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Methodological approaches to determining the marine radiocarbon reservoir effect

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Abstract

The marine radiocarbon reservoir effect is an offset in ^{14}C age between contemporaneous organisms from the terrestrial environment and organisms that derive their carbon from the marine environment. Quantification of this effect is of crucial importance for correct calibration of the ^{14}C ages of marine-influenced samples to the calendrical time-scale. This is fundamental to the construction of archaeological and palaeoenvironmental chronologies when such samples are employed in ^{14}C analysis. Quantitative measurements of temporal variations in regional marine reservoir ages also have the potential to be used as a measure of process changes within Earth surface systems, due to their link with climatic and oceanic changes. The various approaches to quantification of the marine radiocarbon reservoir effect are assessed, focusing particularly on the North Atlantic Ocean. Currently, the global average marine reservoir age of surface waters, R(t), is c.400 radiocarbon years, however, regional values deviate from this as a function of climate and oceanic circulation systems. These local deviations from R(t) are expressed as ΔR values. Hence, polar waters exhibit greater reservoir ages (ΔR = c. +400 to +800 ^{14}C y) than equatorial waters (ΔR = c.0 ^{14}C y).

Observed temporal variations in ΔR appear to reflect climatic and oceanographic changes. We assess three approaches to quantification of marine reservoir effects using known age samples (from museum collections), tephra isochrones (present onshore/offshore), and paired marine/terrestrial samples (from the same context in, for example, archaeological sites). The strengths and limitations of these approaches are evaluated using examples from the North Atlantic region. It is proposed that, with a suitable protocol, accelerator mass spectrometry (AMS) measurements on paired, short lived, single entity marine and terrestrial samples from archaeological deposits is the most promising approach to constraining changes over at least the last 5 ky BP.

Introduction

The marine radiocarbon reservoir effect is an offset in ^{14}C age between contemporaneous organisms that derive their carbon from the terrestrial environment and those organisms that live wholly or partly in the marine environment (e.g. foraminifera, fish, marine mammals, molluscs, etc) or that incorporate marine-derived carbon through ingestion (e.g. human consumption of fish and shell-fish, etc).
A fundamental assumption in ^{14}C dating theory is that there is global uniformity in the ^{14}C activity of living organisms and indeed, this is true for the well mixed atmosphere and the terrestrial flora and fauna that atmospheric carbon supports, provided that due corrections are made for the degree of isotopic fractionation that takes place during ^{14}C transfer through the food chain. In contrast, the oceans and the plant and animal life that they support represents a rather heterogeneous environment (irrespective of corrections for fractionation) that is depleted in ^{14}C relative to terrestrial flora and fauna (figure 1). This is brought about by the fact that a body of water can only take up atmospheric carbon while at the surface. Much of the formation of the ocean's deep waters occurs in the polar regions where gaseous exchange and cooling occur. Consequently, there is an increase in density that causes this water to sink away from the surface, thereby removing it from its carbon source. The slow mixing of water masses, which differ in the time since they were last at the ocean surface, results in an overall ^{14}C deficiency within the oceans relative to the atmosphere. This would not be a major problem if the world's oceans were uniformly mixed since a global age correction factor could be employed. However, circulation and mixing within the oceans are comparatively slow

processes and this leads to (i) marked geographical variations at the ocean surface, and (ii) significant depth variations in the degree of ^{14}C depletion. These will depend upon factors such as the stratification of water masses, rates of current movement, the length of time that a body of water is in contact with the atmosphere and the locations of water mass convergence and upwelling (Gordon and Harkness, 1992). Consequently, in terms of the conventional ^{14}C timescale, which is based on the ideal atmospheric/terrestrial situation, organisms containing marine carbon are all characterised by having a finite ^{14}C age immediately upon death, i.e. a reservoir age. This is an essential consideration when interpreting ^{14}C measurements made on such material and has implications for research within geographical, geological, and archaeological fields, particularly with respect to the construction of paleoenvironmental and archaeological chronologies.

Defining the Marine Reservoir Effect.

In order to determine calendar age ranges from ^{14}C measurements made on samples deriving their carbon from the atmospheric environment, calibration curves that are based on high precision radiocarbon dating of absolute-age tree ring sequences have been produced for the Holocene period to c.11, 000 BP (Stuiver and Braziunas, 1993). This record has been extended further back into Late Quaternary time (c.25, 000 BP) using coral sequences and cross calibrations with U/Th dating (Bard *et al.,* 1990; 1993; Burr *et al.,* 1998). However, it has long been recognised that accurate calibration is more complex when organisms are formed in carbon reservoirs other than the atmosphere, due to differences in initial specific ^{14}C activity (Stuiver *et al.*, 1986). To compensate for a reservoir effect in calibration calculations, an accurate value for the offset in ^{14}C activity is required. If the offset were constant, the correction for the marine reservoir effect could be achieved for by subtracting this factor from the measured sample ^{14}C age. However, because of the heterogeneous nature of the marine ^{14}C reservoir, the offset varies both spatially and temporally. In response to this problem, a calibration curve for marine samples was constructed by modelling the oceanic response to the variable atmospheric ^{14}C signal and a global average offset, R(t), (of approximately 400 radiocarbon years) was estimated between the atmosphere and the surface oceans (Stuiver *et al.*, 1986).

While the global marine calibration curve gives a value for R(t), the reservoir offset in a specific sample location is heavily dependent upon local oceanic and climatic conditions, and the correction factor that is required to obtain an accurate ^{14}C measurement may vary significantly from the global average. These local deviations from R(t) are expressed as ΔR and can have positive or negative values. Precise determination of an appropriate ΔR value is therefore of considerable importance to research within the fields described above. ΔR values are quantified by empirical studies of specific locations, and a range of methodologies, examined here, have been developed to achieve this. There is a significant modern spatial pattern to variations in ΔR(figure 2) (Stuiver and Braziunas 1993).

