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Impact of nuclear fuel reprocessing on the temporal evolution of marine radiocarbon

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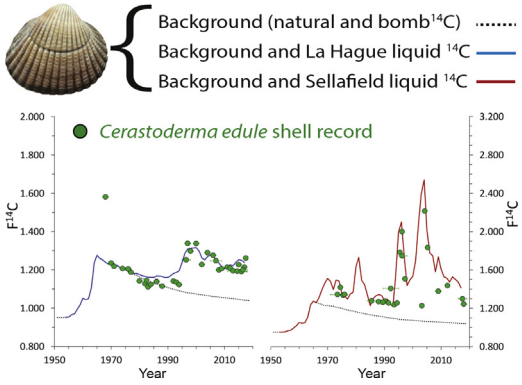
HIGHLIGHTS

- Cockle shells used to reconstruct ^{14}C in sea surface of NW Europe from 1969 to 2019.
- Shell ^{14}C records show large deviations from marine bomb pulse at specific sites.
- Excess ^{14}C mainly caused by liquid releases from Sellafield and La Hague plants.
- Impact from other nuclear sources insignificant compared to Sellafield and La Hague.
- ^{14}C dating and tracer studies challenged by large spatial and temporal variability.

GRAPHICAL ABSTRACT



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ABSTRACT

Radiocarbon (^{14}C) is broadly used in oceanography to determine water ages, trace water circulation, and develop sediment- and sclerochronologies. These applications require an accurate knowledge of marine ^{14}C levels, which have been largely perturbed by human activities. Globally during the last century the above-ground nuclear weapon testings have been the primary cause of the increased atmospheric and marine ^{14}C. However, other anthropogenic sources may have caused important regional deviations from the bomb pulse. For the last 70 years European nuclear fuel reprocessing plants have been major contributors of ^{14}C to air and oceans, yet, their regional impact on surrounding marine ^{14}C has been largely overlooked. Here we use a collection of bivalve shells of known capture date and age collected from various locations, including the North Sea, the Irish Sea, Norway, and the Bay of Biscay to reconstruct the sea surface ^{14}C over the last five decades. The measured ^{14}C values for the period 1969–2019, reported in fraction modern, ranged from 1.1 to 1.6 in coastal waters of the Netherlands and from 1.2 to 3.2 along the coast of the UK, indicating significantly higher levels of ^{14}C than those expected for the marine bomb pulse (0.950–1.150). The ^{14}C peaks revealed by the shells coincide with the increase of liquid ^{14}C releases reported from the reprocessing plants of La Hague into the English Channel, and from Sellafield into the Irish Sea. Conversely, the shells from Norway and Spain showed ^{14}C values close to the range of the global marine bomb pulse. The

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observed large spatial and temporal differences in sea surface ^{14}C show that ^{14}C dating and tracing studies could become problematic in the English Channel, Irish Sea and North Sea for the time period covering the discharge of liquid ^{14}C from the reprocessing plants.

1. Introduction

Radiocarbon (^{14}C) is a radioisotope (half-life ca. 5730 years) widely used for placing materials and events in the right temporal context. In the marine environment, natural and anthropogenic ^{14}C have been employed among other tracers to infer water circulation (Broecker, 1991; Wanamaker Jr. et al., 2012), to establish sediment chronologies (Ohkouchi et al., 2003) and to determine the age and growth rate of fish and bivalves (Andrews et al., 2019; Kalish, 1993; Witbaard et al., 1994). All these applications require an accurate knowledge on the ^{14}C concentrations of the past and present ocean.

Post-1950s, several human activities including above-ground nuclear weapon testing, nuclear power generation, and reprocessing of spent nuclear fuel have resulted and continue to partially result in large perturbations of the natural ^{14}C, here reported as Fraction Modern, $F^{14}C$ (Reimer et al., 2004). The explosion of nuclear bombs during the 1950/60s constitute the most prominent source of anthropogenic ^{14}C with ca. 200 PBq released into the atmosphere (UNSCEAR, 2000). The consequent impacts on atmospheric and oceanic ^{14}C have been reconstructed using dendrochronology (tree rings) and sclerochronology of biogenic structures of marine calcifying organisms, respectively. By the mid-1960s atomic bomb testing roughly doubled the atmospheric $F^{14}C$ from 1 to 1.9 (Fig. 1a) (Hua et al., 2013). In the following decades, the so called *'bomb pulse'* gradually declined to pre-bomb levels mainly due to the mixing of the atmosphere with the ocean and biosphere as well as dilution caused by fossil fuel emissions (Graven, 2015). The transfer of bomb-^{14}C to the marine environment resulted in $F^{14}C$ values generally rising from 0.95 to about 1.15 in the sea surface (Fig. 1a). The marine bomb pulse is smoother in shape and time lagged with respect to the atmosphere because of the slow air-sea transfer of $^{14}CO_2$ and the large marine carbon reservoir (Reimer, 2009).

