The freshwater reservoir effect in radiocarbon dating

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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].
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 CO₂, 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 CO₂ 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 oxidation of old organic matter [24], the inflow of water from a glacier containing old CO₂, or old CO₂ 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 Schlammersdorf 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 Schlammersdorf/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 CO₂(aq), H₂CO₃(aq), HCO₃⁻(aq) and CO₃²⁻(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 HgCl₂ solution. This prevented the growth of algae, which would have converted some of the DIC into organic
carbon. The samples were kept dark and cool until analysis. The water was acidified with 100% H₃PO₄, which converted all DIC into CO₂. N₂ was bubbled through the water to free the CO₂, 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 CO₂ 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 (bpl). The sediments consist of homogeneous grey-brown marine clay gyttja. This study focuses on the part between 467 and 1935 cm bpl which was subsampled at 1–2 cm depth intervals. Material for AMS ¹⁴C 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 KMnO₄ at 80°C. 13–14 mg of pretreated shell was dissolved in 100% H₃PO₄ at 25°C, to produce CO₂ for ¹⁴C-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 CO₂ by combustion in sealed evacuated quartz tubes containing CuO.
Radiocarbon dating

For radiocarbon dating, CO₂ from the combusted or acidified samples was converted to graphite with the H₂ reduction method [42]. It was measured at the AMS ¹⁴C Dating Centre at Aarhus University (AAR-numbers) or at the ¹⁴CHRONO Centre, Queen’s University Belfast (UBA-numbers). The dating results are reported as conventional ¹⁴C dates in ¹⁴C 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 CaCO₃ 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, ¹³C/¹²C, are essential for normalising ¹⁴C-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 CO₂ 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 ¹⁴C Dating Centre at Aarhus University. Most samples yielded enough material for replicate measurements. δ¹³C values are reported as ‰ VPDB. δ¹⁵N 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 CO₂ aliquot from the radiocarbon preparation were performed using a Dual Inlet IsoPrime stable isotope mass spectrometer at the AMS ¹⁴C Dating Centre at Aarhus University. δ¹³C 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 ¹⁴C age between an aquatic sample and a contemporaneous terrestrial sample. It is calculated by subtracting the ¹⁴C age of a terrestrial sample ¹⁴C_T from the ¹⁴C age of the contemporaneous aquatic sample ¹⁴C_A:

\[ R = ¹⁴C_A - ¹⁴C_T. \]

Finding the ¹⁴C 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 ¹⁴C ages are negative, the ¹⁴C age measured on an aquatic sample would underestimate
the reservoir effect. Therefore, both the aquatic sample and a modern terrestrial sample are dated. Measurements on atmospheric $^{14}\text{C}$O$_2$ (e.g. [48]) provide a convenient record of terrestrial references. The reservoir age $R$ in $^{14}\text{C}$ years is calculated from the difference in $^{14}\text{C}$ ratios, which are given as percent modern carbon, pmC ($^{14}\text{C}_\text{A}$ for the aquatic, pmC$_T$ for the terrestrial sample; see [43] for details on notation and reporting of radiocarbon data):

$$R = 8033 \cdot \ln \frac{\text{pmC}_T}{\text{pmC}_A},$$  \hspace{1cm} (2)

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

$$s(R) = 8033 \cdot \sqrt{\left(\frac{\Delta \text{pmC}_A}{\text{pmC}_A}\right)^2 + \left(\frac{\Delta \text{pmC}_T}{\text{pmC}_T}\right)^2}.$$ \hspace{1cm} (3)

For the $^{14}\text{C}$ content of the contemporaneous atmosphere at the time of sample formation, pmC$_T$, measurements from the Black Forest station Schaunsland 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 $^{14}\text{C}$ from a nearby nuclear power plant and $^{14}\text{C}$-free CO$_2$ from industry, heating and transport [49].

