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Anthropogenic ^{236}U in Danish Seawater: Global Fallout vs. Reprocessing Discharge

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ABSTRACT

This work focuses on the occurrence of ^{236}U in seawater along Danish coasts, which is the solely water exchange region between the North Sea/Atlantic Ocean and the Baltic Sea. Seawater collected in 2013 and 2014 were analysed for ^{236}U (as well as ^{238}U and ^{137}Cs). Our results indicate that ^{236}U concentrations in Danish seawater are distributed within a relatively narrow range of $(3.6\text{--}8.2) \times 10^7$ atom/L and to certain extent independent of salinity. $^{236}\text{U}/^{238}\text{U}$ atomic ratios in Danish seawater are more than 4 times higher than the estimated global fallout value of 1×10^{-9} . The levels of $^{236}\text{U}/^{238}\text{U}$ atomic ratios obtained are comparable to those reported for the open North Sea, and much higher than several other open oceans worldwide. This indicates, besides the global fallout input, the discharges from the two major European nuclear reprocessing plants are dominating sources of ^{236}U in Danish seawater. However, unexpected high $^{236}\text{U}/^{238}\text{U}$ ratios as well as high ^{236}U concentrations were observed at low salinity locations of the Baltic Sea. While this feature might be interpreted as a clue for another significant ^{236}U input in the Baltic Sea, but may also be caused by the complexity of water currents or slow turnover rate.

23 Highlights

- 24 • First results of ^{236}U in the mixing area of the North Sea/the Atlantic Ocean and the Baltic Sea are
- 25 reported.
- 26 • Anthropogenic ^{236}U dominates Danish seawater with a relatively homogeneous distribution of ^{236}U
- 27 concentration independent of salinity.
- 28 • Relatively high levels of ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios are observed in Danish
- 29 seawater, which might need to be taken into account when carry out tracer applications of ^{236}U in the
- 30 North Atlantic-Arctic Ocean.
- 31 • If ^{236}U derived from the early era of reprocessing was stored or deposited in the sediment of the
- 32 Baltic Sea and serves now as a major source, ^{236}U might be a potentially useful tracer to investigate
- 33 the turn over and exchange of the water in Baltic Sea, as well as the interaction between the sediment
- 34 and water in the Baltic Sea.

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INTRODUCTION

^{236}U ($t_{1/2} = 2.34 \times 10^7$ y) is produced by thermal neutron capture of the omnipresent ^{235}U via (n, γ)-reactions, as well as through ^{238}U (n, 3n) ^{236}U reactions with fast neutrons. A very minor amount (about 35 kg) of natural ^{236}U was estimated on the Earth's crust surface, mainly in uranium ores,¹ while the majority (more than 1000 kg) of ^{236}U in the environment originate from anthropogenic nuclear activities, e.g., fallout from atmospheric nuclear weapons testing and discharges from nuclear facilities.^{2,3}

Since $^{236}\text{U}/^{238}\text{U}$ isotopic ratios together with the occurrence of other minor U isotopes carry key signatures for uranium sources, ^{236}U has been recognized as a valuable tracer in nuclear safeguards, geology and environmental studies.³⁻¹⁵ In recent years, the potential of ^{236}U as a new oceanographic tracer has been promoted by several studies.^{1,16-21} Based on its conservative behavior and well-established knowledge regarding all other naturally occurring U isotopes in the ocean, ^{236}U would provide an additional transient signal of water masses. In combination with other anthropogenic tracers (e.g., CFCs, ^3H , ^{14}C , ^{134}Cs , ^{137}Cs , ^{129}I , ^{99}Tc), tracer applications of ^{236}U in the world oceans would provide a clearer picture illustrating water mass movements, circulation and mixing patterns of different water flows, which are important and challenging aspects in oceanography. Even though significant work has been devoted to assess its distribution and to develop tracer applications of anthropogenic ^{236}U in the marine environment, worldwide ^{236}U data is limited; especially the distribution of ^{236}U in regional seas, such as the Baltic Sea is not well known. A major challenge in applying ^{236}U to oceanographic tracer studies is to define the source terms of ^{236}U in the marine environment.

To be used as a reliable tracer, knowledge on the source terms of ^{236}U in the Ocean is a prerequisite. It was estimated that global fallout of the atmospheric nuclear weapons testing has released 1000 - 1400 kg of ^{236}U to the environment.^{17,20} It was estimated that about 10^6 kg of ^{236}U has been produced in nuclear power reactors, of which the majority still remain in unprocessed nuclear waste and only a small proportion is released from the reprocessing plants.³ The North Atlantic and Arctic Oceans have been identified as regions of special oceanographic interest, due to their role in the thermohaline

circulation.^{19,22} Several studies using various tracers have been applied in these domains over the past decades, including natural and anthropogenic radionuclides. ^{236}U would be another conservatively behaving water mass tracer to use. However, the source terms of ^{236}U especially in the region of the North Atlantic and Arctic Oceans are not yet clear and the environmental distribution of anthropogenic ^{236}U is still not sufficiently investigated.

