Unravelling 5 decades of anthropogenic ^{236}U discharge from nuclear reprocessing plants

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HIGHLIGHTS

- The ^{236}U circulation tracer is challenged by incomplete data on its input function.
- Bivalves used for reconstruction of ^{236}U discharges to Irish Sea and North Sea.
- Previously unknown large release of ^{236}U into the Irish Sea in the 1970s
- Tracing of ^{236}U confirms small water recirculation into English Channel.
- The large 1970s release may expand ^{236}U circulation studies to the S. Atlantic.

GRAPHICAL ABSTRACT
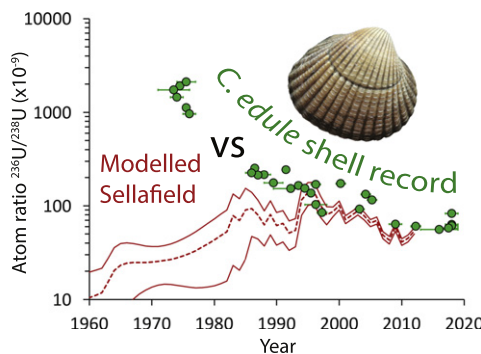
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ABSTRACT

Marine biogenic materials such as corals, shells, or seaweed have long been recognized as recorders of environmental conditions. Here, the bivalve *Cerastoderma edule* is used for the first time as a recorder of past seawater contamination with anthropogenic uranium, specifically ^{236}U. Several studies have employed the authorized radioactive releases, including ^{236}U, from nuclear reprocessing plants in La Hague, France, into the English Channel, and Sellafield, England, into the Irish Sea, to trace Atlantic waters and to understand recent climate induced circulation changes in the Arctic Ocean. Anthropogenic ^{236}U has emerged over recent years as a new transient tracer to track these changes, but its application has been challenged owing to paucity of fundamental data on the input (timing and amount) of ^{236}U from Sellafield. Here, we present ^{236}U/^{238}U data from bivalve shells collected close to La Hague and Sellafield from two unique shell collections that allow the reconstruction of the historical ^{236}U contamination of seawater since the 1960s, mostly with bi-annual resolution. The novel archive is first validated by comparison with well-documented ^{236}U discharges from La Hague. Then, shells from the Irish Sea are used to reconstruct the regional ^{236}U contamination. Apart from defining new, observationally based ^{236}U input functions that will allow more precise tracer studies in the Arctic Ocean, we find an unexpected peak of ^{236}U releases

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to the Irish Sea in the 1970s. Using this peak, we provide evidence for a small, but significant recirculation of Irish Sea water into the English Channel. Tracing the 1970s peak should allow extending ^{236}U tracer studies into the South Atlantic Ocean.

1. Introduction

Recycling of spent nuclear fuel is carried out to separate and recover the fissionable nuclides and involves the authorized discharge of low-level radioactive effluents into the environment. The ensuing contamination is extremely useful to oceanographers to trace the movement and mixing of marine waters. The point-source and temporally variable release of anthropogenic radionuclides from reprocessing plants has labelled European coastal waters with a different isotopic composition since the 1950s or late 1960s (Fig. 1a and b). Based on this principle, several studies have used the released nuclides (e.g. ^{60}Co, ^{106}Ru, ^{125}Sb, ^{129}I, ^{137}Cs and ^{3}H) to investigate water circulation transport pathways and timescales by tracing the labelled waters downstream of the discharge locations (e.g., Bailly du Bois and Guéguéniat, 1999; Smith et al., 2011; Yiou et al., 1994).

The long-lived anthropogenic ^{236}U (T$_{1/2}$ = 23.5 Ma) has become an increasingly important new transient circulation tracer, either alone or in combination with other conservative tracers, such as ^{129}I (T$_{1/2}$ = 15.7 Ma) (e.g., Casacuberta et al., 2018; Wefing et al., 2019). Reprocessing activities constitute the main regional input of ^{236}U in the North Atlantic and Arctic Oceans. The combination of ^{236}U from La Hague and Sellafield with Atlantic waters carrying a background value of ^{236}U that results from the atmospheric nuclear weapon tests (Casacuberta et al., 2014; Sakaguchi et al., 2009; Winkler et al., 2012) forms the so-called tracer input function, representing a valuable tool to calculate tracer ages and to estimate circulation timescales and mixing regimes of Atlantic waters in the Arctic and sub-Arctic regions (Casacuberta et al., 2018; Castrillejo et al., 2018; Wefing et al., 2019).

The application of ^{236}U is, however, compromised by incomplete information on the timing and the amount of ^{236}U releases from the two European reprocessing plants, making estimates of tracer ages and water mass circulation timescales uncertain. The quality of a transient tracer based circulation or mixing age crucially depends, amongst other factors, on the precise knowledge of its input function. It is, thus, essential to construct an accurate (with respect to both, magnitude and timing) ^{236}U input function. So far, a single study defines the tracer input function for ^{236}U from nuclear reprocessing (Christl et al., 2015b). The study showed that the main regional source of ^{236}U to western European seas is Sellafield, UK, with an estimated ^{236}U input of 30–90 kg into the Irish Sea between 1952 and 2013 (Fig. 1a). Due to missing documentation of ^{236}U releases, the modeled ^{236}U input function for the water stream carrying the Sellafield releases (hereinafter Sellafield-branch) has large uncertainties (red arrow in Fig. 1c). The second most important source is La Hague (Christl et al., 2015b), with a well-documented discharge of about 25 kg ^{236}U to the English Channel since 1966 (Fig. 1b).