Besides inputs through nuclear weapon testings, the environment also receives substantial amounts of ^{14}C from the nuclear fuel cycle (Zazzeri et al., 2018). Of major concern to the marine environment are inputs from the reprocessing of spent nuclear fuel. Based on ^{14}C observations from tree rings and algae (Cook et al., 2004; Isogai et al., 2002), and databases and reports available from British, French and European organisations (MAFF, 1982-1994; ORANO, 2017; OSPAR, 2003-2019; RAAD, 2020; RIFE, 1996-2018; Zerbib et al., 2004), between 1950 and 2017 the reprocessing plants of La Hague in Normandy (France) and Sellafield in Cumbria (United Kingom), discharged a total of 1.2 PBq into the Northeast Atlantic. The highest impact on the marine environment resulted from liquid inputs, with a notable increase in their release rate from both reprocessing plants after the mid-1990s (Fig. 1b and c). The liquid releases of ^{14}C account for about 0.5 PBq, i.e. 40% of the total (liquid+gas) discharges, which are roughly 1.5 times the amount of natural ^{14}C expected in the North Sea, Irish Sea and the English Channel.

While the bomb pulse was reconstructed accross the temperate NE Atlantic until the mid-1990s using the shells of the long-lived bivalve *Arctica islandica* (Scourse et al., 2012; Weidman, 1995; Witbaard et al., 1994), there is notably less insight into how regional sources such as nuclear fuel reprocessing affected the temporal and spatial changes of sea surface ^{14}C. The majority of studies dealing with reprocessing ^{14}C have documented the behaviour, transport, biological accumulation and transfer, and radiological impact of the releases (Cook et al., 1995; Fievet et al., 2006; Gulliver et al., 2001; Maro et al., 2004; Muir et al., 2017; Tierney et al., 2018; Tierney et al., 2017a; Tierney et al., 2017b; Wolstenholme et al., 1998). The common finding from these studies was that ^{14}C content was significantly higher in seawater, biota, and sediments than the levels expected from the bomb pulse alone. Very few studies have investigated the transient evolution of marine ^{14}C through the 1970/90s (Cook et al., 2004; Isogai et al., 2002; Keogh et al., 2004), and only short ^{14}C time series in seawater and biota (Cook et al., 2004; Gulliver et al., 2001; Gulliver et al., 2004) exist for the later period of time coinciding with the largest liquid releases of reprocessing ^{14}C (Fig. 1b and c).

We hypothesized that regional sources like reprocessing have changed the ^{14}C content of surface waters across NW European seas, and that consequently, there have been deviations from the bomb ^{14}C in the sea surface sutained through the last 5 decades. To test the hypothesis, we aimed to achieve a comprehensive view on the temporal evolution of ^{14}C in surface seawater between the late 1960s and present at various locations in NW Europe (Fig. 2). We used gas ion source - accelerator mass spectrometry (AMS) techniques to determine the ^{14}C content in the calcium carbonate shell of bivalves with known collection date, accurate age and provenance. Bivalve shells record the isotopic composition of stable carbon isotopes in the surrounding seawater (Beirne et al., 2012) making the available shell collection a suitable archive for the reconstruction of sea surface ^{14}C across several areas. The obtained temporal and spatial evolution of ^{14}C was compared to documented releases of liquid ^{14}C from La Hague and Sellafield, among other sources. The implications for the use of ^{14}C as a dating tool are briefly discussed.

2. Methods

2.1. Study areas

A total of eight intertidal flats were sampled in the southern North Sea, the Irish Sea, the Gulf of Biscay and northern Norway (Fig. 2). The majority of archived shell material was collected from a sandy tidal flat at Balgzand in the western most part of the Wadden Sea, Netherlands and from the sand and mud beach of Traeth Melynog in North Wales, U.K. as part of two long-term benthic fauna sampling programs. The sampling began in 1969 in Balgzand (Beukema, 1982; Beukema and Dekker, 2009; Beukema and Dekker, 2018) and in 1975 in Traeth Melynog (Richardson et al., 1980). These locations were usually revisited once or twice a year until 2018/9. Additional shell material was collected from other parts of the UK's coast in 1999, Norway in 1975 and 2016/18, and Mundaka, Basque Country, in 2004.

Except for Mundaka, all locations are situated along the path of waters labelled with reprocessing nuclides from La Hague or Sellafield (Fig. 2). The pathways (Fig. 2a) followed by the releases are well-known and have been studied in detail elsewhere (Bailly du Bois and Dumas, 2005; Bailly du Bois and Guéguénait, 1999; Christl et al., 2015; Dabrowski et al., 2010; Perianez et al., 2018; Raisbeck et al., 1995). Briefly, the liquid releases from La Hague into the English Channel are transported in less than one year eastward via coastal advective currents, pass through the Strait of Dover and enter the southern North Sea. The liquid releases discharged from Sellafield normally exit the Irish Sea through the North Channel, then follow the Scottish and eastern English coastline to enter the western part of the North Sea. Seasonal revearsals of the main current system in the central Irish Sea can cause the southward transport of Irish Sea water (Dabrowski et al., 2010) and of small amounts of Sellafield releases into the English Channel (Bailly du Bois and Guéguénait, 1999; Castrillejo et al., 2020).