Water DIC $^{14}\text{C}$-concentrations measured in this study will be compared with those of the atmosphere in the month of sampling, and aquatic plant $^{14}\text{C}$-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 $^{14}\text{C}$ 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 $\pm2\%$ 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 $R_{\text{direct}}$ is the difference between the $^{14}\text{C}$ age of the mollusc, $^{14}\text{C}_M$, and the $^{14}\text{C}$ age of the contemporaneous atmosphere, as determined by the $^{14}\text{C}$ age of a terrestrial sample, $^{14}\text{C}_T$:

$$R_{\text{direct}} = {^{14}\text{C}_M(t)} - {^{14}\text{C}_T(t)},$$  \hspace{1cm} (4)

where $t$ represents the calendar age as determined by the terrestrial age-depth model. When the contemporaneous $^{14}\text{C}$ age of the atmosphere cannot be assessed directly, i.e. terrestrial material is not available at the same depth, $^{14}\text{C}_T(t)$ 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

$$R(t) = {^{14}\text{C}_M(t)} - {^{14}\text{C}_T(t)}.$$  \hspace{1cm} (5)

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

$$\Delta R(t) = {^{14}\text{C}_M(t)} - {^{14}\text{C}_\text{MAR}(t)}.$$  \hspace{1cm} (6)

In this case, the calibrated age $t$ of each mollusc sample is converted into a marine $^{14}\text{C}$ age, $^{14}\text{C}_\text{MAR}(t)$, 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 $^{14}\text{C}_M$, i.e. the error on the mollusc $^{14}\text{C}$ 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 $\delta^{13}\text{C}$ measurements on the modern river samples are presented in Table 1 and Figure 3. Radiocarbon ages between -70 and +2620 $^{14}\text{C}$ years lead to estimated reservoir ages of 350 to 3040 $^{14}\text{C}$ years. The atmospheric $^{14}\text{C}$ levels used for estimating reservoir ages are given in Table 1 as well. The mallard feather is the sample with the youngest $^{14}\text{C}$ age. It is not considered a truly aquatic sample and is therefore excluded from this discussion. The $\delta^{13}\text{C}$ values of modern river samples span a large range from -34.2 to -8.9‰.

The ranges in $^{14}\text{C}$ ages for water DIC, plants and fauna overlap. In general, DIC samples are older and more enriched in $\delta^{13}\text{C}$ than the biological materials from the same sampling date (Figure 3). Natural variations in $^{14}\text{C}$ levels between different reservoirs are amplified today.
Table 1 Radiocarbon dates of modern water samples, aquatic plants and animals from Northern Germany

| River, Year | AAR     | Species      | pmC    | \( ^{14} \text{C} \) age | Res. age | \( \delta^{13} \text{C} \) (\%/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±43 | -31.62±0.23 (EA)              |
| Alster, 2010 | 14334   | Nuphar leaf  | 76.83±0.24 | 2117±25                  | 2472±60 | -31.50±0.05 (DI)              |
| Alster, 2010 | 14335   | Nuphar petiole| 78.51±0.23 | 1944±24                  | 2299±60 | -31.24±0.05 (DI)              |
| Alster, 2010 | 14336   | subm. plant  | 100.93±0.44 | -74±35                  | 347±43 | -25.42±0.46 (EA)              |
| Alster, 2010 | 14337   | floating plant| 89.64±0.41 | 879±37                  | 1300±43 | -28.09±0.73 (EA)              |
| Alster, 2010 | 14338   | subm. plant  | 80.93±0.55 | 1700±35                  | 2120±40 | -17.45±1.88 (EA)              |
| Alster, 2010 | 14339   | Nuphar leaf  | 78.80±0.24 | 1914±24                  | 2269±60 | -34.22±0.05 (DI)              |
| Alster, 2010 | 14340   | Nuphar petiole| 97.04±0.30 | 241±25                   | 596±60 | -26.67±1.10 (EA)              |
| Alster, 2007 | 11460   | Mussel shell | 85.98±0.37 | 1214±34                  | 1654±38 | -13.22±0.05 (DI)              |
| Alster, 2007 | 11461   | Snail shell  | 94.75±0.37 | 433±32                   | 870±38 | -15.36±0.05 (DI)              |
| Alster, 2007 | 11462   | Roach BC    | 97.27±0.35 | 223±29                   | 661±38 | -25.46±0.05 (DI)              |
| Alster, 2007 | 11394   | Roach BC    | 96.51±0.38 | 285±32                   | 727±38 | -25.91±0.05 (DI)              |
| Alster, 2007 | 11396   | Roach BC    | 97.01±0.34 | 244±28                   | 685±38 | -24.24±0.05 (DI)              |
| Alster, 2008 | 12874   | Mallard feather| 104.77±0.41 | -374±32                  | 47±43 | -23.99±0.11 (EA)              |
| Alster, 2008 | 12875   | Spined loach | 81.29±0.39 | 1664±39                  | 2085±43 | -27.24±0.09 (EA)              |
| Alster, 2008 | 12876   | Crayfish    | 84.37±0.42 | 1365±40                  | 1787±43 | -27.89±0.46 (EA)              |
| Alster, 2008 | 12878   | Roach, flesh | 99.17±0.40 | 67±32                    | 488±43 | -22.30±0.10 (EA)              |