Comparison of ΔR variations with global oceanic circulation patterns demonstrates the correlation between reservoir age variation and prevailing environmental and oceanic conditions. Warmer surface currents tend to be associated with reduced reservoir ages, whereas regions where deep waters are upwelled show greater reservoir ages. Additional factors that influence the size of local reservoir effects include climatic variations, such as prevailing local wind currents and sea ice indices. These affect the rate of ocean atmosphere CO_2 exchange and consequently the concentration of ^{14}C in surface waters. Therefore, present global surface water reservoir age varies with latitude and climate. Polar and sub polar waters exhibit greater reservoir ages of c.800 1200 yrs (ΔR = c. +400 to +800 yrs), than the c.400 yr reservoir ages of tropical and subtropical regions (ΔR = c.0 yrs) (Austin *et al.*, 1995).

It was assumed that a ΔR correction was time-independent for a specific location, however, recent work strongly indicates that ΔR values may exhibit temporal as well as spatial variations (Heier Nielsen *et al.*, 1995). This appears to be a response to changes in the oceanic and climatic variables that are the determining factors behind ΔR and which are further complicated by variation in ^{14}C production. Therefore, to establish the nature of ΔR values the methodology used in quantification must provide both an accurate and precise assessment. In essence, the exact nature of spatial and temporal variations in ^{14}C content between marine and terrestrial reservoirs is often not well defined; thus, an improved understanding of the variations would have two major benefits. Firstly, accuracy and precision of calibrated ^{14}C age measurements made upon samples containing marine derived carbon could be greatly improved. Secondly,

quantitative measurements of temporal variations in regional marine reservoir ages have the potential to be used as a measure of process changes within Earth surface systems, due to their link with climatic and oceanic changes. As a result, the purpose of this paper is to assess the methodologies used in quantification of regional ΔR variations.

Chronological and environmental perspectives: the North Atlantic in the Late Quaternary

Calibration of radiocarbon age measurements made on samples containing marine derived carbon currently involves application of a standard time independent regional ΔR correction. It is now apparent that ΔR may show temporal variations as a function of oceanic circulation variations, and as a lagged response to changing atmospheric ^{14}C concentrations (Heier Nielsen *et al.*, 1995).

Surface water reservoir ages in the Northeast Atlantic presently exhibit lower ΔR values (centred on ΔR = 0, figure 3) than those experienced in other global locations at a similar latitude (Austin, 1995). This appears due to the present strong northeast flow of the warm North Atlantic current system, resulting in an influx of relatively ^{14}C enriched surface water to the region (Haflidason, 2000).

The time independence of the North Atlantic reservoir correction is therefore conditional on the continued existence of present circulation systems and environmental conditions. It may be reasoned that circulation and climatic variations of certain amplitudes will produce a corresponding variation in reservoir ages.

Climatic and oceanographic variations, such as the changing extent of polar water masses and sea ice, presumed to influence reservoir ages, are features of the North Atlantic in the Late Quaternary. Studies of Younger Dryas and Early Holocene reservoir ages show glacial conditions were accompanied by a 300 to 400 year increase in reservoir ages (figure 4). These decrease with the onset of the Early Holocene, but at that time are still significantly raised from modern values, being systematically older in the Western Nordic Seas (Austin *et al.*, 1995; Haflidason *et al.*, 2000). Reimer *et al.* (2002) analysed 31 sets of paired samples from Irish and Scottish locations, spanning

6100 years. The application of ideal sample protocols (as discussed below) was restricted due to the use of some previously analysed samples not specifically extracted for reservoir age research. The nature of the time series developed did not reveal a clear time dependency in North Atlantic reservoir age, although linear regression suggested temporal deviations in ΔR within the mid to late Holocene. A key implication was that change in ΔR may be significant within interglacial periods, but that gaps within the data set must be filled before temporal trends in regional ΔR can be defined with confidence (Reimer *et al.*, 2002).

While smaller scale (sub glacial-interglacial cycles) climatic changes may also produce discernible reservoir age variations, this possibility has not been fully investigated even within climatically sensitive regions such as the North Atlantic. Within this region, assessment of reservoir ages has primarily concentrated upon the establishment of current ΔR values for a range of locations. The region lacks a comprehensive temporal study, using a unified methodology, to examine potential long and short-term variations in reservoir effect.

In addition to variation in surface water reservoir ages, temporal reservoir variation has been observed in the gradient between surface and deepwater reservoir ages in the Southwest and Eastern Pacific Oceans during glacial times (Shackleton *et al.*, 1988; Sikes *et al.*, 2000). The recognition of these effects aids the reconstruction of glacial period ocean circulation and ventilation rates. The resulting variability in carbon circulation, particularly of changing atmospheric CO_2 concentrations from ocean atmosphere exchange, contributes to the understanding of past climatic regimes.

Approaches to the assessment of marine reservoir effects

Three main approaches have been used to establish ΔR for specific locations and time periods. They are firstly, using known age samples (from museum collections), secondly, tephra isochrones (present onshore/offshore), and thirdly, paired marine/terrestrial samples (from the same context in, for example, archaeological sites).

I. Known age samples from museum or analogue samples

Radiocarbon dating of marine material, where the calendar date of death of the organism is documented, enables the comparison of contemporaneous atmospheric and marine radiocarbon ages. The deficiency in ^{14}C content of the measured marine sample relative to the global atmospheric calibration curve is used to calculate the 'apparent age' of the material, which allows quantification of the local deviation from the global R(t). Marine mollusc shells (Mangerud and Gulliksen, 1975; Harkness, 1983) and marine mammal bones (Olsson, 1980; Birkenmajer and Olsson, 1998) have all been used in this type of study. The samples must have been collected live and reliable records of the date and location of collection, storage methods and handling since collection must be available (Harkness, 1983). Ideally, analogue samples should also be of sufficient age to minimise the impact of artificially produced atmospheric ^{14}C variations. Post 1950, determination of natural surface water ^{14}C content is impossible due to atmospheric nuclear weapons testing, precluding the effective use of post 1950 marine material for reservoir studies (Ingram, 1996). In addition, industrial fossil fuel burning has resulted in the release of ^{14}C-depleted carbon to the atmosphere (also known as the Suess effect). The phase lag introduced in marine systems means that accurate quantification of industrial contamination is possible through direct measurement in younger samples (Harkness, 1983). However, as few such measurements were made prior to the 1950's, the extent of the Suess effect in older samples can only be estimated through theoretical modelling.

