material from the same depth are available. The reservoir age R_{direct} is the difference between the ^{14}C age of the mollusc, $^{14}C_M$, and the ^{14}C age of the contemporaneous atmosphere, as determined by the ^{14}C age of a terrestrial sample, $^{14}C_T$:

$$R_{direct} = {}^{14}C_M(t) - {}^{14}C_T(t), \tag{4}$$

where t represents the calendar age as determined by the terrestrial age-depth model. When the contemporaneous ^{14}C age of the atmosphere cannot be assessed directly, i.e. terrestrial material is not available at the same depth, $^{14}C_T(t)$ is determined using the age model (to estimate t, Figure 2) in conjunction with the atmospheric calibration curve IntCal09 [45] to calculate the reservoir age R(t) as

$$R(t) = {}^{14}C_M(t) - {}^{14}C_T(t). \tag{5}$$

Similarly, the local ^{14}C reservoir age deviation from the global 'model' ocean, $\Delta R(t)$, can be estimated as the difference between a measured marine ^{14}C age, $^{14}C_M(t)$, and the contemporaneous marine ^{14}C age of the global 'model' ocean, $^{14}C_{MAR}(t)$:

$$\Delta R(t) = {}^{14}C_M(t) - {}^{14}C_{MAR}(t). \tag{6}$$

In this case, the calibrated age t of each mollusc sample is converted into a marine ^{14}C age, $^{14}C_{MAR}(t)$, by applying the global marine calibration curve Marine09 [45]. Errors on the calculated $\Delta R(t)$ values are estimated using 95% confidence intervals on the calibrated terrestrial age of each mollusc sample together with the measurement uncertainty on $^{14}C_M$, i.e. the error on the mollusc ^{14}C date.

Results and discussion

This presentation of the results starts with modern samples from Northern Germany. Then archaeological samples from the same region are discussed to assess the effect on samples from the past. Finally, the importance of the freshwater reservoir effect for radiocarbon dating in an estuarine environment is examined.

Modern river samples

On three occasions, in August 2007, September 2008 and July 2010, plants and animals were collected from the Northern German rivers Alster and Trave. Water samples were as well collected on these occasions and additionally in February 2009. Radiocarbon dates and δ^{13}C measurements on the modern river samples are presented in Table 1 and Figure 3. Radiocarbon ages between -70 and +2620 ^{14}C years lead to estimated reservoir ages of 350 to 3040 ^{14}C years. The atmospheric ^{14}C levels used for estimating reservoir ages are given in Table 1 as well. The mallard feather is the sample with the youngest ^{14}C age. It is not considered a truly aquatic sample and is therefore excluded from this discussion. The δ^{13}C values of modern river samples span a large range from -34.2 to -8.9‰.

The ranges in ^{14}C ages for water DIC, plants and fauna overlap. In general, DIC samples are older and more enriched in δ^{13}C than the biological materials from the same sampling date (Figure 3). Natural variations in ^{14}C levels between different reservoirs are amplified today

Table 1 Radiocarbon dates of modern water samples, aquatic plants and animals from Northern Germany

Radiocarbon dates of modern water samples, aquatic plants and animals from Northern Germany						
River, Year	**AAR**	**Species**	**pmC**	**^{14}C age**	**Res. age**	**δ^{13}C (‰VPDB)**
Alster, 2007	11779	Water DIC	78.30±0.30	1967±33	2418±35	-14.96±0.05 (DI)
Alster, 2008	12881	Water DIC	72.18±0.43	2619±48	3044±50	-10.92±0.05 (DI)
Alster, 2009	13612	Water DIC	82.75±0.36	1521±35	1871±38	-14.85±0.05 (DI)
Alster, 2010	14332	Water DIC	75.49±0.24	2259±26	2638±30	-14.27±0.05 (DI)
Trave, 2007	11780	Water DIC	86.45±0.57	1170±55	1623±55	-13.59±0.05 (DI)
Trave, 2008	12882	Water DIC	78.04±0.42	1992±44	2417±46	-11.30±0.05 (DI)
Trave, 2009	13611	Water DIC	86.38±0.35	1176±33	1527±36	-8.94±0.05 (DI)
Trave, 2010	14333	Water DIC	75.52±0.25	2255±27	2634±31	-11.86±0.05 (DI)
Alster, 2008	12873	subm. plant	75.36±0.38	2273±41	2694±439	-31.62±0.23 (EA)
Alster, 2010	14334	*Nuphar* leaf	76.83±0.24	2117±25	2472±602	-31.50±0.05 (DI)
Alster, 2010	14335	*Nuphar* petiole	78.51+0.23	1944±24	2299±602	-31.24±0.05 (DI)
Trave, 2008	12870	subm. plant	100.93±0.44	-74±35	347±439	-25.42±0.46 (EA)
Trave, 2008	12871	floating plant	89.64±0.41	879±37	1300±439	-28.09±0.73 (EA)
Trave, 2008	12872	subm. plant	80.93±0.55	1700±55	2120±440	-17.45±1.88 (EA)
Trave, 2010	14336	subm. plant	78.80±0.24	1914±24	2269±602	-34.22±0.05 (DI)
Trave, 2010	14337	subm./float.	85.45±0.24	1263±23	1618±601	-26.95±0.05 (DI)
Trave, 2010	14338	*Nuphar* leaf	96.48±0.24	288±20	643±601	-27.52±0.05 (DI)
Trave, 2010	14339	*Nuphar* petiole	97.04±0.30	241±25	596±602	-26.67±0.10 (EA)
Alster, 2007	11460	Mussel shell	85.98±0.37	1214±34	1654±381	-13.22±0.05 (DI)
Alster, 2007	11461	Snail shell	94.75±0.37	433±32	870±381	-15.36±0.05 (DI)
Alster, 2007	11462	Roach BC	97.27±0.35	223±29	661±381	-25.46±0.05 (DI)
Trave, 2007	11394	Roach BC	96.51±0.38	285±32	727±381	-25.91±0.05 (DI)
Trave, 2007	11396	Roach BC	97.01±0.34	244±28	685±380	-24.24±0.05 (DI)
Trave, 2008	12874	Mallard feather	104.77±0.41	-374±32	47±438	-23.99±0.11 (EA)
Trave, 2008	12875	Spined loach	81.29±0.39	1664±39	2085±439	-27.24±0.09 (EA)
Trave, 2008	12876	Crayfish	84.37±0.42	1365±40	1787±439	-27.89±0.46 (EA)
Trave, 2008	12878	Roach, flesh	99.17±0.40	67±32	488±438	-22.30±0.10 (EA)