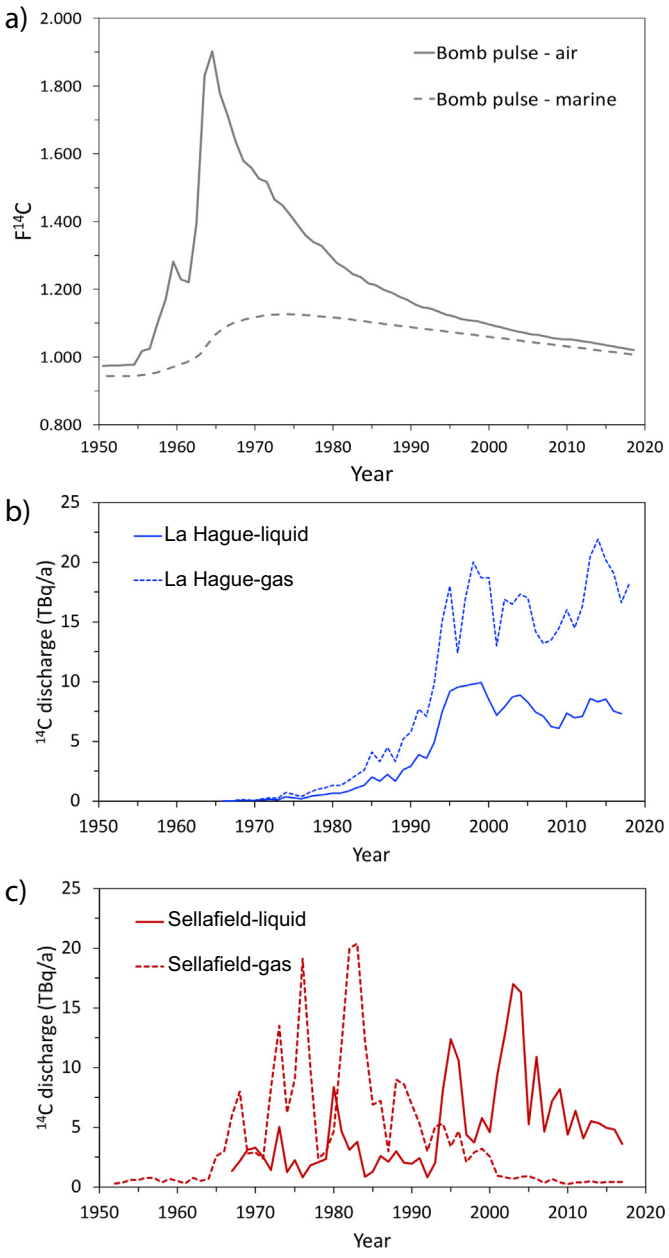

Fig. 1. Decadal changes undergone by ^{14}C. a) Compiled observations of ^{14}C in air and tree rings in the Northern Hemisphere Zone 1 (North of 40°N) for the boreal summers between 1950 and 2010 (Hua et al., 2013). Data from 2010 onwards have been estimated by linear regression using parameters obtained by fitting the last 10 years of observational data. The marine bomb pulse (Marine09) for the upper 75 m of the oceanic water column between 1951 and 1996 (Reimer, 2009). Data from 1996 onwards have been estimated by linear regression obtained from fitting the last 10 years of observational data. Documented discharges of liquid and gaseous ^{14}C from the nuclear reprocessing plants of b) La Hague and c) Sellafield, compiled from various sources (Cook et al., 2004; Isogai et al., 2002; MAFF, 1982-1994; ORANO, 2017; OSPAR, 2003-2019; RIFE, 1996-2018; Zerbib et al., 2004).

Within the North Sea, the releases follow a cyclonic circulation and enter the Nordic Seas following the Norwegian coast.

The Wadden Sea (Fig. 2b) is suitably connected to the southern North Sea via the Marsdiep tidal inlet. This connection allows the rapid tidal flushing of Balgzand with waters carrying the contamination discharged at La Hague, 600 km to the southwest. Traeth Melynog (Fig. 2b) in the southeastern part of Anglesey, is exposed to central Irish Sea waters from the west and the north through the Menai Strait. Thus, this region is subject to increased radionuclide concentrations due to Sellafield discharges 150 km to the northeast and the mixing of waters within the Irish Sea (Castrillejo et al., 2020; Dabrowski et al., 2010).

2.2. Shell material

Detailed information about the bivalve shell collections is listed in Supplemental Table S1 (Appendix A). Most of the shells are common European cockles *Cerastoderma edule* (*C. edule*) collected from the Wadden Sea and Traeth Melynog. Cockle samples collected in 1999 were also available from Morecambe Bay, Thames and the Wash area, Norfolk. Additional shell samples of *Chamelea striatula* (*C. striatula*) and *C. edule* were collected in Ramfjordbotn and Ingøya, Norway, and *Limecola balthica* (*L. balthica*) from Mundaka, Spain. In the case of *C. edule*, the shell surface displays characteristic external dark annual rings that are deposited every winter (October to March). The clear growth pattern allows the rapid visual determination of the animal's lifespan by counting the winter rings (Richardson et al., 1980). We selected specimens of about two year lifespan so that data would have a temporal uncertainty of only ±1 year. The samples of *C. striatula* and L. *balthica* present a less clear growth pattern and their age cannot be determined by simple visual counting of growth rings. Yet, given the species and the size of the shells, they are expected to be <10 years old. All animals were collected alive and their shells labelled, archived and stored after boiling and removal of the flesh. The known capture date and age of the animal allowed plotting ^{14}C results accurately in the temporal context.