The requirement for samples to be unaffected by either nuclear weapons ^{14}C or the Suess effect is often difficult to meet in full, and pragmatic compromises have been made. For example, Mangerud and Gulliksen (1975) used 15 marine mollusc samples to establish a reservoir age of 440 years for the Norwegian coast, some of which were potentially influenced by the Suess effect. As determination of an appropriate correction could not be made directly, a 3-reservoir box model, using tree ring determinations of atmospheric ^{14}C depletion to 1950 was used to infer the corresponding magnitude of the Suess effect at the time of sample formation.

II. Onshore/offshore isochrons

The virtually instantaneous deposition of volcanic ash, or tephra, over wide onshore and offshore areas (Eiriksson *et al.*, 2000) makes them powerful chronostratigraphic markers that are potentially useful for the determination of ΔR values. To determine ΔR, a comparison is made between ^{14}C measurements of materials in close stratigraphic association with the same tephra layer, both onshore and offshore. This usually involves the dating of foraminifera or mollusc shells extracted from marine sediments and plant material from terrestrial settings, such as peat profiles. Using the assumption of a coeval date of organism death for both sample types, ΔR may be calculated using relevant sections of the marine and atmospheric calibration curves.

III. Paired samples

The analysis of contemporaneous marine and terrestrial material to determine ΔR is not restricted to areas of tephra deposition. Pairs of same-age marine and terrestrial organisms can be extracted from a range of terrestrial deposits, especially from archaeological sites. If the organisms share dates of death and deposition, the local ΔR for a specific time may be calculated through a comparison of the ^{14}C measurements. Furthermore, the accuracy and precision of ΔR determinations will increase with the application of strict sampling protocols. In addition to archaeological deposits, other possible sources of material are buried near-shore sediments representing ancient shorelines, land based exposures of post-glacial uplift and coastal storm or tsunami deposits (Southon *et al.*, 1992).

Methodological strengths and limitations

I. Known age samples

This approach permits the comparison of an absolute calendar age (due to known collection date) with a coeval measured sample ^{14}C activity for the marine organism.

The atmospheric ^{14}C age corresponding to the known age BC/AD (collection date) of the organism is derived from the atmospheric calibration curve. The measured ^{14}C age of the shell is then compared with this data to determine a reservoir effect. Although standard errors are associated with both values for the measured ^{14}C shell age and the derived atmospheric ^{14}C age, no requirement exists for separate radiocarbon analyses of both terrestrial and marine material. This means that measurement uncertainties are associated only with the calculated ^{14}C deficiency of the marine sample, thereby increasing the precision and accuracy of the ΔR derivation.

Unfortunately, the availability of appropriate samples is inherently limited. The effects of atmospheric nuclear weapons tests and the Suess effect complicate the analysis of post 1890 material; therefore, samples are ideally required from pre 1890 collections. As these collections may have acquired an historical significance they may not always be available for destructive radiocarbon analysis. For a fundamentally similar reason, the known age sample approach is also limited over wider temporal scales because few suitable collections exist from prior to c.1700 AD. As existing historical collections cannot be supplemented, major spatial and/or temporal restrictions are imposed, and opportunities for multiple or repeat sampling are severely limited. This may pose a problem where the influence of contamination (*e.g.* geological carbon from the substrate) is suspected. Identification and quantification of such effects is difficult in samples whose provenance is not absolutely certain (Yoneda *et al.,* 2001). In addition, accurate determination of the appropriate atmospheric ^{14}C concentration (*i.e.* atmospheric ^{14}C age) for the sample depends upon accurate records of collection date. Unfortunately, where the only available information concerns the date at which a sample entered the collection, there is no assurance of a precise calendar age for its death. This uncertainty may also apply to the sample location, where the collection records are insufficiently precise. In these cases, the extent to which spatially referenced ΔR may be determined is limited.

II. Onshore/offshore tephra isochrons

Some extensive tephra deposits can be found both onshore and in deep-sea cores, where they can constrain ^{14}C measurement and radiocarbon dating over wide spatial areas. Where several different tephra horizons are present at a single site, temporal changes in

regional reservoir age may be established. This approach has been used to establish significant ΔR variations during the Younger Dryas/ Holocene transition, and in the early Holocene period (Austin *et al.*, 1995; Haflidason *et al.*, 2000; Sikes *et al.*, 2000), illustrating the significant potential of the method. This methodology may also allow spatial variations in ΔR to be tracked through comparison of radiocarbon ages associated with tephra falls in a variety of locations.

There are a number of limitations to this approach, perhaps the most fundamental are the spatial distribution of individual identifiable tephra layers (which will be linked to sedimentation rates and surface mixed layer (SML) depths) and the frequency of tephra deposition through time. At present, comparatively few studies have used tephra isochrons, but inevitably there will be significant spatial and temporal gaps in any data sets based exclusively on this approach. In addition, the accumulation rates of the sediments enclosing the tephra will have a large impact upon potential precision and accuracy, with low sediment accumulation rates and significant surface sediment mixing zones increasing potential uncertainties. The tephra constraining the dated sediment must be confidently ascribed to direct fall-out from the atmosphere into the sea, as opposed to lagged processes where, for example, fallout on pack ice or tephra entrained in glacier ice may be stored for decades or centuries before reaching the sea floor. Identification of the past surface horizon at the time of the tephra fall onto the seafloor (the key isochron) depends upon shard concentration. Usually, the modal point of highest shard concentration is chosen for sampling. For example, in an analysis of Vedde ash shards in a Hebridean shelf core, the tephra were located between core depths of 285 and 230 cm while samples were then taken from the peak concentration level at 265 cm depth (Austin, 1995). Where such peaks are ill defined, or several smaller peaks exist, the appropriate location of a consistent isochron and point of sample extraction is unclear. Mean or median tephra distribution points may fall substantially higher or lower than the modal concentration in the core.