Several studies have reported $^{236}\text{U}/^{238}\text{U}$ ratios up to 10^{-8} in young surface waters and sediments in Northwest Europe.^{18,19} Anthropogenic ^{236}U has also been detected at more than 4000 m depth in the equatorial Atlantic Ocean.^{1,20} The two European nuclear fuel reprocessing facilities La Hague (France) and Sellafield (UK) are considered as important ^{236}U sources in the Atlantic-Arctic Ocean. In seawater collected in 1993 from the Irish Sea affected by the radioactive waste release from the Sellafield reprocessing plant, $^{236}\text{U}/^{238}\text{U}$ atomic ratios were reported to be 2×10^{-6} .⁷ Elevated ^{236}U levels ($^{236}\text{U}/^{238}\text{U}$ atomic ratios reached to 2×10^{-8} in 2009) were also observed in seawater near the La Hague reprocessing plant.¹⁸ However, due to limited documentation of the uranium discharge history of the two European nuclear reprocessing plants, little is known about the actual $^{236}\text{U}/^{238}\text{U}$ ratios in the discharges from the reprocessing plants. The only available data is from La Hague, that contributes a minor part to the total amount of ^{236}U released into the North Sea.^{18,19,23} Studies have indicated that the spatial distribution of ^{236}U in the North Sea is consistent with a simple model that involves the two reprocessing plants as the sole sources of ^{236}U in this marine region.¹⁸ However, more experimental data are needed to constrain parameters used in the model in order to reconstruct the discharge history of the two reprocessing plants.

Furthermore, the understanding of uranium environmental behavior in the mixing process of different water currents is another key issue in tracer studies utilizing ^{236}U . Uranium is known to be generally conservative in open oceans under oxygenated conditions.^{24,25} Whereas, several studies have indicated that the behavior of uranium is not strictly conservative in anoxic water systems.^{25,26} For example, in the deeper intermittently anoxic basin of the Baltic Proper (e.g., Gotland Deep, being anoxic below 200 m depth since 1979), uranium was reported to be removed from the water phase and incorporated into the sediment.²⁶ The anoxic intermediate section of the Black Sea contains less U ($1.3 \mu\text{g}/\text{kg}$) compared to the

surface water (1.8-2.0 µg/kg), while the bottom sediments in the central part are enriched in uranium (10-12 ppm).^{27,28} It has been suggested that the mechanism for withdrawal of dissolved uranium from the water phase are reduction of uranium (VI) to uranium (IV), followed by precipitation as UO₂, or adsorption on a reactive phase, e.g., organic material.^{25,26}

The Danish Straits are the sole water exchanging area between the oceanic North Sea/the Atlantic Ocean and the brackish Baltic Sea. Saline water from the North Sea flows near the bottom into the Kattegat, where outflow water of lower salinity from the Baltic remains on the surface. The Danish Straits provide unique advantages to study water mixing between the saline North Sea water and brackish Baltic Sea water and the dispersion of uranium in different water systems, especially transport of ²³⁶U discharged from Sellafield and La Hague reprocessing plants to the North Atlantic Ocean and the Baltic Sea.

In this work, seawater samples collected along the Danish coast were analyzed for ²³⁶U and other radionuclides (²³⁸U and ¹³⁷Cs). We aimed to investigate the mixing behavior and the source terms of ²³⁶U in the North Sea - Baltic Sea region using the levels and distribution pattern of ²³⁶U obtained in this work, thus contribute to assess the dispersion of anthropogenic ²³⁶U in the Atlantic-Arctic Ocean.

MATERIALS AND METHODS

Standards, reagents and samples. Uranium standard solution (1.000 g/L in 2 mol/L HNO₃) was purchased from NIST (Gaithersburg, MD), which was used after dilution as a standard for the ICP-MS measurement to quantify ²³⁸U in seawater. All reagents used in the experiment were of analytical reagent grade and prepared using ultra-pure water (18 MΩ·cm). UTEVA resin (100-150 µm particle size) was purchased from Triskem International, Bruz, France and packed in 2-mL Econo-Columns (0.7 cm i.d. × 5 cm length, Bio-Rad Laboratories Inc., Hercules, CA) for the chemical purification of uranium isotopes. Surface and bottom seawater samples collected from Danish coasts in the summer (June-July) of 2013 and 2014, respectively, were analyzed for salinity, ¹³⁷Cs, ²³⁸U and ²³⁶U. Details of samples information are summarized in Table S-1 and a map of the sampling locations is shown in Figure 1.

Analytical methods for determination of ^{137}Cs , ^{238}U and ^{236}U . To determine ^{137}Cs in each seawater, 45 L of seawater was transferred to a flask and acidified to pH 2 with concentrated HNO_3 . 30 mg of Cs carrier (as CsCl) and 50 g of ammonium 2-molybdophosphate (AMP) was added and the sample was stirred for 1 h for the adsorption of Cs by AMP. After settling for overnight, the supernatant was discarded and the remaining slurry was filtered and dried at 105 °C in an oven for overnight. The AMP powder was weighed to calculate the chemical yield of Cs and then measured by gamma spectrometry using HPGe (high-purity germanium) detectors with about 40% relative efficiency. To reach acceptable levels of detection limits and measurement uncertainties, each sample was counted for 24 h.