Atmospheric ^{14}C-levels, used for estimating reservoir ages			
Timespan	**pmC**	**Timespan**	**pmC**
August 2007	105.80±0.21	growing season up to August 2007	105.64±4.99
September 2008	105.44±0.21	growing season up to September 2008	105.39±5.73
February 2009	104.47±0.21	growing season before February 2009	105.39±5.73
July 2010	104.83±0.21	growing season up to July 2010	104.52±7.82

Radiocarbon ages, estimated reservoir ages and δ^{13}C values of modern samples from Northern German rivers. Atmospheric ^{14}C levels, which were used for calculating reservoir ages, are shown as well (from [48] and pers. comm. I. Levin 2012). DIC: dissolved inorganic carbon. subm.: submerged. BC: bone collagen. DI: analyses on a CO_2 aliquot from the radiocarbon preparation, performed using a Dual Inlet IsoPrime stable isotope mass spectrometer. EA: analyses on pre-treated samples, performed by combustion in a EuroVector elemental analyser coupled to the mass spectrometer.

because of the presence of "bomb ^{14}C", an excess in atmospheric ^{14}C concentrations due to atomic bomb testing [46,47], which lead to a doubling of atmospheric ^{14}C levels until the 1960s. The FRE measured today is therefore not directly translatable to prehistoric samples.

Water

The δ^{13}C values and ^{14}C ages of the water DIC are correlated [32]. This reflects most likely the carbon source: dissolved ancient limestone has infinite ^{14}C ages and δ^{13}C values around 0‰; CO_2 from modern decaying organic

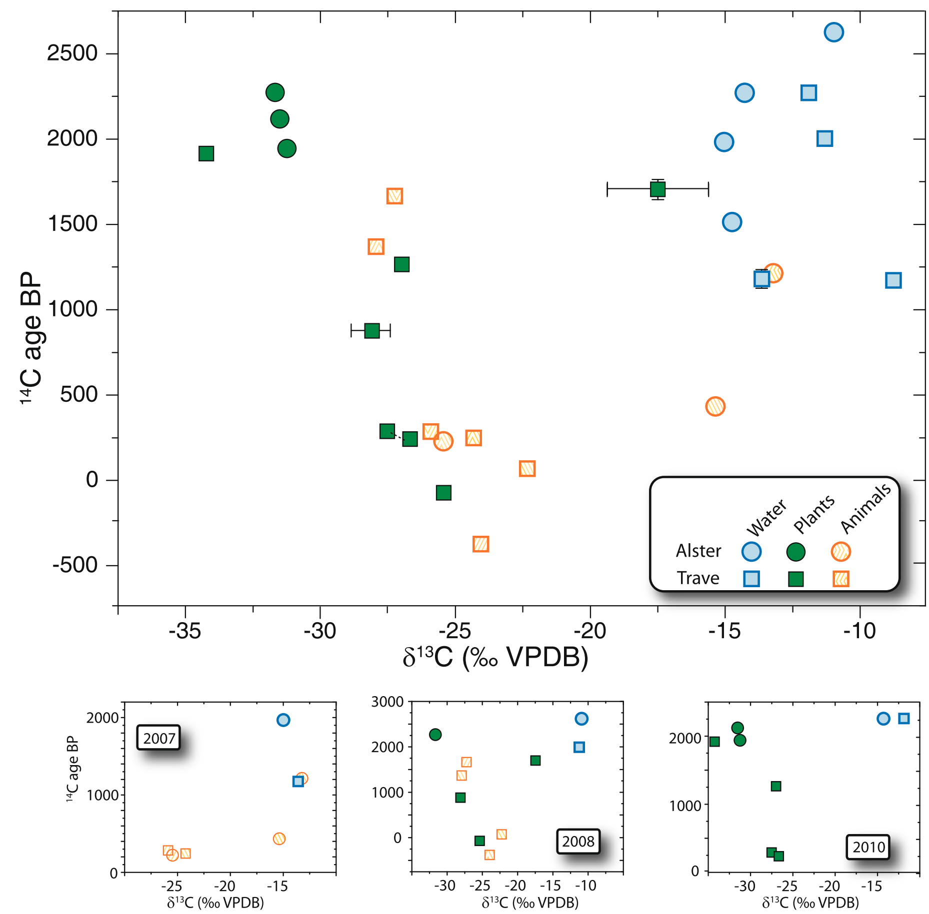

Figure 3 Radiocarbon dating of water, aquatic plants and animals. Radiocarbon ages (uncal. ^{14}C years BP) and δ^{13}C values of modern samples. The values of the water samples were measured on DIC, dissolved inorganic carbon, which is the carbon source for photosynthesis among aquatic plants. The three smaller graphs display the same measurements as the large one, divided after date of sampling. Note the different scales for the small graphs. In February 2009, only water samples were collected. This sampling date is therefore not represented by an extra graph. The error bars are in most cases smaller than the symbols and thus not visible on the graphs. See Table 1 for values and additional information about the samples, such as estimated reservoir ages.

matter has ^{14}C ages close to zero and δ^{13}C values around -25‰ (there is no fractionation between organic carbon and CO_2 under soil conditions as the corresponding biochemical reactions usually proceed to the end [50]). Old apparent ages of water DIC have already been measured in the first studies of the FRE. In 1954, for example, water samples from a hardwater lake in North America yielded ages of 2,200 years [5].

This two-component model, however, is too simple to describe the factors governing the DIC radiocarbon age: The ^{14}C age of Alster DIC is greater than that of Trave DIC for every sampling date but one, 2010; Alster DIC δ^{13}C values are generally lower than Trave DIC, except for 2008 (Table 1). If the only source for large radiocarbon ages were dissolved carbonate minerals, and the only source for small radiocarbon ages soil CO_2, then the low δ^{13}C values of the Alster would be inconsistent with the large ^{14}C ages. There are two possible explanations for this discrepancy: on the one hand, higher ages in the Alster could be caused by mineralisation of old organic matter, such as peat. On the other hand, lower ages in the Trave could be caused by the fact that the Trave flows through the shallow lake Wardersee [51]; this leads to a comparatively long residence time of the water, which facilitates exchange with atmospheric CO_2.