These stratigraphic uncertainties may result from post depositional mixing (*eg.* bioturbation) of core sediments, and can also be inherent in the distribution of microfauna (usually foraminifera), used in reservoir age determination. Although macroscopic tephra layers may inhibit surface mixing by sealing the underlying sediment, microscopic tephra layers do not have this effect. The uncertainties associated

with these processes are amplified in areas with low concentrations of tephra or related microfaunal assemblages and by the fact that localised sedimentation rates are highly variable (Jones *et al.*, 1989; Paull *et al.*, 1991). To extract sufficient carbon for dating marine microfauna such as foraminifera, many individual specimens are combined, meaning that the resultant ^{14}C measurement is representative of an average of the ^{14}C content of many individual organisms. Mixing effects within the SML may introduce specimens of widely different age to a single core stratum, compromising accuracy of the "marine" ^{14}C age obtained. Rate of incorporation, residence time and degree of mixing in the SML is a function of the sedimentation rate, to which inherent dating uncertainties increase with inverse proportion.

Size selective bioturbation effects within the SML can mean that larger planktonic fractions appear consistently older than bulk or fine carbonate fractions, due to the exhumation of older sediments by burrowing benthic organisms (McCave, 1988, Broecker *et al.*, 1991, Thomson *et al.*, 1995). In this case, the magnitude of the observed age offset depends upon the size separation technique employed (Wheatcroft, 1992). In addition, longer SML residence can result in break up and dissolution of foraminifera (a phenomenon difficult to detect), inducing preferential selection of younger specimens (Peng and Broecker, 1984). Austin (1995) recommends selection of dissolution resistant or larger species that are less mobile following deposition. The processes involved in mixing and bioturbation effects are difficult to identify and quantify (Broecker *et al.*, 1991), and are generally indirectly calculated by modelling or estimation (*e.g.* the Berger Heath model) (Berger *et al.*, 1978). In addition to mixing of material in a specific core stratigraphy, extensive vertical and lateral sediment transport may occur prior to deposition of both tephra shards and the carbonate fraction.

Recommendations to limit the impact of mixing on the derivation of accurate reservoir ages include comparison of ^{14}C ages above and below the tephra deposit, determination of sharp basal contacts, the identification of upward fining of the tephra deposit, and characteristics of atmospheric deposition (Sikes *et al.*, 2000). In studies of more ancient sediments, larger dating uncertainties associated with the methodology may be acceptable. Within later Holocene studies the variety and extent of mixing effects may lessen the suitability of the tephra isochron approach to a restricted range of areas and times.

III. Paired samples

The paired sample methodology depends upon the contemporaneity of marine and terrestrial material. In common with the tephra isochron approach, factors of post depositional bioturbation and mixing must also be considered when selecting terrestrial deposits from which to extract paired samples. However, very rapid sediment deposition rates are possible, particularly on archaeological sites, where individual dumps of material may be identified, corresponding to activity over a period of days. In addition, identification and quantification of sediment disturbance can be established both *in situ* and during post excavation analysis through soil micromorphology, mineral magnetism, and other provenancing techniques. Optimal results are therefore obtained through rigorous site and sample selection, based upon several criteria. In particular, layers that exhibit visible signs of bioturbation, or slow accumulation rates, can be avoided. For example, the presence of articulated fish, and/or small mammal bones, and an absence of root penetration indicate stability and a lack of reworking within strata. In addition, sample replication can confirm that marine and terrestrial materials within a single layer are representative of a short deposition period. This can be achieved with sets of 'single entity' age measurements on, for example single cereal grains or marine mollusc shells. An anomalous result in an otherwise coherent set of ages from a single deposit demonstrates intrusive or reworked material. Statistical analyses (*e.g.* chi squared tests (Ward and Wilson, 1978)) may be performed upon groups of terrestrial or marine radiocarbon determinations to ensure that these are representative of a single deposition date, and therefore greatly enhances the accuracy of any ΔR values calculated using this approach.

The selection of cereal grains and marine mollusc shells presents one possible pairing of terrestrial/marine materials. These may not be present and other combinations present additional analytical concerns. For example additional isotopic analyses (*e.g.* $\delta^{13}C$ and $\delta^{15}N$) are required upon bone collagen, as residual reservoir effects may be present due to consumption of marine resources (*e.g.* seaweed) by terrestrial mammals (Arneborg *et al.*, 1999). If the terrestrial samples are of charcoal or larger wood fragments (*e.g.* trunk sections); problems may arise due to the potential for extended periods of growth.

Certain tree species (*e.g.* oak) may live for several hundred years, meaning that a sample of charcoal or wood, not composed of the outermost rings, may give a deceptively old terrestrial radiocarbon age that results in an underestimation of the marine reservoir age; in this instance, the two samples will represent the ^{14}C concentrations of the two reservoirs (ocean and atmosphere) at quite different points in time. Thus, if terrestrial radiocarbon ages are to be derived from charcoal or wood samples it must be established that the material represents the outermost layers and final growth periods in order to determine an accurate reservoir age. The problem is exacerbated by recycling of building timbers, or burning of old driftwood after an extended period in the environment, and is known as the "old wood effect". The use of short-lived samples, such as plant caryopses (representing one growth season), and identifiable twigs or leaves, is therefore advocated (Facorellis, 1998; Albero *et al.*, 1986; Reimer *et al.,* 2002), particularly when single entity dating is applied (Ashmore, 1998).