The concentration of ^{238}U in seawater was directly measured by ICP-MS (X Series^{II}, Thermo Fisher Scientific, Waltham, MA) after 10 times dilution. The ICP-MS instrument was equipped with an Xt-skimmer core and a concentric nebuliser under hot plasma conditions. The typical operational conditions of the instrument have been given elsewhere.²⁹ Indium (as InCl_3) was used as an internal standard and 0.5 mol/L HNO_3 solution was used as a washing solution between consecutive assays.

The detailed analytical method for the determination of ^{236}U in seawater has been reported elsewhere.³⁰ It should be noted that the seawater samples collected in 2013 were not filtered before analysis while the samples collected in 2014 were filtered through a Munktell 00K paper filter. In short, to 5 or 10 L seawater, conc. HNO_3 was added to adjust pH to 2 and purified FeCl_3 solution (0.05 g/mL of Fe) was added to a final Fe concentration of 0.1g/L. The sample was vigorously stirred with N_2 bubbling for 5-10 minutes. 10% $\text{NH}_3 \cdot \text{H}_2\text{O}$ was slowly added to adjust the pH to 8-9. The sample was kept still for 0.5-1 h, and the supernatant was decanted. The sample slurry was centrifuged at 4000 rpm for 5 minutes and the supernatant was discarded. 20 mL of conc. HNO_3 was added to the residue and the solution was heated at 200 °C until near dryness. The final residue was dissolved with 15 mL of 3 mol/L HNO_3 and the solution was loaded onto a 2-mL UTEVA column which was pre-conditioned with 20 mL of 3 mol/L HNO_3 . The UTEVA column was rinsed with 40 mL of 3 mol/L HNO_3 , followed by 20 mL of 6 mol/L HCl . Uranium absorbed on the column was eluted with 10 mL of 0.025 mol/L HCl . The flow rate for the chromatographic separation was controlled manually to 1.0-1.5 mL/min.

A 100-μL aliquot of U eluate was taken and diluted 1000-10000 times with 0.5 mol/L HNO₃ for measurement of ²³⁸U by ICP-MS to calculate the chemical yield of uranium as well as for the calibration of the actual ²³⁶U/²³⁸U atomic ratio in the AMS target as described below. To the remaining U eluate, 3 mg of Fe (as FeCl₃ solution) was added, and the sample was adjusted to pH>9 with ammonia to co-precipitate U. The precipitate was dried in an oven at 100 °C and then was baked in a furnace for 2-3 hours at 700 °C. The sample was then ground to a fine powder, mixed with a similar volume of silver powder and pressed into aluminum sputter target holders for the AMS measurement of ²³⁶U/²³⁸U. The AMS measurement was carried out at the 3-MV tandem accelerator facility VERA (Vienna Environmental Research Accelerator) at the University of Vienna, Austria. The detailed method for AMS measurement of ²³⁶U has been reported elsewhere.³¹

The blanks were prepared using the same procedure as the samples for every batch of samples (4 to 8 samples), and the actual ²³⁶U/²³⁸U atomic ratio (R_s) in the sample was calculated based on the following equation.

$$R_s = \frac{238 (m_m R_m - m_b R_b)}{236 (m_m - m_b)}$$

Where m_m is the ²³⁸U mass in the eluate measured by ICP-MS, R_m is the ²³⁶U/²³⁸U ratio measured in the AMS target, m_b is the ²³⁸U mass in the eluate of the procedure blank measured by ICP-MS, and R_b is the ²³⁶U/²³⁸U ratio measured in the AMS sputter target of the procedure blank.

In principle the actual m_m and m_b should be the corresponding ²³⁸U mass in the final sputter sample for AMS instead of the eluate. Due to the large variation of signal intensity (beam current) of ²³⁸U in the AMS measurement of the targets without isotopic spike, more accurate ²³⁸U values measured by ICP-MS were used to reduce the analytical uncertainty based on the assumption of quantitative U recovery in the sputter target preparation step, which has been confirmed previously.³⁰ It should be noted that with the use of pre-purified chemicals, the contributions of ²³⁶U ($m_b \cdot R_m$) and ²³⁸U (m_b) from procedure blanks are rather negligible compared to their contents in individual samples,³⁰ therefore the differences between R_s and R_m are within the reported uncertainty ranges (averagely 10%) for most samples analysed.

RESULTS AND DISCUSSION

Distribution of ^{236}U concentration and $^{236}\text{U}/^{238}\text{U}$ ratio in Danish seawater

The overall results for ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios (as well as salinities, ^{137}Cs and ^{238}U concentrations) obtained in this work are summarized in Table S-1. The geographical distribution patterns of ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios in seawater along the Danish coasts for the 2013 - 2014 are illustrated in Figure 2 and 3, respectively. In general, the ^{236}U concentrations, $^{236}\text{U}/^{238}\text{U}$ atomic ratios as well as salinity obtained in 2013 compare well with the values obtained in 2014 for samples from the same locations, reflecting the relatively slow water exchange rate in the investigated region.