When scrutinizing precipitation records for Schleswig-Holstein, it was found that the amount of precipitation in the week prior to sampling is correlated negatively with the radiocarbon age and the δ^{13}C values of the water DIC. The more rain in the period before sampling, the younger the ^{14}C age, and the more negative the δ^{13}C values. During periods with less precipitation, on the other hand, the relative amount of groundwater with ancient dissolved carbonates appears to be larger in the rivers. See [32] for details.

Aquatic plants

Modern aquatic plants were found to have radiocarbon ages between -70 and +2270 BP, corresponding to estimated reservoir ages of 350–2690 ^{14}C years (Table 1). The average reservoir ages are 2490±200 ^{14}C years for the Alster and 1270±770 ^{14}C years for the Trave. A FRE of this order of magnitude is not uncommon for aquatic plants. From ^{14}C measurements of living aquatic plants and the contemporaneous atmosphere by Olsson et al. [52,53], reservoir ages of up to 2,000 years could be calculated for Swedish lakes. Also in Estonian hardwater lakes, a large range of reservoir ages, up to 2,700 ^{14}C years, has been measured [26].

The large age range, substantially more than 2000 ^{14}C years, and the great variability of ^{14}C ages of aquatic plants, is most likely caused by the multitude of available carbon sources for these plants. These include atmospheric CO_2, different DIC species in the water, CO_2 from decaying organic matter in the sediment, and nutrients stored in the rhizome of e.g. *Nuphar lutea*. These different carbon sources have potentially very different ^{14}C ages. Sediment organic matter, for example, can be recent, or some decades old and thus heavily affected by bomb carbon. However, as the plant samples were not pretreated (see page 3), minute amounts of DIC could have been present and might have caused older ages. Future studies will compare samples of aquatic plants with and without acid wash, and thus clarify this matter. The purely terrestrial date of a mallard feather that had been found floating on the river water, however, indicates that this risk is low.

The most striking result of the analysis of aquatic plants is the fact that floating leaves of aquatic plants do not have younger ^{14}C ages than submerged plants. A submerged plant with an estimated reservoir age of only 350 ^{14}C years contrasts with a floating plant, collected on the same day at the same part of the river, with a much higher reservoir age of 1300 ^{14}C years (Table 1). Floating and submerged parts of the same plant have the same radiocarbon age, as exemplified by two individuals of *Nuphar lutea*, where both the tip of the leaf and the end of the petiole were dated (Table 1).

Water lilies add a complicating factor to the multitude of possible carbon sources, as atmospheric air is transported from the younger leaves through petioles and rhizome to the older leaves, where most of the CO_2 from this transport is photosynthesized [54]. This continuous air transport is most likely the reason for petioles and leaves having the same ^{14}C ages. The large ages of the water lilies (Table 1) indicate a surprisingly large contribution from water CO_2 (CO_2, and not bicarbonate, is the DIC species *N. lutea* uses for photosynthesis), and a surprisingly little contribution from sediment CO_2. The CO_2 concentration in the sediment is much larger than that in the water or atmosphere, and sediment organic matter can be some decades old and therefore have a considerable excess of ^{14}C due to atomic bomb tests. It was reported that the aquatic plants which are capable of using sedimentary CO_2 are inhabitants of softwater environments, such as isoetids or similar plants; so far, no hardwater or marine species have been found to show significant root uptake of carbon [55].

These 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 [5,26]. The specimen of *N. lutea* analysed by Olsson and Kaup [26], however, originated from a softwater lake. The reservoir age of this water lily was calculated by comparing its ^{14}C activity with the ^{14}C activity of the contemporaneous atmosphere at Schauinsland [26,56]. Its leaves had a reservoir age of 39 years, while the stems had a negative reservoir age of -416 years. This is most likely caused by the fact that the plant grew during the decreasing part of the bomb peak: the stem was build using nutrients from the preceding growing season, stored in the rhizome [26].

In another study, however, *N. lutea* showed a full hardwater effect of about 500 years, while the white water lily *Nymphaea alba* had a terrestrial radiocarbon age [57].

Howsoever, I strongly recommend not to regard the floating leaves of any aquatic plant as terrestrial samples, even though the respective species might be known to assimilate atmospheric CO_2.

Aquatic animals

Radiocarbon ages between 70 and 1660 BP were measured on fish and molluscs from Alster and Trave. This leads to estimated reservoir ages between 490 and 2090 ^{14}C years (Table 1). The age range is thus almost as large as that of the aquatic plants. The average reservoir age of the animals from both rivers is 1120±620 ^{14}C years (excluding the mallard feather). For the Alster alone, the average reservoir age is 1060±520, and for the Trave, 1150±730. The large variability of radiocarbon ages for fish and other freshwater animals (Table 1) is not surprising, regarding the large variability on the basis of the food web, including water DIC and aquatic plants [58]. Furthermore, DIC (for photosynthesis of aquatic plants) is not the only carbon source for aquatic animals. Filter feeders can for example rely on organic carbon in the water. Variation of the FRE both between fish species as well as within species have been measured in modern and archaeological samples from lakes and rivers [59].

Some of the fish with high reservoir ages were used for cooking experiments, which showed that a food crust on pottery has the same reservoir age as the ingredients [18,31,60].

Interestingly, the average reservoir ages 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 reservoir ages than the plants. In the Trave, on the other hand, aquatic plants and animals have similar average reservoir ages. We have not yet been able to find a satisfactory explanation for these similarities and differences, and more samples are needed to draw any firm conclusions.

A high FRE has been measured in a multitude of other studies. Many modern mussels and fish from rivers and freshwater bodies from the Netherlands, for example, had apparent ages of over 2,000 years; the flesh of one fish even 4,430 years [61]. A present-day pike from Lake Aunsø, Denmark, had an apparent age of 684 ^{14}C years [62]. In Lake Tissø, Denmark, ten modern fish and mollusc samples had an average reservoir age of more than 1,000 ^{14}C years [16]. Aquatic plants collected from a river near Tereze, North Caucasus, have an estimated reservoir age of 800 years, while fish from the same river had a FRE of approximately 600 years [63]. At Elk Hills, California, a consistent freshwater reservoir offset of 340±20 ^{14}C years was measured for paired samples of freshwater shells and charcoal [64]. A FRE of 1,600 years in an Antarctic lake was probably caused by penguin guano, as the reservoir age of Antarctic sea water is between 1,000 and 1,700 years [23].