Sampling issues also apply to marine material. Short-lived, sedentary species (*e.g.* marine molluscs) afford the most reliable estimate of regional reservoir ages. The radiocarbon content of migratory marine species may represent reservoir effects from several localities forming the seasonal or annual ranges. Information concerning the effect of inter species variability upon returned reservoir age indicates that feeding behaviour and habitat selection may exert a considerable influence upon the reliability of radiocarbon ages. Shell carbonate may not be in complete equilibrium with the ocean's dissolved inorganic carbonate due to these factors (Barrett *et al.*, 2000). Tanaka *et al.* (1986) determined that up to 50% of shell carbonate might be derived from a metabolic component. This presents particular difficulties with deposit feeders, which are situated on carboniferous substrates. In a study of Hawaiian reservoir effects, Dye (1994) established that mollusc shells collected from limestone coasts were *ca.*620 years older than those from volcanic coasts, due to metabolism of carbonate from geological sources (limestone). Marine material must therefore be sourced to a local environment, and samples from areas of carboniferous bedrock used with caution. This also applies to areas where there is a high input of terrigenous material containing 'old' carbon to the marine environment (*e.g.* estuarine locations).

The extensive controls that are required to obtain coherent results through this paired sample approach may constrain the number of suitable sampling sites and these may consequently be absent in the region of research interest. Despite the high density of coastal archaeology on the Atlantic seaboard of Europe, anthropogenic deposits with appropriate integrity for this methodology are rare beyond c. 6000 BP and investigation of a wider temporal range necessitates the use of naturally deposited material. Although there is great potential contained within natural deposits, these resources have not yet been fully investigated and as a consequence are under-utilised. Archaeological sites therefore remain the most promising deposits for application of this methodology. The abundance of archaeological excavations and analysis in certain areas enables extensive use of paired samples within the temporal limitations imposed by the distribution of past cultures. Archived samples and site records provide a simple method of obtaining sample material, and reservoir age research objectives can usually be included in current excavation objectives with little difficulty.

The case for a new protocol for the use of archaeological materials:

The paired sample approach offers certain specific advantages over tephra isochron and analogue studies of extensive temporal and spatial marine reservoir effect variations. With appropriate sampling parameters, high degrees of precision and accuracy may be obtained. At present, studies using paired samples generally recommend stratigraphic controls, but no standardised methodological approach or guidelines exist to optimise results. Such an approach would greatly increase efficacy of the method and encourage its wider application. Major factors for consideration when using the paired sample methodology, which could be included in such a standardised protocol, are outlined below:

Samples should be extracted from contexts that meet rigorous criteria in the field as follows:

- Obviously bioturbated or otherwise disturbed contexts (or where suspicion of such activity is high) should not be sampled, as the age and duration of sediment deposition will be ambiguous.

- A discard protocol (cf. Higham and Hogg, 1995) should be adopted for samples/contexts that are affected by on-site contamination, including groundwater runoff and input of geological carbonate.

- Where possible, sample pairs should be extracted from deposits containing a large volume of potentially dateable material relative to the deposit size, reducing the possibility that an isolated sample specimen is the result of post depositional movement of soil/sediment. This is particularly relevant with respect to very small individual samples, such as carbonised cereal grains.

- Preferential selection of samples from layers where a short deposition period can be established reduces the possible age range of material within a layer (Albero *et al.*, 1986).

- Statistical analysis of repeat and replicate samples should be used to identify intrusive material (Ingram, 1996; Southon *et al.*, 1992).

- Consideration of organism behaviour, and in particular feeding mechanisms, should be incorporated into research strategies and possible interspecies variability in ^{14}C content should be considered.

- Use of the same species on an inter- and intra-site level will increase the comparability of radiocarbon ages and ΔR values, particularly where repeat sampling is performed. Results may then be compared with contrasting species to ascertain the wider applicability of the ΔR value obtained.

- As site morphology may increase likelihood of contamination, sampling in sheltered locations, bays, estuaries and inlets, and areas with a high proportion of fresh water and sediment run off, should be undertaken with caution. Ideal sites have material derived from well-mixed ocean water, such as the exposed Atlantic coast of Norway or the British Isles.

Conclusions

The marine reservoir effect has a spatial pattern that has changed through time. Some modern variations in the pattern can be explained by oceanographic processes, for example, differences in values of ΔR calculated for sites along the Californian coast (200 to 500 years) are most effectively explained by patterns of upwelling. In contrast, other ranges such as those around the shores of the Mediterranean Sea (ΔR of c.40 to 253 may relate to both natural variability and contrasting methodological approaches.

Temporal variation, such as the changes around the coasts of Iceland from a ΔR of 380 years today to a ΔR of 800 to 1100 years during the Younger Dryas period reflect the impact of climate and environmental changes during a glacial to interglacial transition. Temporal changes in ΔR have also occurred within the current interglacial period but the extent to which change in the later Holocene is time dependent is currently unclear.

The three main approaches used to determine ΔR involve known age samples, onshore/off shore tephra isochrons or paired samples. The 'known age sample' approach is effectively limited to relatively modern samples and, while it has produced important spatial data, it cannot give an effective time dimension. In order to establish changes through time, the paired sample approach can provide the best data where suitable terrestrial (archaeological) deposits are available. There is considerable unrealised potential in this approach, although it is also constrained by the need to have either human activity or appropriate rapid environmental changes to produce the necessary materials. Crucially, however, the effective use of the paired sample methodology depends upon rigorous sample protocols. To establish, with confidence, the range of spatial and temporal reservoir age variations in a region, analysis at a comprehensive range of sites is desirable. Increased sample numbers, spanning wide spatial and temporal dimensions, would lead to increased detection and resolution of reservoir effect variations. In addition, where suitable material for the paired sample methodology is not present, an alternative approach using onshore/offshore tephra isochrons may be feasible.

