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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.

35

36 INTRODUCTION

37 ^{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)-
38 reactions, as well as through ^{238}U (n, 3n) ^{236}U reactions with fast neutrons. A very minor amount (about 35
39 kg) of natural ^{236}U was estimated on the Earth's crust surface, mainly in uranium ores,¹ while the majority
40 (more than 1000 kg) of ^{236}U in the environment originate from anthropogenic nuclear activities, e.g.,
41 fallout from atmospheric nuclear weapons testing and discharges from nuclear facilities.^{2,3}

42 Since $^{236}\text{U}/^{238}\text{U}$ isotopic ratios together with the occurrence of other minor U isotopes carry key
43 signatures for uranium sources, ^{236}U has been recognized as a valuable tracer in nuclear safeguards,
44 geology and environmental studies.³⁻¹⁵ In recent years, the potential of ^{236}U as a new oceanographic tracer
45 has been promoted by several studies.^{1,16-21} Based on its conservative behavior and well-established
46 knowledge regarding all other naturally occurring U isotopes in the ocean, ^{236}U would provide an
47 additional transient signal of water masses. In combination with other anthropogenic tracers (e.g., CFCs,
48 ^3H , ^{14}C , ^{134}Cs , ^{137}Cs , ^{129}I , ^{99}Tc), tracer applications of ^{236}U in the world oceans would provide a clearer
49 picture illustrating water mass movements, circulation and mixing patterns of different water flows,
50 which are important and challenging aspects in oceanography. Even though significant work has been
51 devoted to assess its distribution and to develop tracer applications of anthropogenic ^{236}U in the marine
52 environment, worldwide ^{236}U data is limited; especially the distribution of ^{236}U in regional seas, such as
53 the Baltic Sea is not well known. A major challenge in applying ^{236}U to oceanographic tracer studies is to
54 define the source terms of ^{236}U in the marine environment.

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

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

66 Several studies have reported ²³⁶U/²³⁸U ratios up to 10⁻⁸ in young surface waters and sediments in
67 Northwest Europe .^{18,19} Anthropogenic ²³⁶U has also been detected at more than 4000 m depth in the
68 equatorial Atlantic Ocean.^{1,20} The two European nuclear fuel reprocessing facilities La Hague (France)
69 and Sellafield (UK) are considered as important ²³⁶U sources in the Atlantic-Arctic Ocean. In seawater
70 collected in 1993 from the Irish Sea affected by the radioactive waste release from the Sellafield
71 reprocessing plant, ²³⁶U/²³⁸U atomic ratios were reported to be 2 × 10⁻⁶.⁷ Elevated ²³⁶U levels (²³⁶U/²³⁸U
72 atomic ratios reached to 2 × 10⁻⁸ in 2009) were also observed in seawater near the La Hague reprocessing
73 plant.¹⁸ However, due to limited documentation of the uranium discharge history of the two European
74 nuclear reprocessing plants, little is known about the actual ²³⁶U/²³⁸U ratios in the discharges from the
75 reprocessing plants. The only available data is from La Hague, that contributes a minor part to the total
76 amount of ²³⁶U released into the North Sea.^{18,19,23} Studies have indicated that the spatial distribution of
77 ²³⁶U in the North Sea is consistent with a simple model that involves the two reprocessing plants as the
78 sole sources of ²³⁶U in this marine region.¹⁸ However, more experimental data are needed to constrain
79 parameters used in the model in order to reconstruct the discharge history of the two reprocessing plants.

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

87 surface water (1.8-2.0 µg/kg), while the bottom sediments in the central part are enriched in uranium (10-
88 12 ppm).^{27,28} It has been suggested that the mechanism for withdrawal of dissolved uranium from the
89 water phase are reduction of uranium (VI) to uranium (IV), followed by precipitation as UO₂, or
90 adsorption on a reactive phase, e.g., organic material.^{25,26}

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

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

102 MATERIALS AND METHODS

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

112 **Analytical methods for determination of ^{137}Cs , ^{238}U and ^{236}U .** To determine ^{137}Cs in each seawater,
113 45 L of seawater was transferred to a flask and acidified to pH 2 with concentrated HNO_3 . 30 mg of Cs
114 carrier (as CsCl) and 50 g of ammonium 2-molybdophosphate (AMP) was added and the sample was
115 stirred for 1 h for the adsorption of Cs by AMP. After settling for overnight, the supernatant was discarded
116 and the remaining slurry was filtered and dried at 105 °C in an oven for overnight. The AMP powder was
117 weighed to calculate the chemical yield of Cs and then measured by gamma spectrometry using HPGe
118 (high-purity germanium) detectors with about 40% relative efficiency. To reach acceptable levels of
119 detection limits and measurement uncertainties, each sample was counted for 24 h.