The degree of variability can expected to be lower for prehistoric samples, due to the absence of bomb ^{14}C. However, some variability of the FRE has already been measured for Stone Age samples: the reservoir age on human bones from the graveyard of Ostorf varied between -103 and 835 years, only weakly correlated with δ^{13}C and δ^{15}N values, thus probably indicating different reservoir ages of e.g. fish from different lakes [13]. Also in archaeological fish bone from England, a time and space variable FRE has been measured [27]. Early Neolithic fish bones from Åkonge, Denmark, have a broad FRE range as well: 115–480 ^{14}C years [16]. Variations in the reservoir age of lakes are furthermore determined by variations of e.g. the ratio between lake surface and lake volume (i.e. water depth), as groundwater DIC can enter the lake from the total underground surrounding the lake, while atmospheric exchange only takes place on the surface [65]. If a river, which past FRE is to be reconstructed, runs through a lake, another complicating factor is therefore added to the temporal variability of the FRE.

δ^{13}C values and the FRE

δ^{13}C values of plants and animals from Alster and Trave span a large range between -34.2 and -13.2‰ (Table 2, Figure 3). When excluding the three most enriched values of one aquatic plant and two shell samples, a tendency can be seen: flora and fauna with more depleted δ^{13}C values have older radiocarbon ages (Figure 3). The youngest samples have almost terrestrial δ^{13}C values. This relation seems to be typical of water bodies in regions with developed soils, and it was already indicated many decades ago: Aquatic plants and organic lake mud have been measured to have δ^{13}C values down to -30‰ [3], and fish that spent at least part of their live in freshwater systems were found to have δ^{13}C values significantly more negative than marine fish [66].

In regions or periods with less soil organic matter in the watershed, higher δ^{13}C values in the water and thus in the aquatic plants have to be expected. For example, aquatic plants from an early postglacial lake with age offsets of 1,500 to 2,000 years had average δ^{13}C values of -15.3‰ [67]. This is caused by the fact that most of the CO_2 for mineral weathering will be derived from the atmosphere in these cases, and not from decomposition of organic matter in the soil, as would be the case for mature vegetation and more developed soils [1,68]. This might be the explanation for Early Mesolithic Danish pike and otter bones having δ^{13}C values that would usually be classified as marine [62]. As a consequence, DIC δ^{13}C in freshwater systems can vary greatly, and values between 0 and -25‰ have been measured [69].

Archaeological samples from Northern Germany

Archaeological samples from the sites Kayhude/Alster and Schlamersdorf/Trave were acquired from museum archives. Terrestrial samples, bones of freshwater fish, and pottery sherds with food crusts were selected for analysis. The radiocarbon dates of these samples are presented in Table 2 and Figure 4.

Kayhude/Alster

Two terrestrial samples, four food crusts on pottery and one freshwater fish bone from Kayhude were radiocarbon dated. The samples from Kayhude are believed to be contemporaneous, as they were found embedded in a stone layer (part of the soft ground close to the former river/lake had been stabilised by stones, and the dated samples originated from between those stones). Still, the two terrestrial samples have very different radiocarbon ages: 5440 and 9150 BP. The older sample must be an admixture from earlier layers, as it is older than the oldest finds of the entire Ertebølle culture. This exemplifies that this stone layer 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.

The pike bone collagen is about 3000 ^{14}C years 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.

Table 2 Radiocarbon dates of archaeological samples from inland sites in Northern Germany

AAR	Species/material	^{14}C age BP	C/N ratio	δ^{13}C (‰VPDB)	δ^{15}N (‰AIR)
		Radiocarbon dates from Kayhude, Alster, Northern Germany			
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 mammal	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)	—
		Radiocarbon dates from Schlamersdorf, Trave, Northern Germany			
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; five vertebrae	—	3.27±0.02	-21.40±0.05 (EA)	4.75±23
11401	SL5-2913 BC fish; remaining BF	—	3.25±0.01	26.91±0.04 (EA)	7.91±44
11475	SLA5-2869 BC cyprinid	7770±100	—	—	—
11476	SLA5-2786 TC, red deer	6275±65	—	-23.63±0.05 (DI)	—
11476	SLA5-2786 TC, red deer (BF)	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 remains 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

Radiocarbon dates and stable isotope measurements (δ^{13}C, C/N, δ^{15}N) of archaeological samples from Kayhude/Alster and Schlamersdorf/Trave, Northern Germany. FC: food crust; BC: bone collagen; TC: tooth collagen; BF: bone fragment. DI: analyses on a CO_2 aliquot from the radiocarbon preparation, performed using a Dual Inlet IsoPrime stable isotope mass spectrometer. EA: analyses on pre-treated samples, performed by combustion in a EuroVector elemental analyser coupled to the mass spectrometer.