| Time span | pmC     | Time span | pmC     |
|-----------|---------|-----------|---------|
| August 2007 | 105.80±0.21 | growing season up to August 2007 | 105.64±0.99 |
| September 2008 | 105.44±0.21 | growing season up to September 2008 | 105.39±0.73 |
| February 2009 | 104.47±0.21 | growing season before February 2009 | 105.39±0.73 |
| July 2010   | 104.83±0.21 | growing season up to July 2010    | 104.52±7.82 |

Radiocarbon ages, estimated reservoir ages and \( \delta^{13} \text{C} \) values of modern samples from Northern German rivers. Atmospheric \( ^{14} \text{C} \) 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 CO2 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 \( ^{14} \text{C} \)”, an excess in atmospheric \( ^{14} \text{C} \) concentrations due to atomic bomb testing [46,47], which lead to a doubling of atmospheric \( ^{14} \text{C} \) levels until the 1960s. The FRE measured today is therefore not directly translatable to prehistoric samples. **Water**

The \( \delta^{13} \text{C} \) values and \( ^{14} \text{C} \) ages of the water DIC are correlated [32]. This reflects most likely the carbon source: dissolved ancient limestone has infinite \( ^{14} \text{C} \) ages and \( \delta^{13} \text{C} \) values around 0\( \% \); CO2 from modern decaying organic
matter has $^{14}$C ages close to zero and $\delta^{13}$C values around $-25\permil$ (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 $\delta^{13}$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 $\delta^{13}$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 Wardsee [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 $\delta^{13}$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 $\delta^{13}$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 14C years (Table 1). The average reservoir ages are 2490±200 14C years for the Alster and 1270±770 14C years for the Trave. A FRE of this order of magnitude is not uncommon for aquatic plants. From 14C 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 14C years, has been measured [26].

The large age range, substantially more than 2000 14C years, and the great variability of 14C ages of aquatic plants, is most likely caused by the multitude of available carbon sources for these plants. These include atmospheric CO2, different DIC species in the water, CO2 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 14C 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 age range 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 14C ages than submerged plants. A submerged plant with an estimated reservoir age of only 350 14C 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 14C 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 CO2 from this transport is photosynthesized [54]. This continuous air transport is most likely the reason for petioles and leaves having the same 14C ages. The large ages of the water lilies (Table 1) indicate a surprisingly large contribution from water CO2 (CO2, and not bicarbonate, is the DIC species N. lutea uses for photosynthesis), and a surprisingly little contribution from sediment CO2. The CO2 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 14C due to atomic bomb tests. It was reported that the aquatic plants which are capable of using sedimentary CO2 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 14C 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 14C activity with the 14C 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].

However, 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 CO2.

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 14C 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 14C 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 Aunso, Denmark, had an apparent age of 684 $^{14}$C years [62]. In Lake Tisso, 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 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 $\delta^{13}$C and $\delta^{15}$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.