2.3. Sample processing and ^{14}C analysis

^{14}C measurements were undertaken using gas ion source - AMS at the Laboratory of Ion Beam Physics, ETH Zurich. Sample preparation was carried out following the procedure described by Wacker et al. (2013). In summary, the shells were cleaned with deionized water in an ultrasonic bath, air dried and mechanically ground to powder size using a clean metallic morter. Each sample of about 1 mg of carbonate material was introduced in a septum-sealed vial. After flushing the head space with helium, 100 μL of 80% phosphoric acid was added to release CO_2 from the carbonate. Via an autosampler the gas was collected on a zeolithe trap in the gas interface system and transferred into a syringe, where it was diluted with He to a 5% CO_2 mixture and introduced into the gas ion source of the MICADAS facility (Synal et al., 2007; Wacker et al., 2013). IAEA-C1 (Rozanski, 1991) and a coral sample (nominal value 0.9445 ± 0.0018 (1σ stdev) (Gao et al., 2014)) were prepared in the same way as the samples and used respectively, as a blank and as internal standard. Data were evaluated using the BATS data reduction software (Wacker et al., 2010).

2.4. Simulation of sea surface ^{14}C

A one box model was used to simulate the ^{14}C content of surface seawater at Balgzand and Traeth Melynog. The model was recently used to simulate the transport from the reprocessing plants and to estimate the artificial to natural uranium atom ratio ($^{236}U/^{238}U$) in Balgzand and Traeth Melynog (Castrillejo et al., 2020). For each year (between 1969 and 2019), the annual discharge of liquid reprocessed ^{14}C was fully mixed in a water body. We exclusively considered the input of liquid ^{14}C (Fig. 1b and c) because its impact has been found to largely dominate over gaseous releases in the marine environment (e.g. Cook et al., 2004). The documented discharge rates of liquid ^{14}C from La Hague and Sellafield were used in the simulations for Balgzand and Sellafield, respectively. In addition, the water body embeded a time-varying ^{14}C background resulting from the natural $^{14}C/^{12}C$ and the bomb-^{14}C transient. The corresponding ^{14}C background is defined in Section 3.1 (Fig. 3) and is considered to be robust because it has been either published (Reimer, 2009) or calibrated using independent shell data reported elsewhere (Weidman, 1995). The volume of the water body was specific for each site and was assumed to be

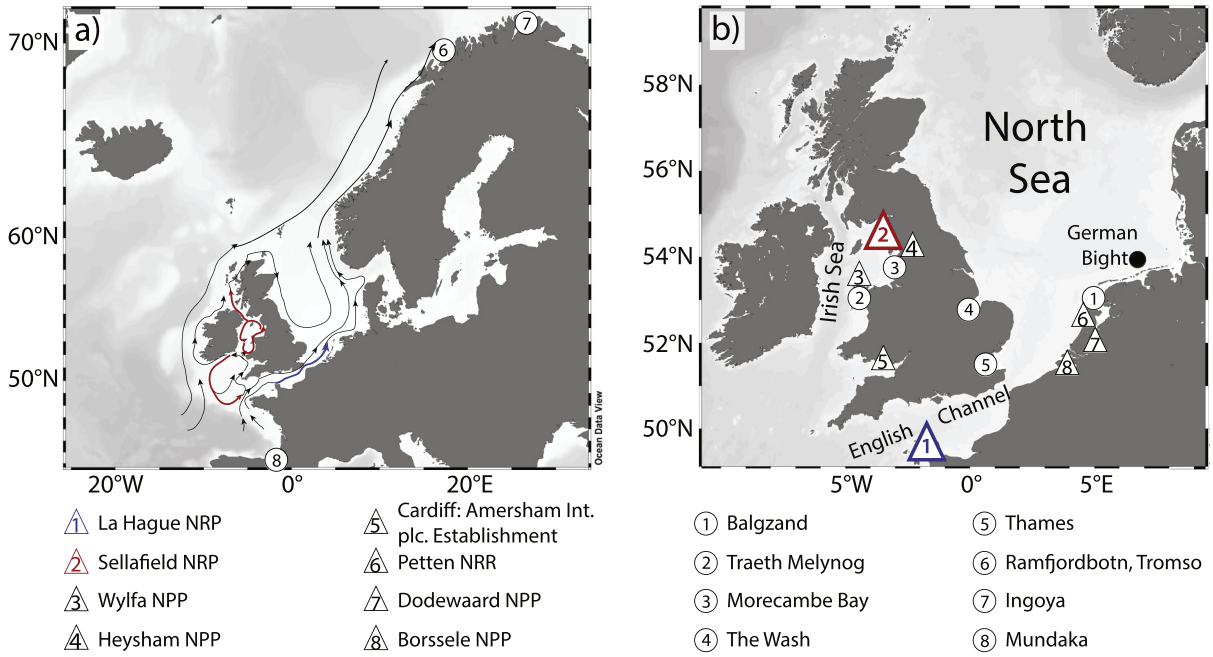

Fig. 2. a) Schematic circulation of water masses and transport of radionuclides from Sellafield and La Hague reprocessing plants and b) position of the study sites (circles) and nuclear facilities (triangles) that could pontentially introduce ^{14}C and impact the study sites. The schematic circulation was adapted from Bailly du Bois et al. (2002). NRP = Nuclear Reprocessing Plant. NPP = Nuclear Power Plant. NRR = Nuclear Research Reactor.

constant throughout the 5 decades of study. The volume was chosen so that simulated sea surface ^{14}C overall matches the $F^{14}C$ measured in the corresponding shell collection. A delay of about 1 year is also applied to releases from La Hague to account for the transit time of the radioactive plume from the La Hague plant to the southern North Sea (Salomon et al., 1995). The used input functions, i.e. amount and timing of introduction of the radionuclide (^{14}C and/or the $^{14}C/^{12}C$ atom ratios), as well as the simulated values are provided as supplemental information (Appendix B).