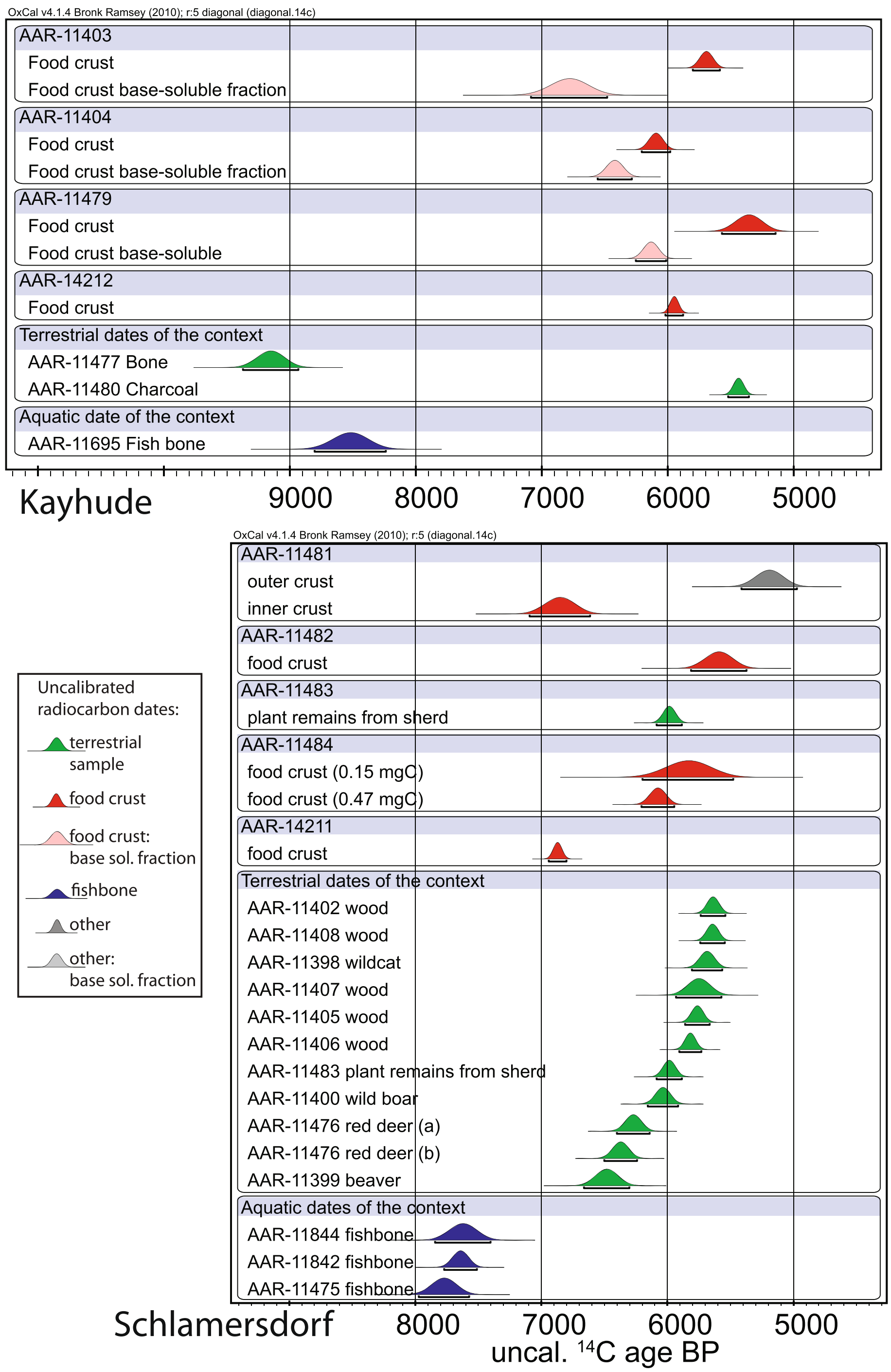

Figure 4 Radiocarbon ages of archaeological samples from Northern Germany. Uncalibrated radiocarbon ages BP of archaeological samples from Kayhude/Alster and Schlamersdorf/Trave, Northern Germany. Different sample types are marked with different colours. The graphs were made using OxCal 4.1.4 [75].

The age divergence of the two terrestrial samples shows that the association of the samples is insecure. However, 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 three other food crusts, AAR-11403, AAR-11404 and AAR-14212, reservoir ages of the order of magnitude of 300 to 600 ^{14}C years can be estimated. Compared to the average reservoir age of modern Alster animals, 1060±520 ^{14}C years, this would indicate 30% to 60% aquatic ingredients in the food crust. If we assume that the pike bone AAR-11695 is contemporaneous with the charcoal and food crust samples, then the reservoir age in the Mesolithic at Kayhude would be about 3000 ^{14}C years. This is very high, but not unrealistic, when comparing with the largest ^{14}C ages of modern plants and fish from this river. In this case, the reservoir ages of the food crusts AAR-11403, AAR-11404 and AAR-14212 would indicate only 10% to 20% aquatic ingredients. These are only thought experiments, though, and not secure calculations of percentage aquatic diet, due to the above-mentioned unsecurity of the context of the samples. If the charcoal sample was influenced by the old wood effect, for example, the reservoir effect calculated here would be underestimated by up to several hundred years.

The base-soluble fraction of three food crusts has also been dated. It may consist of partly original material, e.g. fatty substances [70], 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.

The calibrated ages of the three food crust samples are in the interval 5200–4000 cal BC, younger than the previously dated food crust sample with an age of 5400 cal BC [71].

Schlamersdorf/Trave

From Schlamersdorf at the river Trave, nine terrestrial samples, three fishbones and five food crusts on pottery were dated. The age range of terrestrial samples is very broad, about 1000 years (Figure 4). The food crusts have the same age as the terrestrial samples or are slightly older. The fishbone collagen is significantly older than the terrestrial samples. The terrestrial age range of Schlamersdorf complies with earlier charcoal dates from this site [72]. The broad age range measured here is unlikely to indicate an occupation period of 1000 years. 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: It is unclear whether the pottery from this site is associated with the older or with the younger terrestrial dates.

Three food crusts had previously been dated to around 5300 cal BC (6300–6100 uncal BP) [73]; their δ^{13}C values between -28.6 and -31.9‰ indicate a possibility of freshwater ingredients and thus the possibility of a freshwater reservoir effect [74]. In some cases, also terrestrial ingredients can have such low δ^{13}C values, e.g. caused by a canopy effect. However, this is unlikely, especially for δ^{13}C = -31.9‰, as no terrestrial wood sample from Schlamersdorf has δ^{13}C values below -29‰ (Table 2). Furthermore, the terrestrial animal with the lowest δ^{13}C value, a red deer tooth collagen sample with δ^{13}C = -23.6‰, would have a flesh value of about -29.1‰, assuming a flesh–bone collagen fractionation of 5.5‰. The δ^{13}C value of one of the food crusts is thus significantly lower.

Two of the four food crusts radiocarbon dated from that site are from 5500–6000 BP (which would be about 4000–5000 cal BC), and two around 7000 BP (corresponding to an age range from 5600 to 6000 cal BC; Figure 4). However, as the average reservoir age in modern Trave animals is 1150±730 ^{14}C years, the old ages of the two 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 could likely be about one thousand ^{14}C years. 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 c. 4000–5000 cal BC.