The measured $^{236}\text{U}/^{238}\text{U}$ atomic ratios vary within one order of magnitude for both surface water ($(9.3\text{--}31.6) \times 10^{-9}$) and bottom water ($(5.4\text{--}24.9) \times 10^{-9}$) in the period of 2013-2014. In contrast to the distribution pattern of ^{236}U concentration, higher $^{236}\text{U}/^{238}\text{U}$ atomic ratios in both surface and bottom water are observed in the southeast of Zealand, which is dominated by the inflows of the Baltic seawater.

^{236}U concentrations around the coasts of Zealand vary within relatively narrow ranges for both surface ($(3.6\text{--}8.2) \times 10^7$ atom/L) and bottom ($(4.5\text{--}8.0) \times 10^7$ atom/L) seawater during 2013-2014. Combining the results for seawater from Jutland coasts, it can be seen that there is a decreasing trend of the ^{236}U concentration in the surface seawater from the west coast of Jutland to Kattegat and the Great Belt region. The lowest ^{236}U concentration around Zealand is observed in the surface water of Sundet N (station 11). However, the ^{236}U concentrations increase slightly in the south area (Femern Belt) of Zealand. Among the Jutland surface water, the lowest concentration of ^{236}U (3.2×10^7 atom/L) is observed at Øster Hurup (station 13), which is probably related to the inshore sampling site, where the collected seawater is diluted with fresh water as indicated by its relatively low salinity. In the bottom water around Zealand, lower ^{236}U concentrations are observed along Sundet area (station 10), while relatively higher ^{236}U concentrations are observed for both Kattegat and Femern Belt. The average ^{236}U concentrations in Zealand bottom water (6.1×10^7 atom/L for 2013 and 6.4×10^7 atom/L for 2014) are slightly higher than that in the surface water (5.6×10^7 atom/L for 2013 and 5.7×10^7 atom/L for 2014).

Dispersion behavior of uranium in North-Baltic Sea mixing region

As indicated by the strongly varying salinity (7.6 to 34.7 ‰) and ^{238}U concentration (0.8-3.9 $\mu\text{g/L}$), the investigated region in this work can be sub-divided into four parts: 1) Jutland coast (North Sea and Skagerrak areas), 2) Northern Zealand (Kattegat area), 3) Western Zealand (Great Belt area) and 4) Southeast Zealand (Southern Baltic Sea area). Compared to surface seawater around Zealand, Jutland surface seawater has the highest levels of salinity and ^{238}U concentrations, which represent for surface water of the North Sea. The lowest salinities and ^{238}U concentrations are observed in the surface of southeast Zealand, which represent for Baltic seawater. Northern Zealand (Kattegat) is a mixing zone of North Sea water and Baltic Sea water. The measured salinities in the bottom water at two locations in the Kattegat are close to the salinity in the open seawater (35‰), two times higher than the surface water in the Kattegat and four times higher than western Baltic seawater. This implies that bottom water in the Kattegat is mainly from the North Sea (North Atlantic Ocean), while the surface water in this area is a mixture of the water from the North Sea and Baltic Sea.

The distribution of ^{137}Cs (Figure S-1 and S-2) shows a reversed distribution pattern compared to ^{238}U , with highest ^{137}Cs activity for both surface and bottom water observed in Southeast Zealand (Møn) and the lowest in the northern Zealand (Hesselø and Kattegat-413). This is attributed to the huge fallout of the Chernobyl accident in the Baltic Sea region, which significantly increased the ^{137}Cs concentrations in the Baltic Sea.³² Whereas the North Sea and North Atlantic seawater received much less fallout of Chernobyl accident, meanwhile the discharges of ^{137}Cs from the two European reprocessing plants reduced tremendously since the 1980's.³³ However, the naturally occurring ^{238}U has much higher concentrations in open seawater (about 3-4 ng/ml) compared to the Baltic Sea (0.1-2.6 ng/ml)²⁶ which has significant fresh water (< 0.5 ng/ml) input from the drainage area. All uranium concentrations obtained in this work (N=51) are plotted versus salinity (Figure 5). A linear regression was performed on the data and the equation is expressed as $U (\mu\text{g/L}) = (0.098 \pm 0.003) \times S + (0.115 \pm 0.077)$ with R^2 of 0.973. The slop of this linear regression agrees well with the best-fit line ($U = (0.100 \pm 0.006) \times S - (0.326 \pm$

0.206, $R^2 = 0.78$) for worldwide studies in seawater reported previously.^{34–36} The positive linear ^{238}U -salinity relationship might indicate that natural uranium (^{238}U) in the Baltic Sea mainly originates from seawater introduced from the North Sea and the North Atlantic, its concentration decreases with the increasing dilution by fresh water from riverine inflow to the Baltic Sea. The feed of natural uranium from the catchment through rivers should be very limited compared to the seawater. The positive linear correlation between uranium and salinity might also indicate the relative conservative mixing behavior of uranium during the exchange of the North Sea and Baltic Sea water in the Danish Straits, which is in consistent with previous observations.³⁷