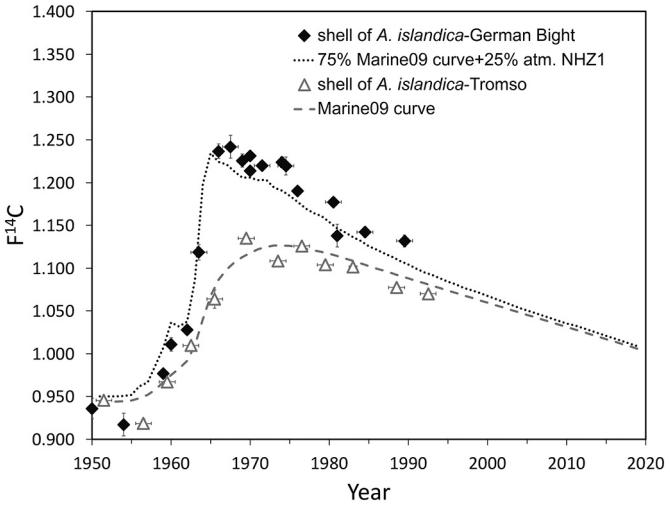

Fig. 3. The content of ^{14}C in shells of the bivalve *Arctica islandica* is used to define the background caused by natural and bomb-^{14}C in the sea surface. *A. islandica* shell data from the German Bight and Trømso were reported in (Weidman, 1995). The Marine09 curve was reported by (Reimer, 2009). The ^{14}C content in the atmosphere for the northern hemispheric zone 1 (NHZ1) was reported in (Hua et al., 2013).

3. Results and discussion

3.1. Background ^{14}C from bomb tests

Shell ^{14}C results of the long-lived bivalve *Arctica islandica* compiled in Scourse et al. (2012) reveal large regional differences in the expression of the marine bomb pulse across the temperate N. Atlantic. Thus, in this section we determine the marine bomb pulse for each study area to enable us to distinguish between bomb- and reprocessing-^{14}C in the analysed shell material. We are supported by published shell ^{14}C data from *A. islandica* that were captured in the mid-1990s, and thus, did not integrate the time period of largest liquid ^{14}C discharges from reprocessing activities (Fig. 1b and c). It can be seen for the Norwegian region (Fig. 3) that the Marine09 curve (Reimer, 2009) represents the marine bomb pulse displayed by an *A. islandica* that was collected near Trømso in 1993 (Weidman, 1995). We assume that bomb ^{14}C concentrations in surface waters of the North Sea and Irish Sea are probably best represented by the ^{14}C composition of the *A. islandica* that was collected in 1990 at similar latitudes in the German Bight (Fig. 2b) (Weidman, 1995). The ^{14}C from *A. islandica* (Fig. 3) displays a larger peak in concentrations that can be accounted for by combining 25% of the atmospheric bomb-^{14}C signal for the Northen Hemisphere Zone 1 (Hua et al., 2013) with 75% of the Marine09 curve (Reimer, 2009). The two marine bomb pulses displayed in Fig. 3 will be used as baseline values (hereinafter called *background*) to discuss the impact of reprocessing releases on sea surface $F^{14}C$ levels in Section 3.3.

3.2. Range of ^{14}C measured in shells

The bivalve shells analysed in this study show $F^{14}C$ values between 1.042 ± 0.007 and 3.149 ± 0.014 lying in most cases significantly above the contemporary background values expected from the bomb tests (Supplemental Table S1 and Fig. 4). The cockles inhabiting Balgzand between 1967 and 2018 generally displayed shell $F^{14}C$ values between 1.100 and 1.300 (Fig. 4a), while the range was greater, 1.200 and 2.200 (Fig. 4b), in shells collected from Traeth Melynog during a