An interesting case is the potsherd AAR-11481 of which both 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 approximately 2000 years, or more, if the outer crust had been affected by an old wood effect. As this outer crust is younger than all the other terrestrial samples, it could be 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, if the carbon content of both samples was the same. Here, the carbon yield of the outer crust is with 4.8% significantly higher than that of the inner crust (1.7%). The outer crust would therefore be affected *less* by contamination. It is therefore unlikely that its surprisingly young age is caused by modern contamination.

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 v4.1.2 [75] and the IntCal04 atmospheric curve [76]. The probability for the pottery being older than 5000 cal BC is thus less than 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, assuming that the time of forming and time of using the pottery were closely together.

The hardwater effect at Schlamersdorf and Kayhude seems to be larger than the effect reported by Fischer and Heinemeier (2003, [16]), at least for the fish bones.

In their study area, the Åmose on Zealand, Denmark, the fish was 100 to 500 ^{14}C years older than the archaeological context, while the food crusts were up to 300 ^{14}C years older. However, the lack of clearly associated samples from Kayhude and Schlamersdorf makes it difficult to give more than rough estimates of the FRE.

Although some researchers doubt the existence of the FRE in food crusts on pottery [77], there seems to be more and more indications of its presence. For example, Sergant et al. 2006 [78] reported age offsets between pottery and short-lived terrestrial samples of several hundred years. Swifterbant pottery food crusts from a Belgian site were on average 320±159 ^{14}C years older than plant material, and only three food crust ages overlapped with the age range of terrestrial plants [15]. As all these food crusts had $\delta^{13}C$ values below -25‰, the FRE was suggested to be the cause for the age offset [15]. On Åland, food crusts from Östra Jansmyra I and Vargstensslätten II were dated to around 5,000 BC, while hazelnut shells from Östra Jansmyra II were about 1,000 years younger [79]. The FRE might explain the surprisingly old food crust dates, although it is difficult to be certain, as the samples were not associated directly. Food crust dates on Estonian pottery with textile impressions were 1,000 years older than hitherto assumed [80].

The FRE is also a potential error source in radiocarbon dating of pottery from coastal sites, where a predominance of marine resources would be expected. On coastal Lithuanian sites such as Nida on the bank of the Currish Lagoon, $\delta^{13}C$ values below -25‰ indicate freshwater resources, and food crust ^{14}C dates appeared 400 to 500 years older than the earliest terrestrial dates from the same site [81]. Pottery from the Danish fjord sites Bjørnsholm and Norsminde showed evidence for the heating of fish oils, but interestingly, not for marine ingredients, in spite of the availiability of marine resources [82].

The marine reservoir effect in pottery should not be neglected, though. A special risk lies in the fact that partly marine food crusts can have the same $\delta^{13}C$ values as the bone collagen of terrestrial animals. For example, $\delta^{13}C$ values between -22.0 and -24.7‰ of food remains on pottery belonging to the Pitted Ware Culture were interpreted as reflecting terrestrial origin, although the radiocarbon dates were older than expected [83]. However, terrestrial plants and fat and flesh of terrestrial animals usually have more negative $\delta^{13}C$ values, around ca. -25‰, while the bone collagen of terrestrial animals is more enriched. Food crust values which are more enriched than -25‰ indicate therefore the presence of marine resources. Similarly, the $\delta^{13}C$ values of food crusts from Tybrind Vig, mean $\delta^{13}C$ = -23±1‰, indicate a strong marine component [84], but were originally interpreted as being terrestrial [85].

FRE are also of possible concern in areas which are usually not connected with subsistence based on the exploitation of aquatic resources. Clay pots of the Catacomb Cultures of the North-West Caspian steppe, for example, contain evidence for fish processing such as bones and scale remains of freshwater fish [14]. Generally, fishing is almost always underrepresented in the archaeological record relative to traces of hunting [86].

Another complicating factor is the possibility of different pieces of food charring on different locations in the vessel. This has been found in experiments [31], but also in one prehistoric vessel: An age difference of 1100 years was measured on food crusts on sherds that were believed to belong to the same vessel [87]. Furthermore, some ingredients char more easily on the vessel walls than others [31,60,88].

Different experiments have shown that isotopic ratios of food only change slightly during cooking [88-92], and that food crust isotope ratios do not change during burial [89], or only change slightly [93]. Stable isotope measurements can therefore be useful for roughly distinguishing different food sources. It is important here not only to measure $\delta^{13}C$ values, but also $\delta^{15}N$ values, as "terrestrial" $\delta^{13}C$ values can be the result of mixed marine and freshwater resources [61].

Sediment core samples from the Limfjord

As described in section "Materials and methods", terrestrial samples and molluscs from the sediment core were radiocarbon dated, a terrestrial age model was constructed, and ΔR values were calculated. The radiocarbon results and the age model are shown in Figure 2.

The ΔR values range from -140 to 300 ^{14}C years (Figure 5), which is within the same order of magnitude as the values measured on 19th and 20th century (pre-bomb) shells from the Limfjord [28].

Based on the temporal variability of the local reservoir age deviation ΔR, the core has been visually divided into four time intervals, denoted zones 1–4 (Figure 5). This division is supported by other proxies, as described in [33] and [31]. Figure 5 displays the development of ΔR from c. 5400 BC to AD 700.

In zone 1, the reservoir age is slightly larger than the marine 'model' age. In zone 2, ΔR varies between -150 and +300 ^{14}C years, corresponding to reservoir ages between 250 and 700 ^{14}C years. Throughout zone 3, the reservoir age decreases slightly, but steadily, from small positive to small negative ΔR values. Variability increases again in zone 4.