Considerable benefits may be gained from constraining both spatial and temporal reservoir variations. This would deliver improved dating accuracy and, potentially, a significant palaeoenvironmental archive. Conceivably, well-constrained variation in ΔR

could be used to infer the key environmental processes that lead to its formation, adding spatial perspectives to detailed time series of data such as the Greenland ice core record.

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Figure list:

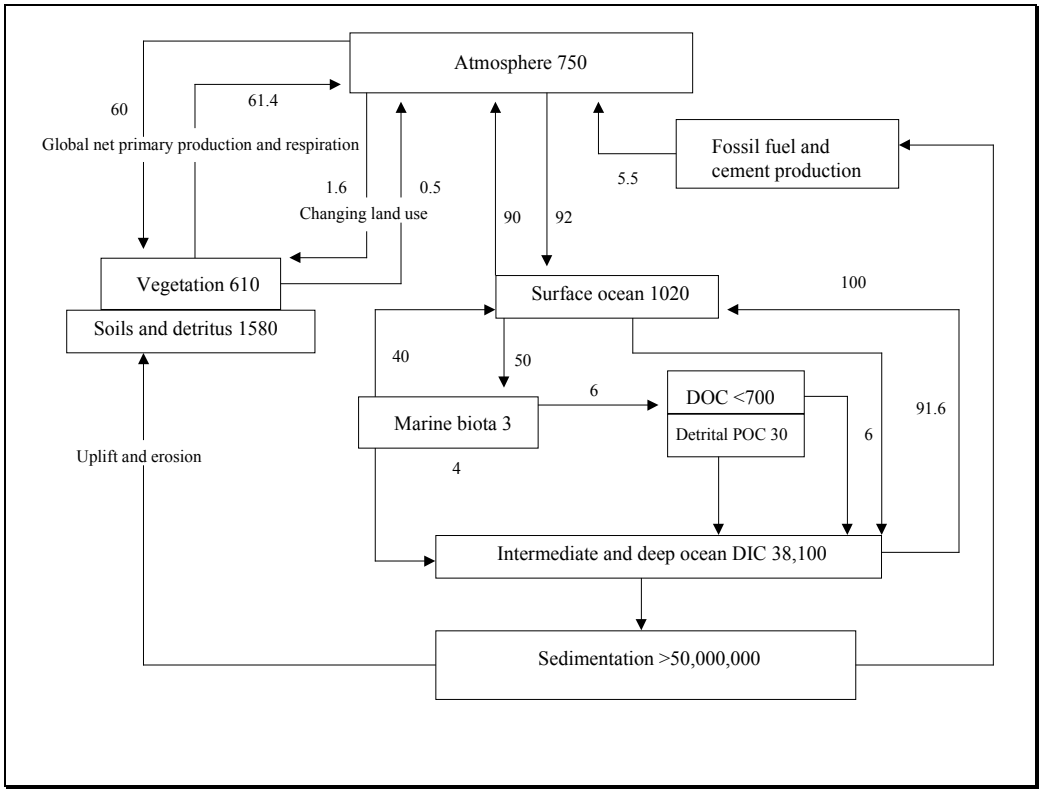

Fig 1: The biogeochemical carbon cycle in Earth surface systems. Estimates of reservoir volumes (in 10^{15}g C or billions of metric tons [BMT]), and fluxes (in 10^{15}g C/y or BMT/y).

Adapted from Schimel et al. 1995.