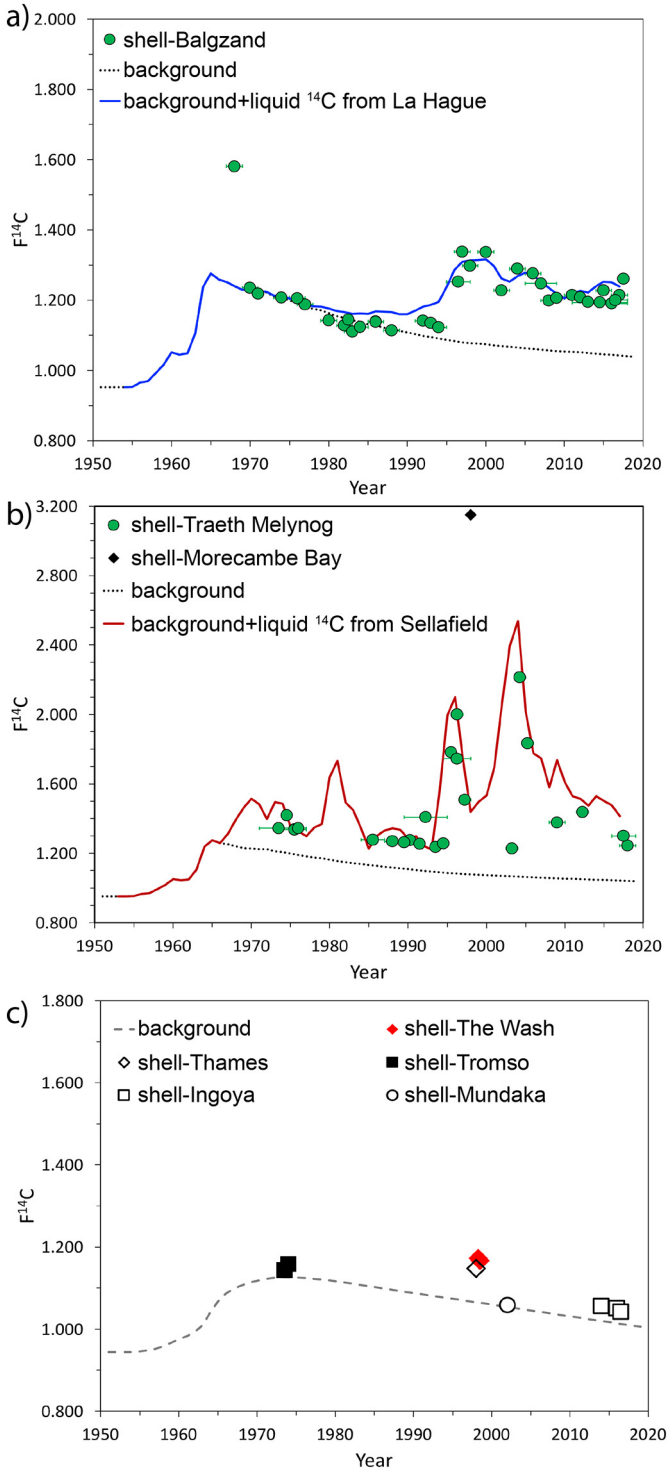

Fig. 4. Levels of ^{14}C measured in shells are displayed together with the corresponding background (defined in Section 3.1) and the simulated ^{14}C content for the sea surface. Data are represented in three sub-groups according to their geographical location and the range of ^{14}C values. a) Balgzand. b) Traeth Melynog and Morecambe Bay. c) Thames and The Wash in the UK, Ingoya and Tromso in Norway, and Mundaka in Spain.

similar time window. Two shell samples showed exceptionally high ^{14}C concentrations. The first sample collected from Balgzand and dating back to the late 1960s displayed a $F^{14}C$ value of 1.581 ± 0.008 (Fig. 4a). A possible explanation is that this cockle lived when the bomb pulse reached its peak (mid 1960s, $F^{14}C$ ca. 1.9 in Fig. 1a) and covered more of the maximum than the rest of the animals from the later Balgzand collections. The cockle shell $F^{14}C$ is about 0.4 higher than for contemporaneous ^{14}C concentrations recorded in a shell of *A. islandica* collected from the German Bight in the southeastern North Sea (Weidman, 1995; Witbaard et al., 1994). Such a finding is compatible with an attenuated bomb pulse for the German Bight, as the *A. islandica* was living at greater depth than the intertidal cockle and permanently covered by a 40 m deep water column. The other cockle displaying the highest $F^{14}C$ value in this study, 3.149 ± 0.014 (Fig. 4b), was collected in Morecambe Bay in 1999 (Fig. 2b) that is only 50 km south from Sellafield and this short distance most likely explains the elevated ^{14}C. Another possibility is that the cockle from Morecambe Bay was affected by releases from the nearby, Heysham nuclear power plant (Fig. 2b). Yet, the reported releases from this facility are much smaller than for the Sellafield reprocessing plant making it more likely that the high shell ^{14}C value is related to reprocessing activities. As expected, the shells sampled further away from the Sellafied reprocessing plant between 1975 and 2018 showed more diluted ^{14}C concentrations that were only slightly higher or in close agreement with background levels, 1.042–1.173 (Fig. 4c). In the southeastern UK (Fig. 4c), shell ^{14}C concentrations were somewhat above the background in agreement with elevated ^{14}C values reported for seawater and biota collected along the eastern coast in the 1990s (Cook et al., 1998; Gulliver et al., 2004). According to the authors, the excess of ^{14}C could not be entirely explained by the marine transport of Sellafield-derived radionuclides. Instead, they suggested that a non-authorized release of ^{14}C could have taken place from a non-nuclear-power related source (Gulliver et al., 2004). The shell from Mundaka, Spain (Fig. 2) is distant from regional nuclear sources, thus expectedly follows the average value of the Marine09 bomb pulse. Similarly, the shells from Norway are located so far away from Sellafield or La Hague that they displayed no distinguishable deviation from the temperate bomb-^{14}C pulse. Overall, the observed shell ^{14}C values and their spatial distribution appear to be related to a large extent to the distance from the two reprocessing plants, and the transport and dilution of the radioactive plume by ocean currents. Our results are therefore in agreement with previous studies investigating the distribution of ^{14}C and transport of reprocessing releases in the English Channel, Irish Sea and the southern North Sea (e.g. (Bailly du Bois and Dumas, 2005; Cook et al., 1998; Maro et al., 2004)).