In three cases, R_{direct} can be calculated by comparing the ^{14}C ages of a shell sample and a terrestrial sample from the same depth (Table 3). The differences between R_{direct} and $R(t)$ values are 8±151, -79±200 and

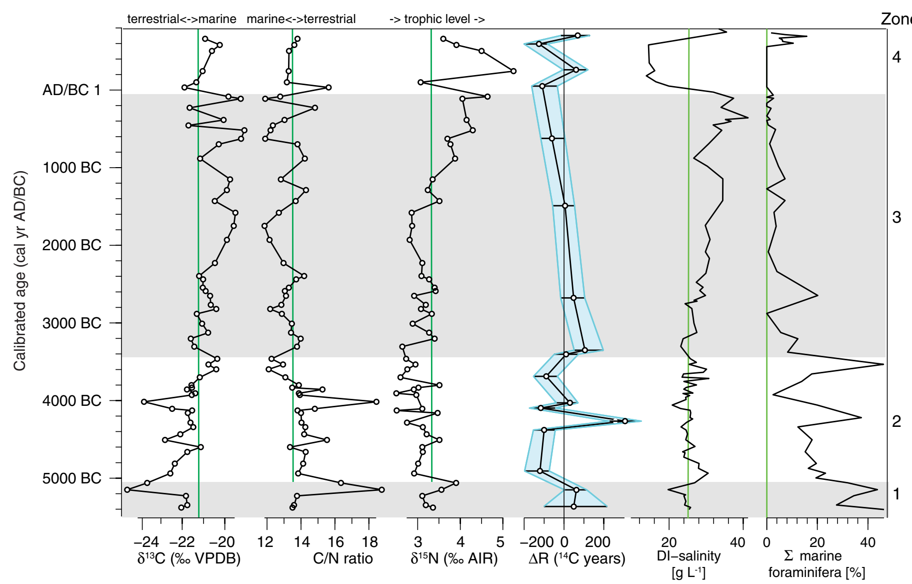

Figure 5 Palaeoenvironmental proxies and reservoir ages in the Limfjord. ΔR and supporting palaeoenvironmental proxies: δ^{13}C, C/N and δ^{15}N of bulk sediment organic matter, diatom-inferred salinity (DI-salinity) and percentage marine foraminifera species. The time axis is given as calibrated ages AD/BC. ΔR is the deviation from marine reservoir age, as described in section "Materials and methods".

57±78 ^{14}C-years. The values thus agree within errors. There is no correlation between shell species and reservoir age, suggesting that species effects due to different feeding habits or burrowing depths have no significant influence on the reservoir age. A similar conclusion was reached by studies of three other Danish fjords [29] and the North Icelandic shelf [94]. In other studies, though, an influence of the habitat and diet of shellfish on the reservoir age has been observed (e.g. [95]).

During inferred marine conditions, it can be expected that the Kilen reservoir age R is c. 400 years ($\Delta R \approx 0$). More variable reservoir ages may be expected during inferred brackish conditions. Very high reservoir ages ($\Delta R > 0$) most likely indicate influence of ^{14}C free carbonates, i.e. the hard-water effect, from groundwater or river discharge of dissolved carbonates. In contrast, low reservoir ages ($\Delta R < 0$) can be caused by increased CO_2 exchange at the water-atmosphere boundary, or by surface-water runoff or mineralisation of contemporaneous terrestrial organic matter. Similar variations were found in other Danish fjords [29], with reservoir ages up to 900 years [28]. Other coastal environments show high reservoir ages as well: In a Swedish isostatically isolated basin, reservoir effects as high as R = 1,100 to 700 ^{14}C years were measured on clay gyttja that was deposited during the most saline coastal Litorina phase [96]. On the coast of Oman, a reservoir age of 645±40 ^{14}C years was measured on samples from graves from the 4th millennium BC [97].

In Norwegian mollusc samples, freshwater influence lowered the reservoir effect [98]: reservoir ages were found to be lower in the fresher, uppermost surface water along the inner coast and in the fjords (ΔR between -150 and -100 years). Also on the coast of central Queensland, Australia, estuarine ^{14}C dates are highly complex due to variations in terrestrial carbon input and exchange with the open ocean [30].

Lastly, variations in the marine reservoir age itself should be kept in mind. Small fluctuations in the Kilen reservoir age might be result of these variations. However, this is more likely to happen in regions with variations in the upwelling of deep-sea water [95,99,100].

The supporting proxies presented in Figure 5 are stable isotope measurements on bulk sediment organic matter: δ^{13}C, C/N ratio and δ^{15}N; salinity reconstructed from diatom assemblages; and the percentage of all marine foraminifera species [33]. δ^{15}N values most likely reflect δ^{15}N values of source organic matter. Increasing δ^{15}N values after c. 4000 cal. BP (c. 2000 BC) are here interpreted as a manuring signal from the surrounding grassland, due to increased dependence on cattle farming [33]. δ^{13}C values and C/N ratios are strongly correlated [33]. They indicate source organic matter and distinguish between allochthonous terrestrial organic matter and autochthonous organic matter. A linear mixing of marine and terrestrial organic matter can be observed.

The percentage of marine foraminifera species indicates bottom-water salinity [33,36]. The surface-water salinity

Table 3 Kilen radiocarbon dates

Radiocarbon dates from Kilen, Limfjorden, Denmark						
Sample ID	**Depth (cm bpsl)**	**Species/ Material**	**^{14}C age (uncal. BP)**	**Model age (cal yr BP)**	**ΔR (^{14}C years)**	**$\delta^{13}C$ (‰VPDB)**
AAR-12150	459-460	1 lf, 1 *Betula* sp. fruit, 2 bss, 1 *Cyperaceae* seed	1315±65			*-27*
AAR-13213	463-464	*Tapes sp.* [28-33]	1733±34	1247±64	61±112	1.59
AAR-12151	472-473	1 flower *Quercus* sp.	1440±65			*-27*
AAR-13214	473-474	*Corbula gibba* [15-20]	1684±34	1357±53	-142±69	1.78
UBA-16568	503-504	*Corbula gibba* [15-20]	2161±35	1689±68	57±66	14*
AAR-13215	522-523	*Cerastoderma edule* [6]	2193±33	1899±72	-102±75	2.85
AAR-12152	523-524	1 *Scirpus* seed	1880±60			*-27*
AAR-13216	601-603	*Abra alba* [20]	2754±46	2572±116	-55±87	0.89
AAR-12142	603-605	1 lf	2464±40			-26.87
AAR-12143	745-747	1 tf + bark	3215±35			-28.38
AAR-13217	751-753	*Cardium* sp.	3556±39	3439±48	-1±62	1.44
AAR-12144	975-977	1 tf + bark; cf *Salix* sp.	4132±45			-27.27
AAR-13218	975-977	*Abra alba* [20]	4500±48	4628±79	41±71	0.58
AAR-12145	1149-1151	1 lf	4635±75			-28.19
AAR-13219	1149-1151	*Corbula gibba* [15-20]	5028±50	5301±66	59±108	1.89
AAR-13220	1169-1171	*Corbula gibba* [15-20]	5096±34	5353±62	70±85	0.70
AAR-11463	1171-1175	206 lfs, 3 *Betula* sp. fruits, 1 bud, 1 bs	4635±40			-28.36
AAR-12146	1279-1281	1 *Alnus* sp. t + bark	4848±42			-28.61
AAR-13221	1279-1281	*Abra alba* [20]	5199±46	5638±47	-91±66	1.09
AAR-12147	1399-1401	97 lfs	5225±40			-27.52
AAR-13222	1403-1405	*Abra alba* [20]	5621±39	5974±45	28±66	0.47
UBA-16569	1427-1429	*Abra alba* [20]	5545±58	6047±49	-106±61	5.6*
AAR-12148	1483-1487	11 lfs	5260±90			*-27*
AAR-13223	1487-1489	*Bittium reticulatum* [25]	6090±65	6214±59	298±108	2.54
UBA-16570	1527-1529	*Corbula gibba* [15-20]	5825±29	6329±66	-105±98	1.8*
AAR-13224	1711-1713	*Corbula gibba* [15-20]	6241±34	6857±95	-140±89	1.12
AAR-12149	1715-1717	43 lfs	6120±65			*-27*
UBA-16571	1819-1821	*Corbula gibba* [15-20]	6616±30	7100±89	58±103	4.3*
AAR-11464	1923-1927	25 lfs	6405±60			*-25*
AAR-13225	1927-1929	*Tellimya ferruginosa* [30]	6850±150	7314±71	55±172	0.96