Recent work showed that ^{236}U/^{238}U atom ratios from seawater are recorded in aragonitic corals (Sakaguchi et al., 2016; Winkler et al., 2012) with negligible fractionation (Chen et al., 2016; Weyer et al., 2008). In seawater, U is present as a highly soluble and stable uranyl-carbonate complex (Langmuir, 1978), which is readily (and preferentially) incorporated into aragonitic skeletons of marine calcifying organisms (Kaufman et al., 1971). Bivalves inhabit most coastal marine and estuarine environments and many construct their shells of aragonite. Bivalve sclerochronology (shell rings and shell growth lines) has been used to unravel temporal changes (Richardson, 2001) of marine pollution over time, including studies monitoring natural U discharges from industrial activities (Carilli et al., 2015; Price and Pearce, 1997). Amongst marine bivalves, the common European cockle *Cerastoderma edule* (*C. edule*) presents potential advantages as a chronological archive
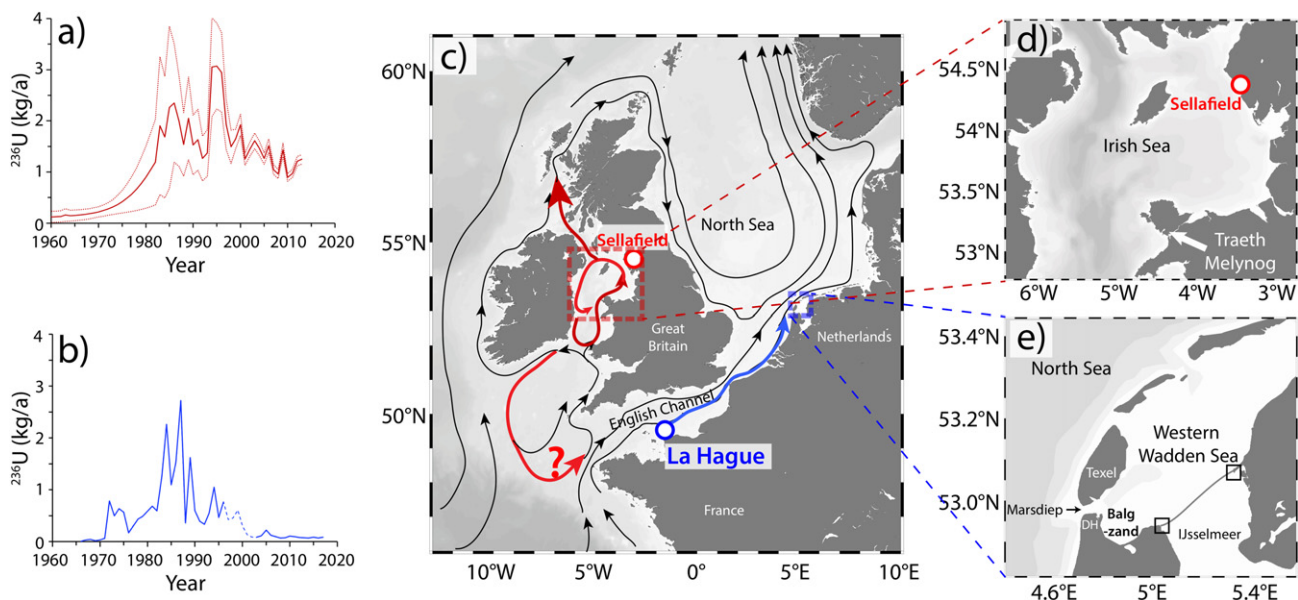
Fig. 1. a and b) Liquid ^{236}U discharge from European nuclear reprocessing plants. In red, modeled Sellafield ^{236}U releases with lower, middle and upper estimates from Christl et al. (2015b). In blue, documented and model-based (discontinuous line between 1997 and 2003) La Hague ^{236}U releases compiled by Christl et al. (2015b). The La Hague ^{236}U inputs from 2013 to 2017 were kindly provided by ORANO group. c) Map of the west European seas showing the location of the nuclear reprocessing plants of Sellafield (red) and La Hague (blue), and a simple scheme of the general water circulation. d and e) the two study areas of Traeth Melynog in the central Irish Sea, and Balgzand in the western Wadden Sea. DH = Den Helder.

of past U-isotopic composition in western European Seas. Firstly, their shell is composed of aragonite, which tends to accumulate greater amounts of U than calcite shells (Kaufman et al., 1971; Price and Pearce, 1997), sufficient to allow the determination of $^{236}U/^{238}U$ in a few gram of shell material by Accelerator Mass Spectrometry (AMS), the only technique capable of covering the full range of $^{236}U/^{238}U$ in marine samples (Christl et al., 2015a). Secondly, the shell structure presents a very clear growth pattern, which allows an accurate determination of its age and thus, timing of ^{236}U incorporation. A *C. edule* shell grows rapidly between April and October, although in young cockles slow growth continues during autumn and almost ceases in the winter months (December to January). This results in the deposition of an external dark annual winter ring on the shell surface, allowing the rapid, visual determination of the animal's lifespan (Milano et al., 2017; Richardson et al., 1980). Another advantage is that *C. edule* is highly abundant in temperate coastal intertidal mud and sand, and thus provides good spatial and temporal coverage in areas influenced by La Hague or Sellafield. The shells used in this study belong to two unique archives of *C. edule* that were collected annually from the late 1960s to 2019 (Beukema, 1982; Beukema and Dekker, 2018; Beukema and Dekker, 2009; Richardson et al., 1980). The animals were collected alive with accurate provenance (i.e. location and tidal height) and known collection date. Their lifespan was determined by counting the number of external winter rings and we mainly selected specimens with a two-year lifespan as a tradeoff between good temporal resolution and sufficient sample material. Older, large shells were discarded because the rings were narrowly spaced at the shell margin and difficult to discern for age determination. The resulting absolute timescale for the reconstruction of $^{236}U/^{238}U$ in each respective region is assumed to have no uncertainty.

In this study, we report $^{236}U/^{238}U$ ratios measured in *C. edule* shells, sediment, and seawater collected from regions exposed to radionuclide discharges from Sellafield (a sand and mud beach located 150 km to the SW named Traeth Melynog in North Wales, Fig. 1d) and La Hague (a sandy tidal flat with peat outcrops located 600 km to the NE named Balgzand, in the western Wadden Sea, Fig. 1e; see also Table S1). First, we confirm that $^{236}U/^{238}U$ ratios from seawater are reliably recorded by *C. edule* without significant influence from the seabed. Second, we reconstruct the $^{236}U/^{238}U$ ratios in seawaters carrying the La Hague signal covering more than five decades, and compare this dataset to the most reliable La Hague ^{236}U input function. After this validation step, we reconstruct the historical $^{236}U/^{238}U$ levels in the Irish Sea over the past ~50 yr to constrain the less known ^{236}U input into the Irish Sea. Finally, we present new and more accurate input functions for waters leaving western Europe and briefly discuss their impact on the oceanographic application of ^{236}U.