3.3. Temporal evolution of ^{14}C

A major objective of this study was to investigate the relationship between reprocessing releases and temporal changes in sea surface ^{14}C over the last five decades. In Fig. 4 the historical reconstructions of ^{14}C provided by the two long-term shell collections are compared with the simulated ^{14}C values for the sea surface. The latter (see Section 2.4) were estimated separately for Balgzand and Traeth Melynog by including the diluted reprocessing-^{14}C discharge from the respective nuclear reprocessing plant as well as the marine bomb pulse defined in Section 3.1.

The recorded ^{14}C in *C. edule* shells from Balgzand and Traeth Melynog appears to be closely linked to simulated ^{14}C concentrations in the sea surface water (Fig. 4). At Balgzand (Fig. 4a), shells display a similar ^{14}C to the background until the late 1980s, whereupon post-1995 the high shell $F^{14}C$ of 1.2–1.4 can be explained by the documented addition of liquid ^{14}C releases from La Hague. The 1990s ^{14}C increase coincides with an increased discharge of liquid ^{14}C at La Hague, from about 2.5 TBq/a to about 7 TBq/a (Fig. 1b). At Traeth Melynog (Fig. 4b), there is an excess of about 0.15 $F^{14}C$ between the lowest shell values and the background throughout most of the reconstructed period of time. The positive offset and the high variability of shell ^{14}C in the Irish Sea are captured by the simulated ^{14}C values in sea surface waters (Fig. 4b). The degree to which the shell data deviates from background values can be explained, to a large extent, by temporal changes in the release rate of liquid ^{14}C from Sellafield (Fig. 1c). Additionally, unexpected

low shell ^{14}C values were observed that are close to the background level, e.g. Traeth Melynog in 2004. A plausible explanation for this is that the tidal flat might have been unusually well flushed by open ocean Atlantic water in the previous years, thus transporting away the reprocessing ^{14}C signature. Such a factor would not be accounted for in our very simple model that considers a constant degree of dilution for the reprocessing releases over time, i.e. a steady state water circulation.

A more quantitative data analysis using multiple linear regressions was used to assess the dependence of the shell ^{14}C content on the bomb- and reprocessing-^{14}C.

$$^{14}C_{shell} = a\ (^{14}C_{ocean}) + b\ (\text{Liquid Release}_{reprocessing}) + \text{Constant}$$

To obtain two separate, annually-resolved shell ^{14}C datasets (for each area), a weighted mean was calculated when shell growth periods overlapped in time and the time periods without shell material were left empty (missing values). The regression models were estimated separately for Balgzand and Traeth Melynog, but the two locations had in common that the contribution from the bomb-^{14}C, i.e. the background estimated in Section 3.1 was assumed similar, while only the liquid releases from the respective reprocessing plant were considered, i.e. La Hague for Balgzand and Sellafield for Traeth Melynog. In the case of Balgzand, we opted to exclude the very high ^{14}C values in the late 1960s (1967 to 1969), as the first model estimations showed that they behaved as outliers and resulted in a non-normal distribution of the residuals of the regression. Thus, for Balgzand we effectively estimated the contribution of oceanic background $^{14}C_{ocean}$ and the contribution of liquid releases on top of that, for the time period 1969–2017. For Traeth Melynog, the period covered (1971–2017) was highly discontinuous and lacked data for multiple time periods (1977–1984, 1998–2002, 2006–2007 and 2010–2011).

For Balgzand, the above proposed full model explained 87% of the variance and was highly significant ($p < 0.001$) and residuals were normally distributed. Comparison with regression models with only $^{14}C_{ocean}$ or only the liquid relaease by La Hague did not yield satisfactory results and these models were unable to describe the time trend in $^{14}C_{shell}$ (indicated by a strong trend and non normality of residuals). The above results confirm that both anthropogenic sources are important contributors to the shell ^{14}C content of Balgzand. Also the accurate description of ^{14}C in coastal seawater and biota between La Hague and the southern North Sea is now possible, upon knowledge of reprocessing-^{14}C discharges and of the regional bomb-^{14}C pulse.

Compared to Balgzand, the same data analysis performed with the Traeth Melynog shells resulted in weaker relationships. The multiple linear regression model indicated a significant dependence (adjusted $R^2 = 0.63$, $p < 0.001$) of the shell ^{14}C content with reprocessing-^{14}C ($p < 0.001$), but the relationship with bomb-^{14}C was weak and insignificant ($p = 0.240$). Thus, the Traeth Melynog shells suggest that at this location the ^{14}C signal is mainly dependent on the discharges from Sellafield (adjusted $R^2 = 0.62$, $p < 0.001$), while the bomb-^{14}C appears to be weakly illustrated by its insignificance (adjusted $R^2 = 0.05$, $p > 0.1$).

For the Traeth Melynog shells both the full regression model as well as the partial models fitted poorly and moreover showed a non-linear trend in the residuals. We anticipate that this was mainly caused by a poorer time coverage of the shell material (see Supplemental Table S1), the large temporal variability of the reprocessing-^{14}C release rate after the 1990s from Sellafield (Fig. 1c) and the high shell ^{14}C values in the mid 1990s and 2000s (Fig. 4b). If the time coverage of shell material for Traeth Melynog was more complete, the data analysis would probably have provided stronger evidence of the impact of both the bomb and reprocessing releases into the Irish Sea. Both datasets however showed evidence for the measurable effect of liquid reprocessing releases in the observed temporal evolution of ^{14}C levels in the calcium carbonate of cockles.