Radiocarbon dates of shells and terrestrial macrofossils from a sediment core at Kilen, Limfjorden, Denmark. *lf* leaf-fragment, *lfs* leaf-fragments, *bs* bud-scale, *bss* bud-scales, *t* twig, *tf* twig-fragment. *Scirpus* seed: *Scirpus maritimus/ lacustris*. Numbers in squared brackets denote minimum salinity tolerances according to Sorgenfrei (1958). δ^{13}C marked by an asterisk were measured by the accelerator and can only be used for normalisation of the ^{14}C dating, not for drawing palaeoenvironmental conclusions. Some samples were too small to allow for δ^{13}C measurements; in these cases, δ^{13}C = -27‰ was assumed to normalise the ^{14}C dating.

was reconstructed from diatoms [36]. The δ^{13}C values also correlate with a diatom-inferred quantitative reconstruction of surface salinity and can thus be used as a proxy for salinity estimation in the photic zone. During brackish conditions, sediment organic matter is dominated by terrestrial input, whereas marine conditions enhance autochthonous production [33]. The potential of sediment δ^{13}C values as salinity proxy was already suggested by Hedenström and Possnert, 2001 [96], and further explored by e.g. Mackie et al. [101,102].

The salinity changes observed in zones 3 to 4 are suggested to show increased marine influence in the western part of the Limfjord (through the western opening of the fjord towards the North Sea), whereas the northern openings diminished as a result of isostatic uplift, aeolian sand transport and redeposition of sediment by ocean currents, mainly the Jutland Current. Additionally, reduced connection of Kilen to the Limfjord should be considered. Further work from sites in the northern Limfjord is needed, however, to explore this.

As the reservoir ages are highly variable in zones 1, 2 and 4, no single value for a reservoir correction can be obtained. Between 5000 and 2000 cal yr BP, however, a marine reservoir age of $\Delta R=0$ (R=400 ^{14}C years) can be applied to samples from the Limfjord.

Conclusion

In modern river samples, the freshwater reservoir effect is large and variable even on short time scales. The reservoir age of water DIC depends on precipitation amounts prior to sampling. Differences between adjacent rivers can be caused by differences in residence time, or differences in concentrations of ^{14}C-deficient carbonates or organic material in the watershed. The radiocarbon age range of modern aquatic plants spans more than 2000 ^{14}C years. This is most likely caused by the multitude of carbon sources available for these plants, including different DIC species, atmospheric CO_2, and CO_2 from decaying vegetation in the river sediments or in the catchment. It should be stressed that floating leaves of aquatic plants, although assimilating atmospheric CO_2, can not be regarded as terrestrial samples. These results indicate that it is impossible to find a single freshwater reservoir age for a given river system. A few samples of water, plants or fish from a river are not sufficient to characterise the ^{14}C age of a water body. However, the freshwater reservoir effect might still be “correctable” for archaeological samples: Reservoir age fluctuations are expected to be less pronounced for pre-bomb samples; organic matter with an actual age of a few decades can be heavily affected by bomb carbon and thus reduce a sample’s radiocarbon age significantly. Furthermore, samples accumulating carbon over longer time scales, such as human bones, show average reservoir ages. These might be quite uniform for individuals with similar nutrition habits.

Analyses on archaeological samples indicate the necessity of direct pottery dating, as securely associated terrestrial samples are difficult to find for the assumedly earliest pottery in Northern Germany. A freshwater reservoir effect is likely for the food crusts on pottery from the Ertebølle sites Kayhude and Schlamersdorf. A strong indicator for this is a sherd where both inner and outer crust have been dated, yielding an age difference of approximately 2000 years. The true age of the pottery at Schlamersdorf might be indicated by the radiocarbon date of a plant remain found within the ceramic matrix. A radiocarbon age of about 6000 BP implies that the pottery most likely was produced after 5000 cal BC. In all probability, the earliest pottery from inland sites in Schleswig-Holstein has the same age as Ertebølle pottery from coastal sites. The origins of pottery in Schleswig-Holstein can thus equally likely derive from Eastern European hunter-gatherer pottery traditions, as well as from southwestern influences from agricultural communities in central Germany.

Reservoir age measurements from a core from the Limfjord exemplify that freshwater influence can cause fluctuations of the coast-near marine reservoir ages of up to several hundred years. Freshwater influence can both increase and decrease the reservoir age. A marine reservoir correction can thus not be applied to estuarine samples. So far, stable isotope measurements on shells or sediment organic matter can not be used to predict the reservoir effect. The variable coastal reservoir effect should be kept in mind when radiocarbon dating marine samples, pottery or human bones from coastal sites, as coast-near fishing and shell collection are ascertained for many prehistoric periods.

Competing interests
The authors declare that they have no competing interests.

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