2. Materials and methods

2.1. Sample location and collection

Most shells belong to two collections (see Section 2.2). The shell material was collected from areas that are under the direct influence of waters labelled by reprocessing releases (Fig. 1). Delimited by Den Helder in the south and the island of Texel in the north, Balgzand is a 50 km^2 tidal flat located in southwestern Wadden Sea (Fig. 1e). This region is well flushed by the La Hague-branch that enters through the Marsdiep tidal inlet. The second collection is from Traeth Melynog, a 2 km wide sand/mud bay at the southern end of the Menai Strait, Anglesey, North Wales (Fig. 1d). The tidal flat is connected through the Menai Strait to both the southeastern and central Irish Sea. The mean shallow anticyclonic circulation in the Irish Sea and the coastal currents are shown to bring highly contaminated waters to Traeth Melynog and remain in that region for several months (ca. 400 days) after the tracer release at Sellafield (Dabrowski et al., 2010). Seawater and sediment samples were simultaneously collected together with fresh collections

of *C. edule* from Balgzand in April 2018 and from Traeth Melynog in January 2019 (Table S1). Sediments were collected manually using a trowel from the surface 2–3 cm and oven dried at 60 °C. The surface seawater overlying the mud flats on the flood tide was collected using a bucket and immediately acidified to pH <2 using home-distilled ultrapure nitric acid.

2.2. The two shell collections of C. edule

Cockles were collected during two long-term benthic fauna sampling programs that commenced in 1969 in Balgzand (Beukema, 1982; Beukema and Dekker, 2018; Beukema and Dekker, 2009) and in 1975 in Traeth Melynog (Richardson et al., 1980). The sampling took place annually or bi-annually with the exception of a few longer time gaps (Table S1). A small number of shells were also collected further downstream of Sellafield and La Hague branches in other parts of UK and Norway covering only a few years (Table S1). The animals were captured alive and their lifespan was determined by counting the surface annual winter rings, making elaborate age determinations (such as shell sectioning) unnecessary. The flesh was removed after boiling and the shells archived. From the whole collection, specimens were selected according to their capture date and lifespan (Table S1). Shell selection was based on individuals with two growing seasons (i.e. 2 years) so that the measured data could be placed in a narrow temporal context with an uncertainty of ±1 year. The error bar symbol represented in the figures (in time axis) indicates the age range of each individual specimen. The measured data points are always plotted in the middle of the growth span.

2.3. Initial sample treatment

The shell material was cleaned with deionized water in an ultrasonic bath and dried. Each sample consisting of 7-40 valves (20-30 grams) was homogenized by mechanical crushing down to small grains. A subsample of ~ 10 grams (equivalent to 2-6 valves) was weighted in a 250 mL LDPE bottle, mixed with 30 mL of deionized water and spiked with about 3 pg of ^{233}U. The ^{233}U spike was provided by the German Physikalisch-Technische Bundesanstalt (ref.: 2014-1126, Pommé et al., 2009), diluted in ETH-Zurich and concentration was cross-checked with TIMS at University Heidelberg. The amount of shell material was chosen based on initial tests aimed at investigating the sample mass required to obtain good counting statistics (^{236}U) as well as good ion currents (^{238}U) in the AMS measurement. The following steps included the complete digestion of the shell material using 15-20 mL of concentrated suprapure nitric acid, 1-2 mL of suprapure hydrochloric acid and few drops of hydrogen peroxide. The acidic solution was evaporated and reconstructed to about 100 mL with 0.01 M suprapure nitric acid. Then, the uranium was co-precipitated with iron hydroxides by adding 150 mg of Fe^{3+} as an U-free 5 M Nitric solution, and concentrated suprapure ammonia to rise the pH to 8.5. The bottle was centrifuged and the supernatant removed by syphoning. The iron precipitate was re-dissolved with concentrated suprapure nitric acid and evaporated 3 consecutive times.

In the case of sediments, 5-8 grams of substrate were weighed in a 250 mL LDPE bottle, mixed with 30 mL of deionized water and spiked with 1-3.5 pg of ^{233}U. The uranium was leached using suprapure concentrated nitric acid, hydrochloric acid, and hydrogen peroxide, and mixed with a shaker overnight. The sample was centrifuged, and the supernatant was filtered (0.45 mm pore size) and transferred to a new bottle. We repeated the leaching and centrifugation steps 3 times by adding 10 mL of 8M Nitric acid to ensure that the majority of the leachable uranium was recovered from the sediment. The solution was evaporated to dryness and reconstructed with 8M Nitric acid 3 consecutive times to remove acid impurities.

For the seawater, between 1.7 and 2.9 L of the unfiltered seawater were weighted and spiked with 1 to 3.5 pg of ^{233}U. The uranium was

co-precipitated by adding 250 mg of U-free Fe^{3+} solution and concentrated suprapure ammonia to rise the pH to ~8.5. After removal of the supernatant, the iron precipitate was redissolved in 8M suprapure nitric acid and evaporated to dryness 3 consecutive times.

2.4. Chemical separation and measurement of uranium

The same U extraction and AMS target preparation was applied to shells, sediments and seawater following a method described previously (e.g. Casacuberta et al., 2014; Christl et al., 2013). The reproducibility (Table S1 and Figure S4) of the method was tested by using replicates of 2-year old *C. edule* specimens collected in Balgzand (n= 7) and Traeth Melynog (n=4). The measurement of ^{233}U, ^{236}U and ^{238}U was carried out with the compact 0.5 MV Tandy AMS system at ETH-Zurich following previously described methods (Christl et al., 2015a). Measured $^{236}U/^{238}U$ and $^{233}U/^{238}U$ ratios were blank corrected and normalized to the ETH Zurich in-house standard ZUTRI, which has a nominal value of $(4055 \pm 200) \times 10^{-12}$ and $(33170 \pm 830) \times 10^{-12}$, respectively (Christl et al., 2013). Procedural blanks ($n = 14$) prepared with deionized water were processed in the same way as each sample type in the laboratory and run regularly together with the samples. The blanks in each measurement wheel were used to correct the corresponding samples for $^{236}U/^{233}U$ background, which was typically at the order of 10^{-5} ($^{236}U/^{233}U$) corresponding to <40 ag of ^{236}U. The abundance sensitivity of the Tandy AMS system is at a level of ~10^{-12} in the mass range of the actinides, which results in an estimated instrumental $^{236}U/^{238}U$ background in the order of ~10^{-14}.