^{236}U source terms in Danish Seawater

In all samples, the $^{236}\text{U}/^{238}\text{U}$ atomic ratios of $(5.4\text{--}31.6) \times 10^{-9}$ are much higher than the theoretically estimated pre-anthropogenic level of $10^{-14} - 10^{-10}$.^{3,38} This indicates seawater analyzed in this work are dominated by anthropogenic ^{236}U . There are several possible sources of anthropogenic ^{236}U : 1) global fallout of ^{236}U from nuclear weapons testing; 2) advective transport of ^{236}U from the North Sea originating from discharges of the two major European nuclear reprocessing plants at Sellafield and La Hague; 3) outflows of Baltic seawater carrying ^{236}U from the Chernobyl accident, river run-off and remobilization of ^{236}U from sediment; 4) other local input (e.g., civil and military nuclear reactors).

Global fallout

Large amounts of radionuclides (including ^{236}U) were released during the era of atmospheric nuclear weapons testing in 1952–1963, especially on the Northern Hemisphere. Hence global fallout of ^{236}U should undoubtedly be distributed in all the world oceans. Based on measured ^{236}U data from an annually resolved coral core collected in the Caribbean Sea, a total ^{236}U global fallout input of 1060 kg was estimated via a semi-empirical model.¹⁷ Based on this number, it has been estimated that a $^{236}\text{U}/^{238}\text{U}$ ratio of about 1×10^{-9} is representative for the global fallout signature in modern ocean surface waters.¹

Taking into account the inhomogeneous distribution of global fallout radionuclides, higher $^{236}\text{U}/^{238}\text{U}$ ratios than 1×10^{-9} should be expected in temperate regions, while lower values should be expected at equator and the Antarctic. Actual $^{236}\text{U}/^{238}\text{U}$ atomic ratios for surface Atlantic Ocean seawater (presumably global fallout is the major source for ^{236}U for this area) have been reported to be $(1.9 \pm 0.6) \times 10^{-9}$ by Eigl et al.²¹ and 0.7×10^{-9} by Christl et al.¹, respectively. Casacuberta et al.²⁰ reported $^{236}\text{U}/^{238}\text{U}$ ratios of $(0.9-1.5) \times 10^{-9}$ for North Atlantic seawater (51.82N, 45.73W) collected from the similar latitude band as the Danish seawater analyzed in this work (Figure 4).

Using a $^{236}\text{U}/^{238}\text{U}$ ratio of 1.0×10^{-9} and assuming the ^{238}U concentration in the open ocean is $3.0 \mu\text{g/L}$, a ^{236}U concentration of $0.8 \times 10^7 \text{ atom/L}$ can be estimated as the global fallout level provided no mixing at depth would be taken into account. If a similar concentration of ^{236}U originating from global fallout is applicable to brackish seawater such as Baltic Sea, our ^{236}U concentrations of $(3.6-8.2) \times 10^7 \text{ atom/L}$ are 4-10 times higher than the estimated global-fallout value. This indicates that direct global fallout from the atmospheric nuclear weapons testing is a minor contribution ($< 25 \%$) to the total ^{236}U inventory in Danish seawater.

Reprocessing plants at Sellafield and La Hague through advective transport

Significant amounts of anthropogenic radionuclides have being discharged from the two European nuclear reprocessing plants since 1952 (Sellafield, UK) and 1966 (La Hague, France), which were transported to the North Sea and further dispersed. So far, the highest $^{236}\text{U}/^{238}\text{U}$ atomic ratio of $(2.8 \pm 0.9) \times 10^{-6}$ in seawater was observed in the vicinity of Sellafield in the Irish Sea.⁷ $^{236}\text{U}/^{238}\text{U}$ atomic ratios of $(6.4-15.8) \times 10^{-9}$ have been found in seawater along the eastern coast of Scotland and England reflecting the influence of ^{236}U originating from Sellafield.¹⁸ A $^{236}\text{U}/^{238}\text{U}$ atomic ratio up to 21.6×10^{-9} was reported in the vicinity of La Hague and $(5.2-11.6) \times 10^{-9}$ in the central North Sea as well as along the European continental and Norwegian coasts.¹⁸

Our results for the $^{236}\text{U}/^{238}\text{U}$ atomic ratios of $(9.3\text{-}16.2) \times 10^{-9}$ in seawater collected from the western coast of Jutland are slightly higher than the ratios of $(5.2\text{-}11.6) \times 10^{-9}$ reported for the central North Sea, and comparable to the ratios of $(8.4\text{-}17.7) \times 10^{-9}$ for the European continental coastal areas of the North Sea in 2009.^{18,19} This might be due to the fact that contaminated water from La Hague (as well as that from Sellafield) moves northward along the European continental coast,^{39,40} and therefore the ^{236}U concentrations in the central North Sea are lower than those from coastal areas. Nevertheless, the general concentrations of ^{236}U in Danish seawater are at the same magnitude as the North Sea water, and 10-100 times higher compared to other open oceans including the Atlantic, the Japan Sea (after the Fukushima accident) and the Pacific that were mostly affected by ^{236}U input from global fallout.^{1,16,20,22,41,42} it should be noted that, ^{236}U concentrations in saline Kattegat bottom seawater (stations 3 and 12) are nearly two times higher than those in low salinity surface water. The notably elevated ^{236}U level in Danish seawater and the ^{236}U difference between surface and bottom water in Kattegat suggests the ^{236}U input to Danish seawater from the North Sea originating from the two European reprocessing plants.