$\delta^{13}$C values and the FRE
$\delta^{13}$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 $\delta^{13}$C values have older radiocarbon ages (Figure 3). The youngest samples have almost terrestrial $\delta^{13}$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 $\delta^{13}$C values down to -30‰ [3], and fish that spent at least part of their live in freshwater systems were found to have $\delta^{13}$C values significantly more negative than marine fish [66].

In regions or periods with less soil organic matter in the watershed, higher $\delta^{13}$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 $\delta^{13}$C values of -15.3‰ [67]. This is caused by the fact that most of the CO2 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 $\delta^{13}$C values that would usually be classified as marine [62]. As a consequence, DIC $\delta^{13}$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 | \(\delta^{13}C\) (‰VPDB) | \(\delta^{15}N\) (‰AIR) |
|-----|------------------|-------------------|-----------|------------------------|------------------------|
| 11403 | KAY8-432,01 FC pretreated | 5695±65 | 8.77±0.38 | -28.63±0.05 (CD) | 6.99±0.43 |
| 11403 | KAY8-432,01 FC not pretreated | — | 8.93±0.50 | -29.01±0.03 (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 (CD) | 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±80 | — | — | — |
| 11480 | KAY8-176,0 Charcoal | 5438±81 | — | -24.83±0.05 (CD) | — |
| 11695 | Pike BC | 8520±80 | — | -22.41±0.05 (CD) | — |
| 14212 | KAY8-435 FC pretreated | 5948±35 | 15.46±24.63 | -26.72±0.10 (EA) | — |
| 14212 | KAY8-435 FC not pretreated | — | 17.41±1.06 | -26.55±0.10 (EA) | 7.44±1.00 |
| 14212 | KAY8-435 FC base-soluble | 6130±80 | — | — | — |

Radiocarbon dates from Schlumersdorf, Trave, Northern Germany

| AAR | Species/material | \(^{14}C\) age BP | C/N ratio | \(\delta^{13}C\) (‰VPDB) | \(\delta^{15}N\) (‰AIR) |
|-----|------------------|-------------------|-----------|------------------------|------------------------|
| 11402 | SLA5-10000 Wood | 5638±49 | — | -26.49±0.05 (CD) | — |
| 11405 | SLA5-10001 Wood | 5762±48 | — | -27.25±0.05 (CD) | — |
| 11406 | SLA5-10002 Wood | 5818±43 | — | -28.78±0.05 (CD) | — |
| 11407 | SLA5-10003 Wood | 5750±90 | — | -27.03±0.05 (CD) | — |
| 11408 | SLA5-10004 Wood | 5642±48 | — | -27.47±0.05 (CD) | — |
| 11398 | SLS-2784 BC Wild cat | 5685±60 | 3.25±0.13 | -19.27±0.03 (CD) | 6.49±0.29 |
| 11399 | SLS-2761 BC beaver | 6480±90 | 3.59±0.11 | -22.42±0.03 (CD) | 4.68±0.89 |
| 11400 | SLS-2883 BC wild boar | 6035±60 | 3.24±0.01 | -21.39±0.05 (CD) | 5.01±0.13 |
| 11401 | SLS-2913 BC fish; five vertebrae | — | 3.27±0.02 | -21.40±0.05 (EA) | 4.75±0.23 |
| 11401 | SLS-2913 BC fish; remaining BF | — | 3.25±0.01 | -26.91±0.04 (EA) | 7.91±0.44 |
| 11475 | SLA5-2869 BC cyprinid | 7770±100 | — | — | — |
| 11476 | SLA5-2786 BC, red deer | 6275±65 | — | -23.63±0.05 (CD) | — |
| 11476 | SLA5-2786 BC, red deer (BF) | 6370±65 | — | -23.54±0.05 (CD) | — |
| 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 | -20.04±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 (CD) | — |
| 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 (CD) | — |
| 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 (CD) | 6.93±0.15 |