3. Results and discussion

3.1. Contemporary $^{236}U/^{238}U$ ratios in shells, seawater and sediments

To demonstrate that *C. edule* faithfully captures a record of the U-isotopic composition of modern seawater we compared $^{236}U/^{238}U$ ratios measured in both seawater and shells covering the same temporal range (Fig. 2). In our study, the measured $^{236}U/^{238}U$ ratios of the shells are used for interpretation instead of ^{236}U and ^{238}U concentrations, because the latter, for example, depend on the concentration factor of each animal, and thus, do not represent a suitable proxy of the seawater U-isotopic composition. The full dataset is listed in Table S1.
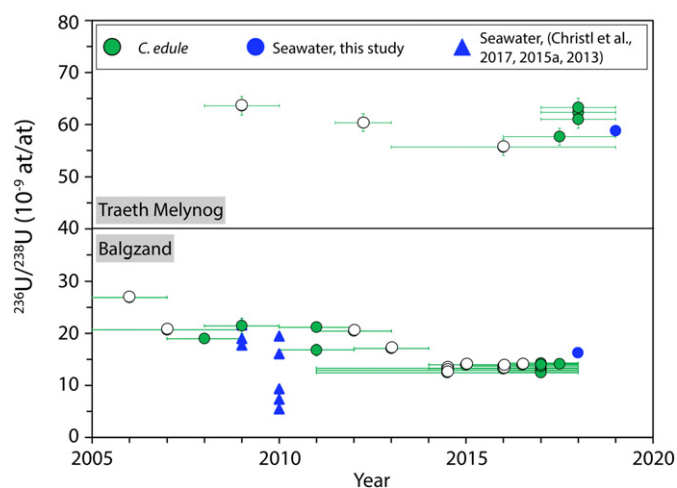
Figure 2. The $^{236}U/^{238}U$ atom ratio in *Cerastoderma edule* shells and surface seawater collected in Traeth Melynog (top panel) and Balgzand (bottom panel). Only shell data used for the comparison are shown as filled green symbols, while the open symbols were not considered in the calculations presented in the main body of text. For a more complete comparison, $^{236}U/^{238}U$ ratios of surface seawater collected in 2009 and 2010 are also plotted (Christl et al., 2017, 2015a, 2013). These samples were collected close to the path of the La Hague-branch, parallel to the coastline between France and Germany, between 51 and 55°N.

Our results show that recent $^{236}U/^{238}U$ ratios in shell material resemble modern $^{236}U/^{238}U$ ratios in seawater reasonably well (Fig. 2). *C. edule* living in Traeth Melynog between 2016 and 2019 display an average $^{236}U/^{238}U$ ratio of $(61 \pm 2) \times 10^{-9}$ (n=4), which is in agreement with a $^{236}U/^{238}U$ ratio of $(59 \pm 2) \times 10^{-9}$ (n=1) measured in the overlying seawater collected in January 2019. At Balgzand, in the western Wadden Sea, shells record an average $^{236}U/^{238}U$ ratio of $(13.5 \pm 0.7) \times 10^{-9}$ (n=8) for the 2016 - 2018 period. These results are lower than in seawater, however, considering that the seawater collected in April 2018 represents a snapshot compared to the time integrated by the shell material, we concluded that shell data agree well with the seawater ratio of $(16.2 \pm 0.5) \times 10^{-9}$ (n=1). Additional data on $^{236}U/^{238}U$ has been reported for surface North Sea water collected in 2009 and 2010 (Christl et al., 2017; Christl et al., 2015a; Christl et al., 2013). A subset of this data, corresponding to seawater sampled in or close to the La Hague-branch between 51 and 55°N was compared to the $^{236}U/^{238}U$ ratio in the Balgzand cockle shells over the same time period (Fig. 2). Maximum North Sea water values of $(19 \pm 2) \times 10^{-9}$ (n=5), representing the core of La Hague-branch, showed comparable $^{236}U/^{238}U$ ratios to Balgzand shells, $(20 \pm 2) \times 10^{-9}$ (n=6). The North Sea waters with values lower than 10×10^{-9} were collected further offshore, thus they expectedly showed a more diluted signal of the La Hague-branch.

Results displayed in Fig. 2 support previous experimental work concluding that oceanic ^{236}U is conservative in oxic seawater coditions (e.g., Casacuberta et al., 2014; Castrillejo et al., 2017; Chamizo et al., 2016; Sakaguchi et al., 2012). Yet, we wanted to verify wether surface sediments in which cockles are living would affect the U isotopic composition of the shells. In the case of sediments, we did not investigate the $^{236}U/^{238}U$ ratio, because the strong acid leaching could have dissolved part of the crustal ^{238}U diluting the $^{236}U/^{238}U$ ratio. Instead, we compared the ^{236}U concentrations in samples collected during 2018/19 that were $(2 - 7) \times 10^{6}$ at/g in shells and $(3 - 10) \times 10^{6}$ at/g in sediments from Balgzand, while the same values in Traeth Melynog were $(18 - 72) \times 10^{6}$ and $(22 \pm 0.5) \times 10^{6}$ at/g, respectively. The fact that shell ^{236}U concentrations were similar or larger than in sediments implies that, the desorption of U from the sediment or the ingestion of particles, would only incorporate a small fraction of the sedimentary U into the shell. The U desorbed from the sediments would rapidly dilute within seawater that is periodically renewed on the tidal flat. And, the ingestion of particles has a small impact on the shell composition (Beirne et al., 2012), being the physicochemical form of the U species in seawater (stable carbonate complex; Langmuir, 1978) the main factor controlling the U composition in marine biogenic carbonates (e.g. Aliyev and Sari, 2003; Keul et al., 2013). Therefore, we conclude that *C. edule* suitably records the U-isotopic composition of the seawater.

3.2. Validation of C. edule as a proxy for past $^{236}U/^{238}U$ ratios in seawater

In this section, the whole dataset of $^{236}U/^{238}U$ ratios from Balgzand shells is presented and compared to the modelled La Hague-branch from Christl et al. (2015b) that is based on the mixing and dilution of well documented ^{236}U releases (Fig. 1b) in a calibrated volume of water. With this independent validation (Fig. 3a), we tested whether *C. edule* could be used as a proxy for past ^{236}U releases from nuclear reprocessing plants.