However, at first glance it appears unexpectedly that the difference in ^{236}U concentrations between surface and bottom seawater in Kattegat is much smaller compared to other anthropogenic radionuclides, e.g., ^{129}I concentrations in bottom seawater are 1-2 orders of magnitude higher than in surface seawater in this region in 2007.⁴³ This might be explained by the facts that 1) ^{236}U release histories from the two nuclear reprocessing plants are significantly different from those of ^{129}I . Release of ^{129}I from the two reprocessing plants have increased since the 1990's and reached a maximum around 2000, while releases of ^{236}U as well as other actinides have declined significantly since the 1990's, which is attributed to the implementation of an actinide removal processes in the reprocessing plants. Therefore, most of the ^{236}U in European seawater should originate from early releases before the 1990's, especially during the 1970's and 1980's. 2) The ^{129}I discharges from the two European reprocessing plants account for more than 95% of ^{129}I in the environment, which are two orders of magnitude higher than the entire releases from atmospheric nuclear weapons testing. While the total inventory of ^{236}U released from the two European

reprocessing plants has been estimated in the range of 115 to 250 kg,²⁰ which is less than one fourth of the estimated input from global fallout of atmospheric nuclear weapons testing.

Advective transport of ²³⁶U via outflow from the Baltic Sea

It has been reported that more than 95% of ¹²⁹I in the Baltic Sea originates from European reprocessing facilities, especially from La Hague.⁴⁴ More than 30% of ¹²⁹I in the south Baltic and >93% in the Kattegat originates from marine discharges and is transported by marine currents. Being similarly conservative as ¹²⁹I, ²³⁶U should also be transported through the Kattegat into the South Baltic. However, the ²³⁶U concentrations in seawater from south of Zealand are slightly lower but still at the same level as those from Kattegat. For example, in the samples collected at Møn in the Baltic Sea, as high as $(4.7-5.7) \times 10^7$ atom/L of ²³⁶U were measured during 2013-2014, which is about two times higher than the ²³⁶U concentrations in the Black Sea water and Danube river which feeds into Black Sea.^{21,45}

It can be seen from Figure 6 that ²³⁶U concentrations observed in this work for Danish seawater are fairly independent of salinity, while the ²³⁶U/²³⁸U ratios increase with the decreasing salinity which results in even higher ²³⁶U/²³⁸U atomic ratios in the low salinity Baltic Sea samples than in the North Sea region. This unexpected high level ²³⁶U in the Baltic Sea area and relatively homogenous distribution of ²³⁶U along the Danish coasts suggest that, an unknown source of ²³⁶U might exist in the Baltic Sea, which contributes with a similar magnitude as those presently from Sellafield and La Hague. Consequently, special consideration must be given to clarify possible source terms in the Baltic Sea, when applying ²³⁶U as an oceanographic tracer in the North Atlantic-Arctic Ocean.

A simple binary mixing model was applied to shed some light on the source terms in the Baltic Sea. The variations of ²³⁶U/²³⁸U atomic ratio and ²³⁶U concentration with the salinity were simulated in this model assuming there were two major endpoint sources of ²³⁶U in the investigated region. One endpoint source of ²³⁶U was the high salinity North Sea water carrying high reprocessing ²³⁶U (salinity=35‰, ²³⁸U=3.3 ug/L and ²³⁶U=8 × 10⁷ atom/L), while the other endpoint source was the fresh Baltic Sea water carrying

unknown source of ^{236}U ($^{238}\text{U} = 0.2 \text{ ug/l}$, $^{236}\text{U} = 3 \times 10^7 \text{ atom/L}$, $^{236}\text{U}/^{238}\text{U}$ atomic ratio is about 1.2×10^{-9} and salinity = 2‰). Interestingly, the simulated variations of $^{236}\text{U}/^{238}\text{U}$ vs. salinity and ^{236}U concentration vs. salinity (Figure 6) are in good agreement with the measurement data in this work. This confirms that besides the reprocessing input, a source from the Baltic Sea also contributes to ^{236}U in the investigated region. ^{236}U in the Baltic Sea might originate from a number of inputs as discussed below.

Chernobyl accident

It is well known that the Chernobyl accident has caused high deposition of radionuclides in the Baltic Sea and the catchment areas. Our ^{137}Cs results show that the average ^{137}Cs activity is much higher in surface water (25 Bq/m^3) than in bottom water (9 Bq/m^3) and the overall ^{137}Cs activity in Danish seawater has a negative linear correlation ($R^2 = 0.984$) with salinity. This indicates seawater transport of the Chernobyl-derived ^{137}Cs through the Danish Straits from the Baltic Sea to the North Sea and in the opposite direction for lower level ^{137}Cs from the North Sea to the Baltic.