3.4. Other inputs of anthropogenic ^{14}C

The above agreement between shell and simulated ^{14}C (Fig. 4) also indicates that gaseous ^{14}C releases from reprocessing activities (Fig. 1), nuclear power plants and research facilities in the study area (Fig. 2) are not significant compared to the liquid discharges of ^{14}C documented for the reprocessing plants and the bomb-^{14}C. If this was not the case, higher ^{14}C values recorded in shells of Traeth Melynog through the 1970/80ies (Fig. 4b) would be expected because of the large gaseous ^{14}C releases reported for Sellafield (Fig. 1c). Similarly, the nuclear power plants of Wylfa, Anglesey and Heysham, Lancashire, and the Amersham International facility in Cardiff (Fig. 2c), show no distinguishable impact on the sea surface ^{14}C at Traeth Melynog. In Balgzand, the deviation between shell and modelled ^{14}C would be expected to be even more enhanced than the observed ^{14}C between the 1990s and present (Fig. 4a) if gaseous releases from La Hague had a significant influence (Fig. 1b). Finally, there are three other nuclear facilities that could have perturbed the ^{14}C levels along the Dutch coast (Fig. 2b): the nuclear power plants at Borsele and Dodewaard, and the nuclear research reactor in Petten, the latter situated only 30 km south of Balgzand. For Borsele and Dodewaard only the gaseous releases were reported and these were 2 to 3 orders of magnitude smaller than the gaseous discharges from La Hague (RAAD, 2020). To the best of our knowledge there is no information on ^{14}C releases from Petten and no ^{14}C releases have been reported either from other European research reactors. Considering all the information and the fact that ^{14}C is a target radionuclide in research reactors (for research and medical use), it is reasonable to assume that releases of ^{14}C from Petten, if there were any, would have been minimal compared to the discharge from La Hague. Although our results do not allow us to discount a small input of gaseous ^{14}C from other sources than La Hague or Sellafield, they serve to demonstrate that liquid ^{14}C released from the two reprocessing facilities has dominated the temporal changes of sea surface ^{14}C over the last five decades.

3.5. Implications for ^{14}C applications

In most studies where modern samples are dated by ^{14}C, the measured ^{14}C is compared to the values displayed by the bomb pulse in order to retrieve a calendar age. While temporal records of the bomb pulse are valid for this purpose in most global areas, the shell-based reconstructions of ^{14}C reported in this study suggest that the marine bomb pulse may not suitably represent the ^{14}C concentrations of regional, northwestern European seawater. This is particularly the case for the southern North Sea between the mid-1990s and present, and for the Irish Sea over the last five decades. The additional inputs of liquid ^{14}C from the reprocessing plants have altered the seawater content of this radioisotope in a way that the range of ^{14}C concentrations in the surface ocean waters could be even larger than that displayed by the atmospheric bomb pulse. The implications for using time series ^{14}C to provide high resolution dating of marine materials are important. Firstly, our results demonstrate that the identification of a single peak, as is usually protocol with the bomb pulse, is not sufficient to enable a correlation with specific dated peaks, e.g. the 1995 and 2005 peaks in Traeth Melynog (Fig. 4). Secondly, the large difference in ^{14}C content of shells from Morecambe Bay and Traeth Melynog in the late 1990s (Fig. 4b) expectedly shows that the impact of reprocessing varies spatially due to regional water circulation. These findings should be considered when applying ^{14}C as a dating or tracing tool in northwestern Europe and since the time of first liquid discharges of ^{14}C from the reprocessing plants.

4. Conclusion

The impact of liquid reprocessing releases on the temporal changes in the ^{14}C content of surface seawater in NW European seas were assessed using a unique collection of shells with known capture age

and lifespan. The ^{14}C record reconstructed from shells deviates significantly from what we expect from the marine bomb pulse normally seen in sea surface waters, particularly at Traeth Melynog, Morecambe Bay and Balgzand. Temporal changes recorded in shell ^{14}C correspond to the variability of the documented liquid ^{14}C release rate from the two reprocessing plants and consequently enabled the attribution of the excess of ^{14}C in sea surface waters to the discharge of liquid waste from Sellafield and La Hague. Modelling suggests that the contribution of ^{14}C from gaseous sources is not significant confirming that liquid reprocessing-^{14}C is the major source to these regional waters. Because the ^{14}C concentration was well above the marine bomb pulse during the last 4 to 5 decades, and due to the significant differences in ^{14}C over relatively small spatial and temporal scales, ^{14}C dating could become problematic for samples from the English Channel, the Irish Sea and the North Sea. Therefore, we suggest in future ^{14}C studies of material from these regions the presented temporal records of ^{14}C are considered when planning field work and interpreting ^{14}C results.

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CRediT authorship contribution statement

Maxi Castrillejo: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Validation, Visualization, Writing - original draft, Writing - review & editing. **Rob Witbaard:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Validation, Writing - review & editing. **Christopher A. Richardson:** Conceptualization, Funding acquisition, Investigation, Resources, Methodology, Writing - review & editing. **Rob Dekker:** Funding acquisition, Investigation, Methodology, Resources, Writing - review & editing. **Caroline Welte:** Formal analysis, Methodology, Writing - review & editing. **Lukas Wacker:** Formal analysis, Methodology, Writing - review & editing. **Marcus Christl:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Validation, Writing - review & editing.

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