The Balgzand shell dataset presents a range of $(10-160) \times 10^{-9}$ for the $^{236}U/^{238}U$ ratios since 1967 to 2018, which is a smaller variation than that of the modeled La Hague-branch of $(<1-300) \times 10^{-9}$ for the same time interval (Fig. 3a). The modeled values in the La Hague branch are based on documented ^{236}U releases covering most of the operational period of La Hague from 1966 onwards (references in Christl et al., 2015b). Following same steps as in Christl et al. (2015b), the La Hague branch waters were modeled with a simple one box model. It was assumed that the annual releases of ^{236}U from La Hague are fully mixed with the annual volume of Atlantic Water that passes through the
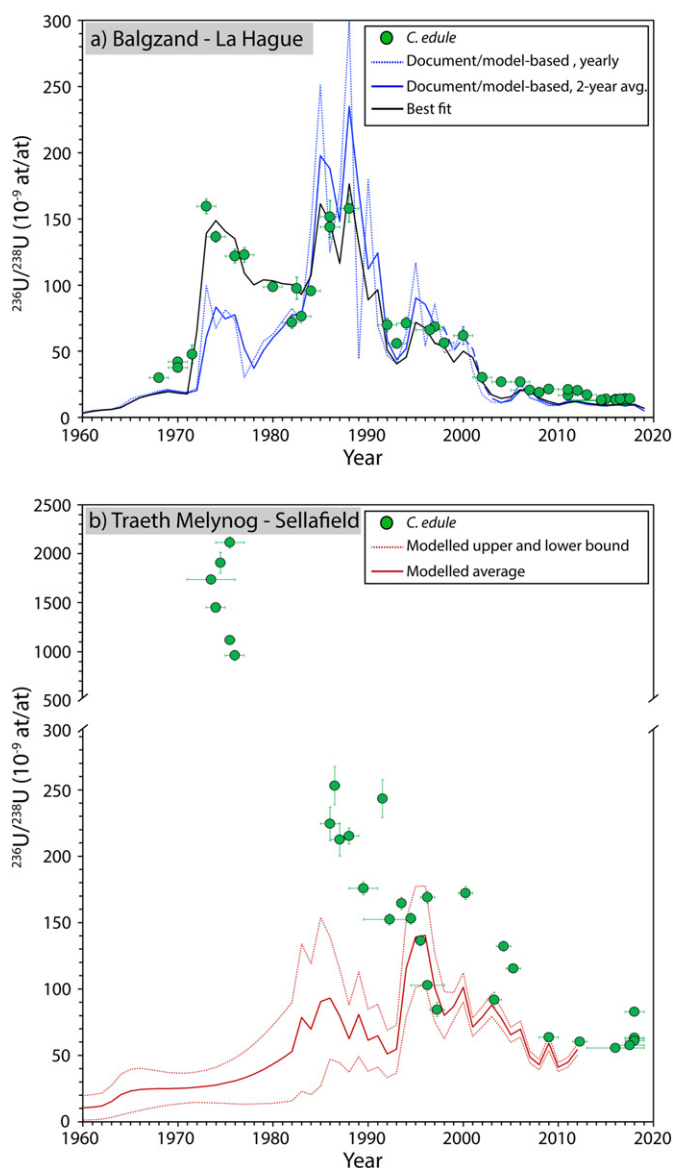
Figure 3. a) The comparison between the $^{236}U/^{238}U$ ratio in *C. edule* shells from Balgzand and the estimated input functions for the La Hague-branch (blue lines, calculated for 1 and 2-year averaged ^{236}U releases) serves as validation of the archive (discussion in Section 3.2). The water flux used to estimate the blue lines is 0.099 Sv, taken from Christl et al. (2015b). The black line is calculated and discussed in Section 3.6. It represents the 2-year averaged La Hague-branch, but with additional inputs of ^{236}U derived from Sellafield. It is calculated with 4% of ^{236}U annual releases from Sellafield and 100% from La Hague, and a flow rate of English Channel waters of 0.13 Sv. b) In Traeth Melynog, $^{236}U/^{238}U$ ratios in the shells show larger discrepancies with the modelled Sellafield-branch, which is calculated using a water flow of 0.29 Sv and ^{236}U input estimates provided in Christl et al. (2015b).

English Channel and via the Strait of Dover into the North Sea. These waters have a global fallout $^{236}U/^{238}U$ signature before the input from the reprocessing plant. The water flux (0.099 Sverdrup, 1 Sv=10^6 m^3 s^{-1}) was calibrated in their model to match the concentrations of ^{129}I (also released from La Hague) measured in the core of the La Hague branch near Balgzand in the North Sea. The transport of radionuclides from La Hague to the North Sea has been well studied (e.g., Bailly du Bois and Dumas, 2005; Delhez and Deleersnijder, 2002; Guegueniat et al., 1995; Herrmann et al., 1995; Salomon et al., 1995). Therefore, in the following we use the modelled $^{236}U/^{238}U$ ratios in the La Hague-branch for validating *C. edule* as a proxy of past $^{236}U/^{238}U$ ratios in seawater.

We observe a discrepancy in the 1970s between the shell-based $^{236}U/^{238}U$ ratios and the modeled values of the La Hague-branch (blue

lines in Fig. 3a) that will be discussed and explained in Section 3.6. The following four decades, the results from the two independent and radically different methodologies are in good agreement. See for example the comparison between the shell and annualy resolved model values (dashed blue lines in Fig. 3a). Because most of the analysed cockle shells had a two-year lifespan, the sum of residuals between shell and model data is improved by 25% when averageing the ^{236}U discharge every two years in the box model (continuous blue line in Fig. 3a). Despite the variable monthly releases of ^{236}U from La Hague (Figure S3), the shells appeared to record a well averaged biennial signal although their main growing period lasts from April to October.

A likely explanation for the good agreement between the shell data and the modelled $^{236}U/^{238}U$ ratios is that the La Hague-branch already integrates radionuclide releases that took place over several weeks to months. Possible processes causing the averaging of the signal are (i) eddies that are retained for weeks near the outlet (Salomon et al., 1988), (ii) a divergent velocity field (faster current speeds off the continent than close to the coastline), as well as (iii) the passage through the Dover Strait into the Southern North Sea, all resulting in enhanced mixing of radionuclide releases (Salomon et al., 1995).

3.3. Shell-based reconstruction of $^{236}U/^{238}U$ in the Irish Sea

After validation of *C. edule* as a reliable recorder of past $^{236}U/^{238}U$ levels in seawater, we now use cockles collected at Traeth Melynog (Fig. 1d), from 1971 to 2018 to reconstruct the historical $^{236}U/^{238}U$ ratios in the Irish Sea.