Radiocarbon dates and stable isotope measurements (\(\delta^{13}C\), C/N, \(\delta^{15}N\)) of archaeological samples from Kayhude/Alster and Schlumersdorf/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.
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 14C 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 14C years. This is very high, but not unrealistic, when comparing with the largest 14C 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 δ13C values between -28.6 and -31.9%o 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 δ13C values, e.g. caused by a canopy effect. However, this is unlikely, especially for δ13C = -31.9%o, as no terrestrial wood sample from Schlamersdorf has δ13C values below -29%o (Table 2). Furthermore, the terrestrial animal with the lowest δ13C value, a red deer tooth collagen sample with δ13C = -23.6%o, would have a flesh value of about -29.1%o, assuming a flesh–bone collagen fractionation of 5.5%o. The δ13C 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 14C years, the old ages of the two oldest pots 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 14C 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 oldest 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 14C 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 harderdata 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 Schlammersdorf 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 $320\pm 159$ $^{14}$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 $-25\%_o$, the FRE was suggested to be the cause for the age offset [15]. On Áland, food crusts from Östra Jansmyra I and Vargstenslätt 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 Curritish Lagoon, $\delta^{13}$C values below $-25\%_o$ 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 Bjornsholm and Norsminde showed evidence for the heating of fish oils, but interestingly, not for marine ingredients, in spite of the availability 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 $-24.7\%_o$ 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. $-25\%_o$, while the bone collagen of terrestrial animals is more enriched. Food crust values which are more enriched than $-25\%_o$ indicate therefore the presence of marine resources. Similarly, the $\delta^{13}$C values of food crusts from Tybrind Vig, mean $\delta^{13}$C = $-23\pm 1\%_o$, 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 $\Delta R$ values were calculated. The radiocarbon results and the age model are shown in Figure 2.

The $\Delta R$ 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 $\Delta R$, 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 $\Delta R$ from c. 5400 BC to AD 700.

In zone 1, the reservoir age is slightly larger than the marine 'model' age. In zone 2, $\Delta R$ 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 $\Delta R$ 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 $8\pm 151$, $-79\pm 200$ and
57±78 14C-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 (ΔR ≈ 0). More variable reservoir ages may be expected during inferred brackish conditions. Very high reservoir ages (ΔR >0) most likely indicate influence of 14C free carbonates, i.e. the hard-water effect, from groundwater or river discharge of dissolved carbonates. In contrast, low reservoir ages (ΔR <0) can be caused by increased CO2 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 14C 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 14C 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 14C 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: δ13C, C/N ratio and δ15N; salinity reconstructed from diatom assemblages; and the percentage of all marine foraminifera species [33]. δ15N values most likely reflect δ15N values of source organic matter. Increasing δ15N 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]. δ13C 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
was reconstructed from diatoms [36]. The δ¹³C 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 δ¹³C 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 by Hedenström and Possnert, 2001 [96], and further explored by e.g. Mackie et al. [101,102].

Table 3 Kilen radiocarbon dates

| Sample ID | Depth (cm bpsl) | Species/Material | ¹⁴C age (uncal. BP) | Model age (cal yr BP) | ΔR ¹⁴C years | δ¹³CVPDB |
|-----------|-----------------|------------------|--------------------|----------------------|--------------|-----------|
| 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 if               | 2464±40            |                      |              | -28.67    |
| 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±40            |                      |              | -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 ferruginoa [30] | 6850±150           | 7314±71              | 55±172      | 0.96      |

Radiocarbon dates of shells and terrestrial macrofossils from a sediment core at Kilen, Limfjorden, Denmark. If leaf-fragment, lfs leaf-fragments, bs bud-scale, bss bud-scales, t twig, ttw twig-fragment. Scirpus seed: Scirpus maritimus/ lacustris. Numbers in squared brackets denote minimum salinity tolerances according to Sorgenfrei (1958). δ¹³C marked by an asterisk were measured by the accelerator and can only be used for normalisation of the ¹⁴C dating, not for drawing palaeoenvironmental conclusions. Some samples were too small to allow for δ¹³C measurements; in these cases, δ¹³C = -27‰ was assumed to normalise the ¹⁴C dating.
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 Schlarmersdorf. 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 Schlarmersdorf 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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