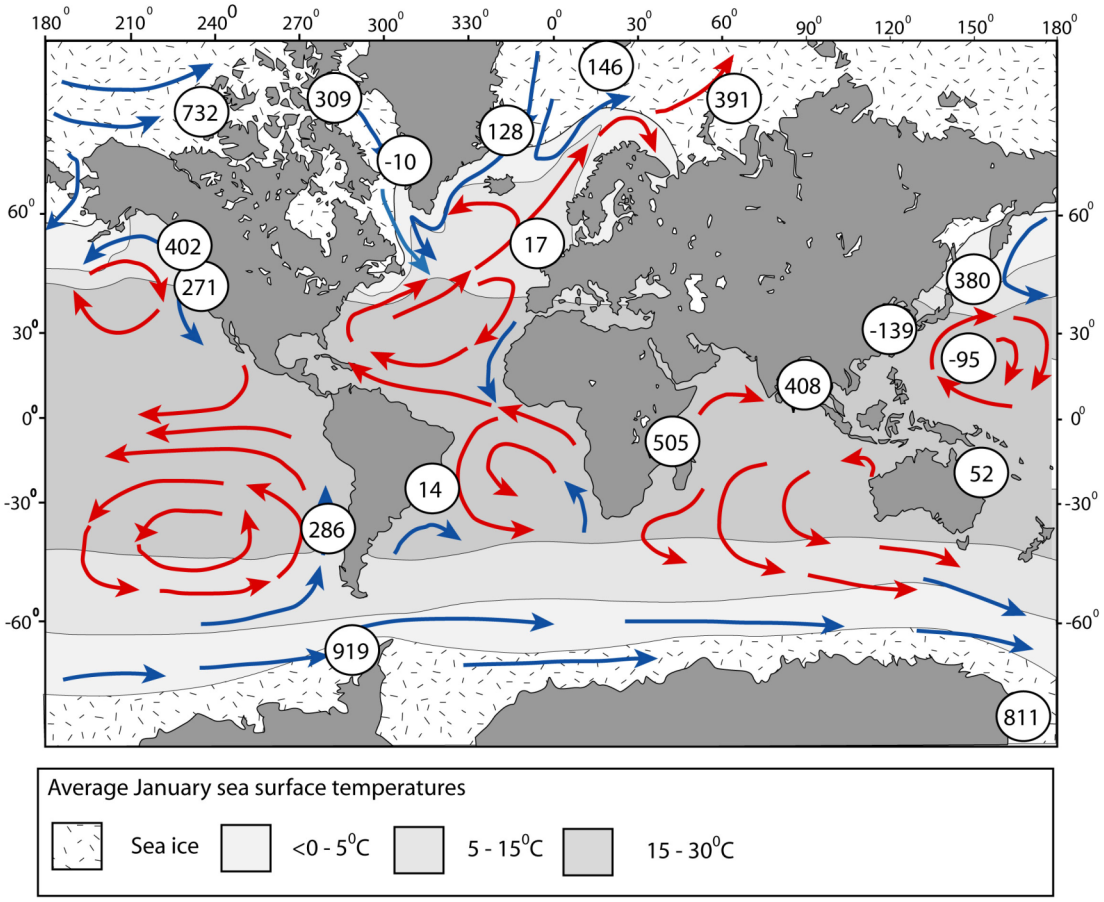

Fig 2: Global ΔR values (in circles from Reimer, 2001) with major global oceanic circulation systems (solid black arrows: warm currents; broken grey arrows: cold currents) and January sea surface temperatures (from Couper, 1983).

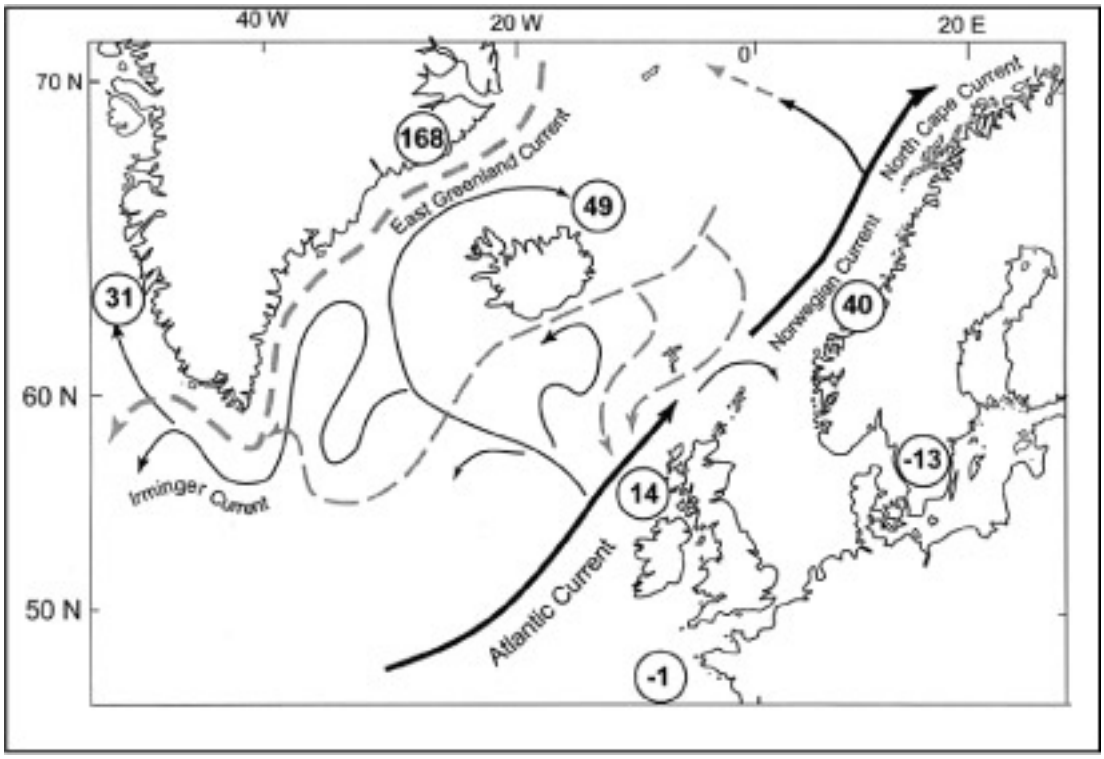

Fig 3: Outline of the modern North Atlantic showing ΔR values (in circles, from Reimer, 2001) with warm (solid black arrows) and cold (broken grey arrows) ocean surface currents.