The $^{236}U/^{238}U$ ratios in the Traeth Melynog collection range between $(56 \pm 2) \times 10^{-9}$ and $(2100 \pm 60) \times 10^{-9}$ (Fig. 3b), spanning a much broader range than observed at Balgzand (Fig. 3a). The shell data are now compared to the modelled Sellafield-branch (red lines in Fig. 3b) that relies on less-well constrained ^{236}U inputs estimated by Christl et al. (2015b). As a first approximation, the ^{236}U is mixed with the same water flow (0.29 Sv) that was used for the Scottish Coastal Current in Christl et al. (2015b). The comparison of the shell data with the modeled $^{236}U/^{238}U$ ratios in the Sellafield-branch shows significant divergence, particularly in the 1970s, when extremely high $^{236}U/^{238}U$ ratios of $(1\text{-}2) \times 10^{-6}$ were recorded, while the agreement is reasonable in the more recent part after the 1980s (Fig. 3b). Remarkably, both the Sellafield and La Hague branches show the largest disagreement in the 1970s (Fig. 3).

3.4. What could have caused the elevated $^{236}U/^{238}U$ ratios in the Irish Sea in the 1970s?

The significant disparity between the modeled Sellafield-branch and shell based observations indicates that, either the model assumptions for the calculation of the $^{236}U/^{238}U$ ratios in the Sellafield-branch are incorrect, and/or that the ^{236}U (and total U) releases into the Irish Sea were much larger than reported in the 1970s and 1980s by Sellafield, and/or the existence of an unknown input of ^{236}U into the Irish Sea. The modeling of early ^{236}U releases from Sellafield is based on two main assumptions (Christl et al., 2015b). First, the annual water mass flow of Atlantic Water through the Irish Sea is assumed to be constant over the whole time period. Second, it is assumed that early U-releases are characterized by low $^{236}U/^{238}U$ ratios of about 1×10^{-4} steadily rising to about 0.005 (Boulyga and Becker, 2002) with increased use of modern reactors running with enriched U-fuels.

We acknowledge that the first assumption of a constant annual Atlantic water mass flow through the Irish Sea is too simplistic. However, to explain two orders of magnitude difference in $^{236}U/^{238}U$ ratios, the water mass flow must have gone down to 1% of its present level. There have been changes in western European seas linked to shifts in the North Atlantic Oscillation (Evans et al., 2003; Wakelin et al., 2003). But, such an extreme climate event has not been reported for the Irish Sea region making the remarkable reduced water mass flow a highly

unlikely explanation for the elevated $^{236}U/^{238}U$ ratios recorded in Traeth Melynog shells.

The second assumption about low $^{236}U/^{238}U$ ratios in the early releases from Sellafield is then analysed. To explain the observed deviation from the observations either the $^{236}U/^{238}U$ ratio of the releases was two orders of magnitude higher in the 1970s or Sellafield released much more total U with a low $^{236}U/^{238}U$ ratio (1×10^{-4}). In the first case, the $^{236}U/^{238}U$ ratio of the releases should have been of the order of 0.012-0.017 to explain the high ratio in shells of Traeth Melynog in the 1970s. This is highly unrealistic, because the ratio is well above the upper limit of 0.005 for recycled fuel used in nuclear power reactors (Boulyga and Becker, 2002). In the second case, a low $^{236}U/^{238}U$ ratio of 1×10^{-4} for low burn-up fuel would imply that total U releases were more than one order of magnitude larger in the 1970s than considered previously (Christl et al., 2015b). Sharp increases in the discharge rate of Pu and Am (Gray et al., 1995) isotopes, among other radionuclides (e.g. ^{137}Cs) have been reported in the 1970s (Fig. 4a). The peaks of $^{239+240}Pu$ and ^{241}Am described by Gray et al. (1995) coincide in time and magnitude (in the case of ^{241}Am) with the high $^{236}U/^{238}U$ ratios measured in Traeth Melynog shells, making the anomalously large total U releases a possible explanation for the observed deviation in the 1970s (Fig. 3b). Gray et al. (1995) associated the increased discharge rate of actinides to larger throughputs and reprocessing of residues. However, they also acknowledged that long storage times of fuel rods in the fuel storage pond might have lead to fuel rod corrosion and increased radioactivity of respective effluents, which were discharged to the sea without treatment until the late 1970s. Further, a separate study reported the presence of ^{236}U in dated sediments collected in Esk estuary, about 12 km to the south of Sellafield. Hamilton (2001) found measurable ^{236}U in the same sediment layer that recorded the peak discharge of ^{241}Am in 1973.

The third explanation would involve an additional source of ^{236}U. The nuclear facility at Springfields, Lancashire (UK), produced nuclear fuel since the mid 1940s, but it has been considered to be a negligible source of ^{236}U by Christl et al. (2015b). Other uranium inputs into the Irish Sea are investigated in Hamilton (2001). According to their study, producers of phosphoric acid discharged about 1100 tonnes of natural uranium off Sellafield between 1954 and 1992. The quantities of ^{236}U in natural uranium ores are however negligible. They also mentioned that the UK Ministry of Defense discharged/fired about 30 tonnes of tank shells containing reprocessing depleted uranium (RDU) and 7000 depleted uranium (DU) shells to the NE Irish Sea. However, such military inputs occurred in the 1980s and 1990s and were characterized by comparably low $^{236}U/^{238}U$ ratios of 1×10^{-7} (Hamilton, 2001).

From the above evidence and discussion, we conclude that the deviation observed in Traeth Melynog shells in the 1970s was most likely caused by incidental releases of uranium from Sellafield (as documented for other actinides in Fig. 4a), although, we cannot rule out smaller contributions from other sources.