$^{236}\text{U}/^{238}\text{U}$ atomic ratios of $10^{-6} - 10^{-3}$ have been measured in soils contaminated with fuel debris in the close vicinity of the Chernobyl power plant. At a site up to a distance of 200 km from the Chernobyl, $^{236}\text{U}/^{238}\text{U}$ atomic ratios were found to be $(2-4) \times 10^{-7}$.³ So far, little is known about the Chernobyl deposition of ^{236}U into the Baltic Sea. However, only minor Chernobyl input of other actinides was observed in the Baltic Sea and the surrounding areas.⁴⁶⁻⁴⁸ It is therefore reasonable to predict that the atmospheric dispersion of ^{236}U into the Baltic Sea may not be of significance either, since uranium is not a volatile element and the Chernobyl accident occurred 500–600 km away from the Baltic Sea.

Input of global fallout ^{236}U in Baltic Sea through direct deposition

The Baltic Sea is a rather shallow (50-60 m on average) brackish regional sea.^{26,49-51} As a consequence, the distribution depth of ^{236}U is restrained within ca. 60 m, compared to open oceans where ^{236}U penetrated into hundreds or even thousands meters depth, higher ^{236}U concentrations in the Baltic Sea introduced by global fallout could be expected.

The areal deposition of global fallout ^{236}U has been estimated to be 17.8×10^{12} atoms/m² based on the analysis of soil samples in Japan.⁵² Several studies on ^{236}U inventories in different marine water columns have obtained values ranging within $(7.7 - 47) \times 10^{12}$ atom/m².^{16,20,22,42,53} Taking 17.8×10^{12} atom/m² as the global fallout deposition of ^{236}U into the Baltic Sea, the surface area of 451000 km² and the volume of 22000 km³, the ^{236}U concentration in the Baltic Sea should have reached 36.5×10^7 atom/L in the 1950-1960s. Since the average residence time of Baltic Sea water is estimated to be 30-35 years (half exchange time of about 20-25 years),^{54,55} after 60 years (the two times of residence time) the global-fallout derived ^{236}U in modern Baltic Sea water would be reduced to about $(1/e)^2=13.5\%$, i.e. 4.9×10^7 atom/L. This value agrees well with those obtained in this work for seawaters collected close to Baltic Sea area, and possibly support the notion of persisting influence of global fallout in the Baltic Sea. However, we do not want to overemphasize this simple estimation.

Input of global fallout ^{236}U in Baltic Sea through river runoff

There are many rivers around the Baltic Sea, which drain 1720000 km² and discharge about 480 km³/y.⁵¹ The fresh water inflow through river run-off has high impact on the Baltic Sea environment. It has been reported that the fresh water carries a significant amount of pollutant including anthropogenic radionuclides into the Baltic Sea.⁵¹ Unlike ^{238}U which mainly exists inside the mineral phase of soil, global fallout ^{236}U is expected to be dissolved or loosely adsorbed on the surface of soil grains. Therefore, ^{236}U can be easily leached out or flushed by precipitation and transported by river run-off.

Relatively high ^{236}U concentrations in fresh water have been reported by several studies, for example, a wide range of ^{236}U concentrations from 4.14×10^6 to 2.14×10^9 atom/L have been reported in water samples from wells and rivers in Austria.⁴⁵ The contribution of global fallout ^{236}U deposited in the catchment area of the rivers draining into the Baltic Sea might be another major source of ^{236}U . Glacier melt water would be especially suspicious to release stored ^{236}U from global fallout (up to 10^{-4} of

$^{236}\text{U}/^{238}\text{U}$ atomic ratio has been reported in an Arctic ice core ⁵⁶⁾ which is relevant for understanding ^{236}U data from the North Atlantic and the Arctic Ocean.

Potential resuspension of the reprocessing derived ^{236}U deposited in the Baltic Sea

Another possible source of high ^{236}U levels in the Baltic Sea might be ^{236}U from the peak discharge era from the reprocessing plants from 1970-1990, which has been transported into and then retained in Baltic Sea water or sediment. It has been reported that the transport of the water mass from La Hague to Hesselø takes about 1.5 year ⁴⁴, while the turnaround time for Baltic Sea water is estimated to be 30-35 years, ^{54,55} Therefore, the recent in-flow of saline water from the North Sea carries the signature of relatively low $^{236}\text{U}/^{238}\text{U}$ atomic ratios would in line with the presently low reprocessing releases of ^{236}U . Whereas the older and more saline water retained in the Baltic main basin may still preserve the higher $^{236}\text{U}/^{238}\text{U}$ ratios of the North Sea water from 1970 - 1990. Coincidentally, the dilution of this saline water in Baltic Sea with fresh water has led to a ^{236}U concentration independent of salinity. Such a dilution by fresh water (without ^{236}U and ^{238}U) would not affect the isotopic ratio $^{236}\text{U}/^{238}\text{U}$ (compare Figure 6b).