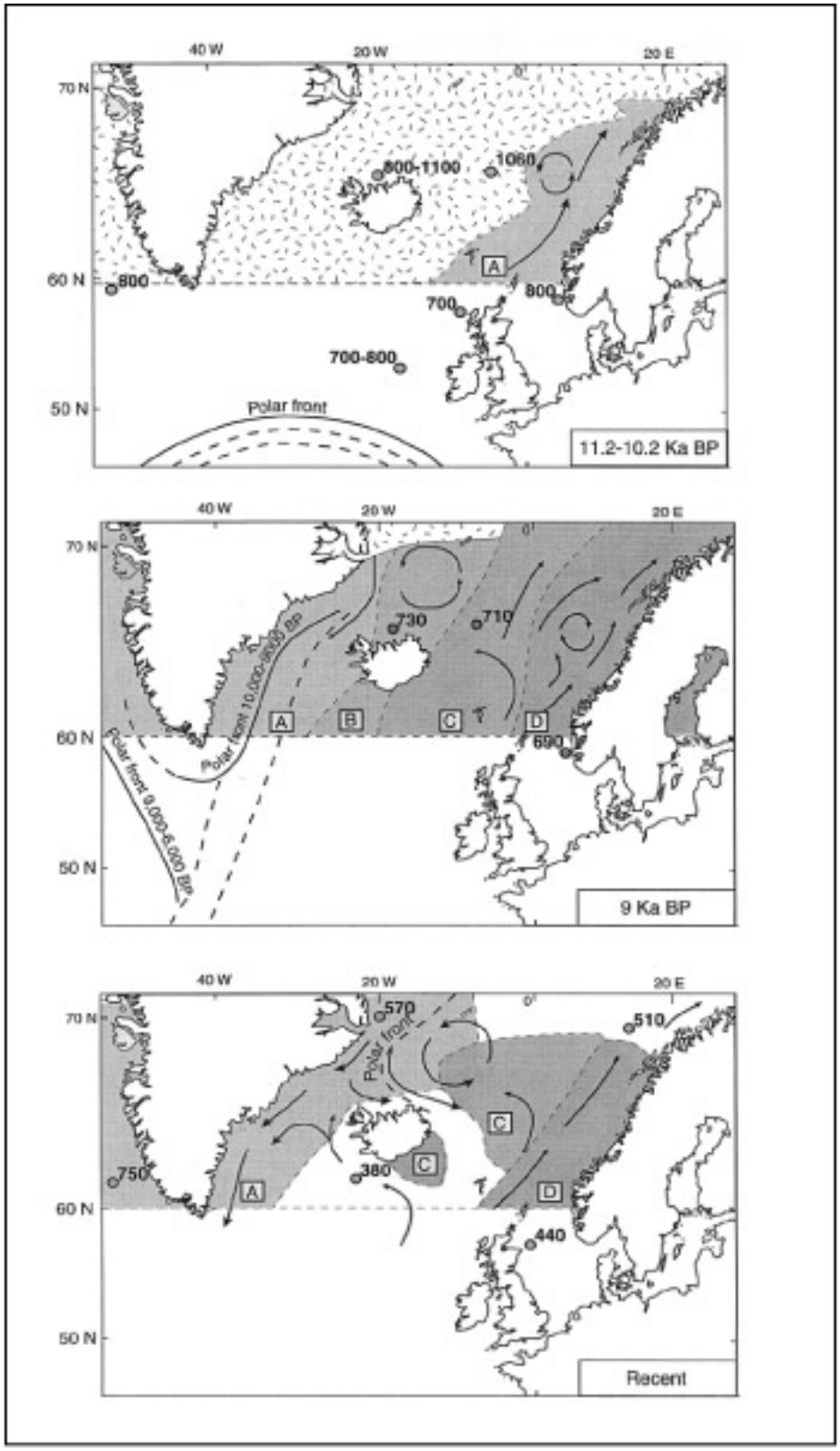

Fig 4: Reconstructions of major surface water mass distributions (after Koç *et al*., 1993), position of the polar front (after Ruddiman and McIntyre, 1981) and calculated reservoir ages (Haflidason *et al*., 2000) at the Younger Dryas (4a), Early Holocene (4b) and at recent (4c). Sea ice cover: dashed pattern; Arctic waters/sea ice assemblage: factor "A". Arctic and Norwegian waters mixing assemblages: factor "B"; Atlantic assemblage: factor "C"; Norwegian/Atlantic current assemblage: factor "D". Arrows indicate major surface currents.

Tables:

Positive site factors	Negative site factors
Presence of sufficient/suitable species for 14C analysis	Lack of suitable species for 14C dating
High sediment accumulation rate	Low sediment accumulation rate
Shallow SML. Low degree of evident bioturbation/mixing	Deep SML. High degree of evident bioturbation/mixing
Macroscopic tephra	Microscopic tephra
Identifiable tephras are present: precise correlation to other parts of the same isochron possible	Identifiable tephras absent or ambiguous correlation to other sites/tephra deposits
Readily identifiable concentration of tephra shards at a single point within the core	Low concentration of tephra shards within the core. Tephra shards 'smeared' over a large portion of the core

Table 1: Some of the positive and negative factors relating to the use of tephra isochrons in determining marine reservoir effects. Combinations of factors are specific to any individual site.

Methodological approaches	Known age samples	Tephra isochrones	Paired terrestrial/marine samples
Range	Effectively modern (300 yr).	Potentially throughout the entire range of ^{14}C analysis.	Defined by presence of a coastal archaeological record (post c. 8000 yr. BP on Atlantic seaboard of NW Europe and British mainland) and/or discreet episodes of marine transgression/recession.
Limitations	Investigations are spatially/ temporally dependent upon previous sample collection. Appropriate samples only available from modern collections (e.g. post AD 1600 within Europe). Difficulties post c. AD 1850 due to industrial ('Suess') effect. Limited post AD 1950 due to atmospheric nuclear testing. No possibility of analysing prehistoric samples, meaning significant temporal studies are impossible. Sample replication within a study may be limited/impossible.	Tephra falls are generally infrequent and may not have occurred at times of interest. The sample location must be within a zone of identifiable tephra deposition of sufficiently high shard concentrations. A well-constrained terrestrial age must exist for the tephra used within a study. Potential for extensive bioturbation/ mixing of core sediments post deposition, limiting dating accuracy. Accurate quantification of these effects may be impossible.	Spatial/temporal limitation to areas where coastal cultures are extant and/or existence of tsunami/marine transgression sequences. Suitable sampling locations must meet specific rigorous criteria. These may not be satisfied for spatial/temporal points of interest. Postdepositional bioturbation/mixing effects limit the extent to which marine and terrestrial samples are contemporaneous. The range of suitable sample material is limited to short-lived, sedentary organisms, e.g., marine molluscs and carbonized plant macrofossils. Material present in larger quantities within the stratigraphy (e.g., charcoal) may not be suitable.
Advantages	The date and location of collection (and hence 'actual age') of the organism may be known with great accuracy and precision. Requirement for ^{14}C analysis to determine 'marine age' only. No associated problems of postdepositional movement/ bioturbation/mixing effects.	Virtually instantaneous deposition of tephras in terrestrial and marine environments allows correlation of a discreet temporal interval in both environments. Tephra deposits may cover wide areas, permitting study in a variety of localities. Comparison of separate discreet tephra falls allows examination of variation in reservoir effects through time.	Individual organisms (single entities) may be dated through AMS, greatly improving dating precision. The potential for replication of dates within a stratigraphic layer, enhancing dating accuracy. Identification and quantification of bioturbation/mixing effects may be achieved through a range of provenancing techniques

Table 2: The range of application, advantages and limitations of the three principal methodologies used in marine reservoir effect determinations.