3.5. New estimate of ^{236}U discharges into the Irish Sea

In this section we reevaluate past ^{236}U inputs into the Irish Sea (Fig. 4b), that is a necessary step towards defining a new ^{236}U input function for the Sellafield-branch. We recalculate the $^{236}U/^{238}U$ ratios in Irish Sea waters between 1971 and 2018 with annual resolution using the cockle shell data from Traeth Melynog (Table S2). A weighted mean is calculated when shell growth periods overlap in time. To fill short time gaps of 1-2 yr without shell material in 1998, 2001, 2006, and 2010, we used an interpolated mean value based on data available immediately before and after. We exclude the larger gap in 1977-1984 from these calculations. The resulting annually resolved $^{236}U/^{238}U$ ratios are then multiplied by the ^{238}U mass present in one liter of seawater (concentration of $^{238}U=3.3ug/l$) and by a volume of water, to obtain the annual ^{236}U content. In this study, the average annual volume of the Sellafield-branch water is determined using the ^{236}U discharges reported by Christl et al. (2015b). As mentioned before, their ^{236}U input function for Sellafield is more uncertain than for La Hague. However, it is thought to be more precise for the time period after the 2000s (Christl et al., 2015b), a period during which we also find good agreement with the Traeth Melynog shell data (Fig. 3b). Therefore, we used the ^{236}U discharges between 2005 and 2013 as calibration period to match the shell data with the modeled Sellafield-branch using the water volume as optimization parameter. The obtained volume of water was 5.52×10^{15} L, resulting from an annual flow of 0.17 Sv. Finally, the small contribution of ^{236}U from the global fallout is subtracted using the modeled global fallout-derived ^{236}U concentration in the ocean mixed layer (Elsässer et al., 2015). From the above calculations, we estimate that large quantities of ^{236}U (165 ± 15 kg) were introduced in a short time period (1971-1976), whereas the discharge since 1985 to present accounted only for 72 ± 6 kg (Fig. 4b). Even when excluding the 1977-1984 gap, the observational, shell-based ^{236}U inputs largely disagree with previous model estimates. Our results actually suggest that ^{236}U releases to the Irish Sea were larger than previous indirect estimates (62 ± 31 kg of ^{236}U in 1952 – 2013, Christl et al., 2015b) and not lower, as proposed by recent modelling work (Periáñez et al., 2018).
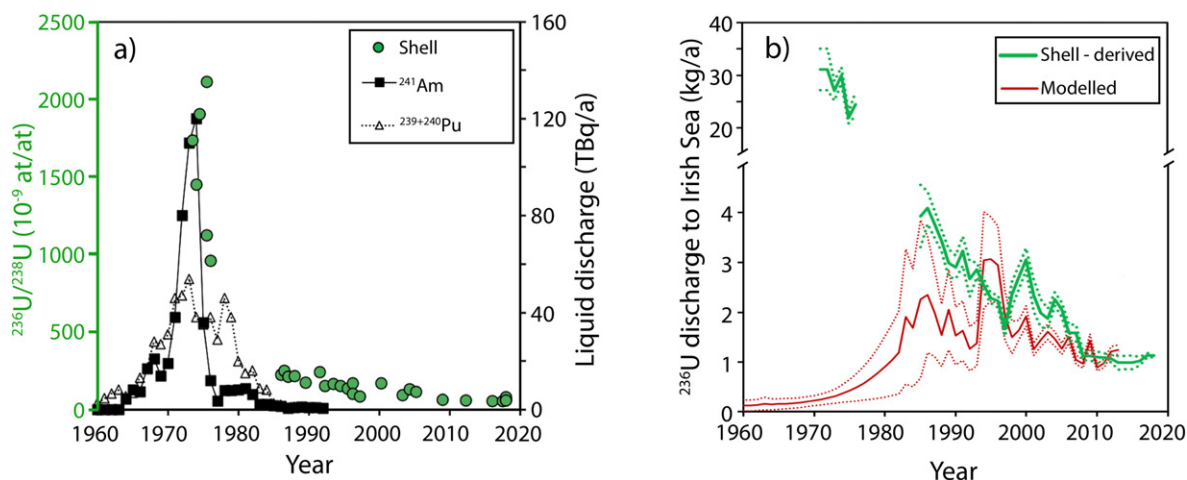
Figure 4. a) The $^{236}U/^{238}U$ ratios measured in shells (left y-axis) are compared to liquid discharges of ^{241}Am and $^{239+240}Pu$ reported for Sellafield (right y-axis) by Gray et al. (1995). b) ^{236}U discharge to the Irish Sea reconstructed from Traeth Melynog cockle shell data (green) is compared to modelled values from Christl et al. (2015b).

3.6. Irish Sea water transport into English Channel evidenced from shell $^{236}U/^{238}U$ ratios

Radionuclide measurements have been extremely useful in the past to intentify circulation pathways and validate hydrodynamic models for the North Sea and adjacent seas (e.g. Bailly du Bois and Dumas, 2005; Bailly du Bois and Guéguéniat, 1999; Dabrowski et al., 2010; Periáñez et al., 2018). These studies showed that waters leaving the Irish Sea usually flow northward and then clockwise along the Scottish coast into the northwestern part of the North Sea (Fig. 1c). Yet, under certain atmospheric conditions Central Irish Sea Waters can flow southward along the west coast of England (e.g. Dabrowski et al., 2010). That reversal of the circulation has been hypothesized to be the cause for the excess of ^{137}Cs measured in surface seawater of the English Channel in 1983-1994 (Bailly du Bois and Guéguéniat, 1999). They argued that an additional input of ^{137}Cs from Sellafield releases was necessary to explain the high radionuclide concentrations in their study area. The $^{236}U/^{238}U$ ratios measured in cockle shells (Fig. 3) support this alternative re-circulation of Irish Sea waters into the English Channel. A large ^{236}U input to the Irish Sea (e.g. Sellafield) would explain the hughe $^{236}U/^{238}U$ ratios displayed by cockles from Traeth Melynog in the early 1970s, and the subsequent transport and dilution of a small part of the ^{236}U releases into the La Hague-branch would justify the smaller, yet visible, peak in $^{236}U/^{238}U$ ratios displayed by shells at Balgzand in the mid 1970s. One could argue that the Irish Waters that entered through the northwestern passage to the North Sea could also influence the ^{236}U shell content in Balgzand. However, the distributions of ^{129}I and ^{236}U measured in North Sea waters indicate that the Sellafield-branch is retroflected northward at great distance off the Dutch coast, and that Balgzand remains isolated thanks to the coastal, advective flow of the La Hague-branch (Christl et al., 2015a).