Sediments constitute another way of storing ^{236}U . The local marine environment in the Baltic Sea is significantly different from the open seas. Most uranium of in the open seawater (90%) exists as U(VI) carbonate complexes. The Baltic Sea water has lower pH (<7) compared to open seawater (pH=8-9). With the depletion of oxygen and even presence of H_2S in deep layers of the central area of the Baltic Proper, the U(VI) maybe reduced and then scavenged by organic particles or collides, etc., deposited into sediment, and later be remobilized. It has been reported that natural uranium is enriched in organic-rich mud from the Gotland Deep in the Baltic Sea with uranium concentration up to 10 ppm.²⁷. Experimental data have indicated that in Baltic Sea mud, the uranium sorbed by soluble organic matter derived from land and by settling of partly decomposed plankton constitutes about one-half of uranium in mud.²⁷ Provided reprocessing derived ^{236}U has a similar environmental behavior as natural uranium, high discharges in the 1970's and 1980's might have been transported to Baltic Sea and deposited in the

sediment. With the dynamic of oxygenated water irregularly flowing into the Baltic Sea, the remobilization of ^{236}U from the sediment might be elevated. However, as per the general conservative behavior based on our results mentioned before and literature report,³⁷ the enrichment of uranium in Baltic sediment might only occur in some anoxic basins (e.g., Gotland Basin). Besides, the remobilization of uranium from sediment depends on the time span of oxygenate conditions in the bottom water. For a short time period with ^{236}U mainly in the surface sediments, the remobilized uranium could very well show enhanced $^{236}\text{U}/^{238}\text{U}$ ratio, but for longer time spans with continuous integration of natural ^{238}U into sediment, it becomes more likely that the remobilized uranium would be diluted to have a lower $^{236}\text{U}/^{238}\text{U}$ ratio. Nevertheless, to make the picture more objective, ^{236}U profiles in Baltic water columns and sediment cores, especially from the long-term anoxic basin of Baltic Sea would be useful.

If the early reprocessing derived ^{236}U stored in Baltic sediments is a major input of ^{236}U into the North Sea, this might affect tracer applications of ^{236}U in the North Atlantic-Arctic Ocean. Regardless of the extra ^{236}U source in the Baltic Sea, the seemingly enriched ratios may have to be considered when using ^{236}U as a tracer. On the other hand, ^{236}U adds to the suit of available geochemical and oceanic tracers that could find use in studies of water exchange, interaction between sediment and water in the Baltic Sea as well as its relationship to the changes of the ecosystem, water condition and the climate in the Baltic Sea

Local input of ^{236}U in Danish seawater

Two Swedish nuclear power plants at Barsebäck and Ringhals may discharge radionuclides into Danish Straits and the Finnish (Lovisa, Olkiluoto and Hanhikivi) and Swedish (Frosmark and Oskarshamn) nuclear reactors may add to the ^{236}U inventory inside the Baltic Sea, but historical records for uranium isotope discharges are not available from these nuclear plants.⁵⁷ However, to the best of our knowledge, no significant levels of radionuclides have been detected in the surrounding environment of these two power plants. Thus, it can be assumed that the contribution of ^{236}U from these local nuclear reactors to Danish seawater might be negligible. During 1950-1990, three nuclear research reactors were built and operated at Risø, Denmark.^{58,59} To evaluate the local input of ^{236}U from the Danish reactors, several

seawater samples were collected in Roskilde Fjord including the discharge point of Risø reactor (DR3). The ^{236}U levels in all collected seawaters are comparable to those obtained for Zealand seawater (Table S-1), indicating no significant contributions from the nuclear reactors at Risø.

ASSOCIATED CONTENT

Supporting Information

Supporting Information summarizes the overall results of ^{236}U and $^{236}\text{U}/^{238}\text{U}$ for Danish seawater in 2013 and 2014, and illustrates the distribution of ^{238}U and ^{137}Cs concentrations in seawater along the Danish coasts, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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578

579 **FIGURE CAPTIONS**

580 **Figure 1.** Sampling stations in this work.

581 **Figure 2.** Distribution of ^{236}U concentration (atom/L) in seawater along the Danish coasts in 2013 and
582 2014

583 **Figure 3.** Distribution of $^{236}\text{U}/^{238}\text{U}$ atomic ratio in seawater along the Danish coasts in 2013 and 2014

584 **Figure 4.** Comparison of $^{236}\text{U}/^{238}\text{U}$ atomic ratios in water samples from different locations

585 **Figure 5.** Correlation ^{238}U and ^{137}Cs concentrations with salinity

586 **Figure 6.** Variation of ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios with salinity

587

588 **Figure 1.** Overview of schematic circulation water mass in North Sea-Baltic Sea region and sampling stations in this work (ECW: English
589 Channel Waters, SCC: Scottish Coastal Current, NCC: Norwegian Coastal Current, BS: outflow of Baltic Sea water).

Figure 2. Distribution of ^{236}U concentration (atom/L) in seawater along the Danish coasts in 2013 and 2014

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