We can use the 1970's mistmatch in Balgzand (blue lines vs shells in Fig. 3a) to estimate the amount of ^{236}U that was transported southward from the Irish Sea into the English Channel and eventually to the Dutch coast. To that end, we employed the simple one box model for the La Hague-branch (see Section 3.2), but this time, we added variable amounts of ^{236}U (as the percentage of Sellafield releases) and adjusted the degree of dilution again by varying the flow rate of English Channel Waters. The results (Table S3) showed that several pairs of ^{236}U inputs and water flows can explain the $^{236}U/^{238}U$ ratios observed in Balgzand. Yet, we find the best fit (black line in Fig. 3a) when the additional ^{236}U is equivalent to 4% of the ^{236}U input into the Irish Sea, and when the water flow in the English Channel is increased to 0.13 Sv. The obtained flow of 0.13 Sv for the 1967-2018 time period is consistent with the mean flow reported for English Channel waters (range 0.06 – 0.17 Sv, Mathis et al., 2015). In general, the magnitude of the flow of radionuclides leaving the Irish Sea and incorporated into the English Channel is larger in our estimates (Tables S3), but in the same order of magnitude, as for the 1% of Sellafield ^{137}Cs releases suggested by Bailly du Bois and Guéguéniat (1999).

3.7. New ^{236}U input functions and their implication for tracing the ocean circulation

One main goal of this study is to provide observational ^{236}U input functions so that tracer studies can calculate accurate timescales of oceanic circulation. To that end, shell data are used (as explained above) to estimate annually resolved $^{236}U/^{238}U$ ratios for the seawater in the Irish Sea and the English Channel. For the Irish Sea waters, we linearly interpolate the data from 1976 and 1985 to complete the gap in 1977-1984. The new input functions are represented in Fig. 5. The comparison with corresponding input functions based on modeled (Sellafield) and documented (La Hague) ^{236}U inputs shows very large deviations before ~1985 and much smaller differences after that time period. The Irish Sea and English Channel waters are known to flow into the North Sea, from where they can follow two main transport pathways. They can
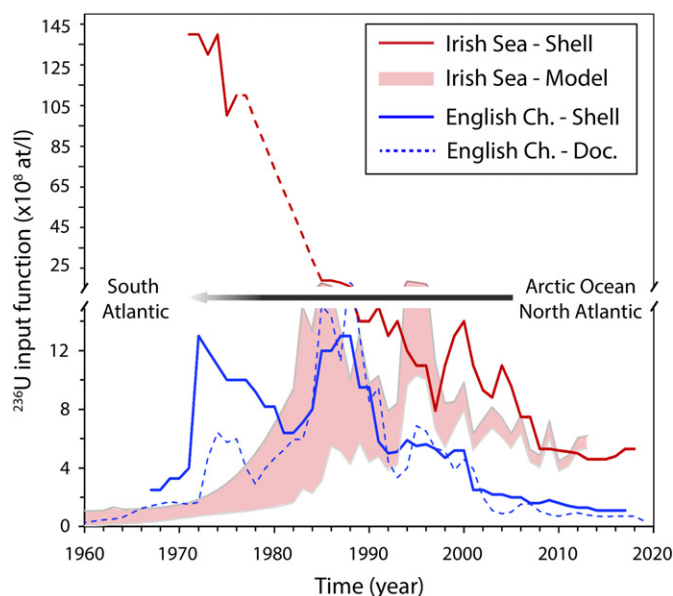
Figure 5. New ^{236}U input function for Irish Sea and English Channel waters estimated from shell-based, annually-resolved $^{236}U/^{238}U$ ratios are compared to the ^{236}U input functions based on modeled and documented ^{236}U discharges from Sellafield and La Hague, respectively. The waters leaving western Europe less than 30 years ago should now be in the Arctic-N. Atlantic region, whereas the 1970s ^{236}U peak should now be flowing towards or within the South Atlantic.

either be transported directly into the N. Atlantic within >5 years (Smith et al., 2005), or the waters can circulate into (and within) the Arctic Ocean for 10 to 25 extra years (Casacuberta et al., 2018; Karcher et al., 2012; Smith et al., 2011; Wefing et al., 2019) before entering the Atlantic (Castrillejo et al., 2018). Therefore, two important conclusions can be derived from Fig. 5. Firstly, the recent studies using ^{236}U and ^{129}I to estimate transport times of water in the Arctic and subpolar North Atlantic are reasonably robust because the time scales of circulation in the region correspond to a time period when substantial agreement was found between the shell based input functions and those employed prior to this study (see arrow in Fig. 5). Secondly, ^{236}U tracer studies carried so far focused on the Arctic and North Atlantic regions primarily because ^{236}U levels were expected to progressively decrease whilst moving towards lower latitudes. However, the unaccounted ^{236}U inputs to the Irish Sea in the 1970s (Fig. 4b) result in exceptionally large ^{236}U concentrations in the input function prior to 1985 (Fig. 5). As consequence, that prominent ^{236}U signal should (although being continuously diluted) now be flowing southward, very likely south of the Equator. Thus, we suggest that ^{236}U can be extended to global oceanographic studies by for example, tracing the 1970s releases as far as the South Atlantic Ocean. So far, no ^{236}U data has been presented for the South Atlantic.

4. Conclusions

This study was designed to constrain the amount and timing of ^{236}U discharges from nuclear fuel reprocessing plants, based on observations. To this end, we measured the $^{236}U/^{238}U$ atom ratio in shells of the bivalve *C. edule* with known capture date and age that lived under the direct influence of La Hague and Sellafield. The comparison of U data from the shells, and co-existing seawater and sediments, as well as, between the shell data and documented La Hague releases, validates the archive to reconstruct past U levels in seawater. Since *C. edule* is abundant in many temperate coastal areas, this approach can be applied to reconstruct other unknown sources of ^{236}U worldwide. This study also highlights on major strength of the ^{236}U tracer, the possibility to look at the past by using carbonate archives. For example, we found major releases of ^{236}U into the Irish Sea in the 1970s that, to our best of knowledge,

were not reported. The results are also important for physical oceanography studies investigating the transport pathways and rates of water circulation. At the regional scale, the 1970s ^{236}U peak provides quantitative evidence of the radioactive plume transport from the Irish Sea south into the English Channel. The comparison between the new input functions based on the shell data and earlier model estimates indicated that ^{236}U is a robust tracer for investigating water circulation and the foreseen changes, in the Arctic and sub-Arctic regions. Finally, we suggest that future ^{236}U tracer studies can search for the 1970s ^{236}U peak and use that information to investigate large-scale water circulation processes, such as ventilation, in the entire Atlantic Ocean.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.137094.

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