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

125 The detailed analytical method for the determination of ^{236}U in seawater has been reported elsewhere.³⁰
126 It should be noted that the seawater samples collected in 2013 were not filtered before analysis while the
127 samples collected in 2014 were filtered through a Munktell 00K paper filter. In short, to 5 or 10 L
128 seawater, conc. HNO_3 was added to adjust pH to 2 and purified FeCl_3 solution (0.05 g/mL of Fe) was
129 added to a final Fe concentration of 0.1g/L. The sample was vigorously stirred with N_2 bubbling for 5-10
130 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,
131 and the supernatant was decanted. The sample slurry was centrifuged at 4000 rpm for 5 minutes and the
132 supernatant was discarded. 20 mL of conc. HNO_3 was added to the residue and the solution was heated at
133 200 °C until near dryness. The final residue was dissolved with 15 mL of 3 mol/L HNO_3 and the solution
134 was loaded onto a 2-mL UTEVA column which was pre-conditioned with 20 mL of 3 mol/L HNO_3 . The
135 UTEVA column was rinsed with 40 mL of 3 mol/L HNO_3 , followed by 20 mL of 6 mol/L HCl . Uranium
136 absorbed on the column was eluted with 10 mL of 0.025 mol/L HCl . The flow rate for the
137 chromatographic separation was controlled manually to 1.0-1.5 mL/min.

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

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

$$151 \quad R_s = \frac{238 (m_m R_m - m_b R_b)}{236 (m_m - m_b)}$$

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

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

163 **RESULTS AND DISCUSSION**

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

165 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
166 concentrations) obtained in this work are summarized in Table S-1. The geographical distribution patterns
167 of ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios in seawater along the Danish coasts for the 2013 - 2014
168 are illustrated in Figure 2 and 3, respectively. In general, the ^{236}U concentrations, $^{236}\text{U}/^{238}\text{U}$ atomic ratios
169 as well as salinity obtained in 2013 compare well with the values obtained in 2014 for samples from the
170 same locations, reflecting the relatively slow water exchange rate in the investigated region.

171 The measured $^{236}\text{U}/^{238}\text{U}$ atomic ratios vary within one order of magnitude for both surface water ((9.3-
172 $31.6) \times 10^{-9}$) and bottom water ((5.4-24.9) $\times 10^{-9}$) in the period of 2013-2014. In contrast to the
173 distribution pattern of ^{236}U concentration, higher $^{236}\text{U}/^{238}\text{U}$ atomic ratios in both surface and bottom water
174 are observed in the southeast of Zealand, which is dominated by the inflows of the Baltic seawater.

175 ^{236}U concentrations around the coasts of Zealand vary within relatively narrow ranges for both surface
176 ((3.6-8.2) $\times 10^7$ atom/L) and bottom ((4.5-8.0) $\times 10^7$ atom/L) seawater during 2013-2014. Combining the
177 results for seawater from Jutland coasts, it can be seen that there is a decreasing trend of the ^{236}U
178 concentration in the surface seawater from the west coast of Jutland to Kattegat and the Great Belt region.
179 The lowest ^{236}U concentration around Zealand is observed in the surface water of Sundet N (station 11).
180 However, the ^{236}U concentrations increase slightly in the south area (Femern Belt) of Zealand. Among the
181 Jutland surface water, the lowest concentration of ^{236}U (3.2×10^7 atom/L) is observed at Øster Hurup
182 (station 13), which is probably related to the inshore sampling site, where the collected seawater is diluted
183 with fresh water as indicated by its relatively low salinity. In the bottom water around Zealand, lower ^{236}U
184 concentrations are observed along Sundet area (station 10), while relatively higher ^{236}U concentrations are
185 observed for both Kattegat and Femern Belt. The average ^{236}U concentrations in Zealand bottom water
186 (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
187 water (5.6×10^7 atom/L for 2013 and 5.7×10^7 atom/L for 2014).

188 **Dispersion behavior of uranium in North-Baltic Sea mixing region**

189 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
190 investigated region in this work can be sub-divided into four parts: 1) Jutland coast (North Sea and
191 Skagerrak areas), 2) Northern Zealand (Kattegat area), 3) Western Zealand (Great Belt area) and 4)
192 Southeast Zealand (Southern Baltic Sea area). Compared to surface seawater around Zealand, Jutland
193 surface seawater has the highest levels of salinity and ^{238}U concentrations, which represent for surface
194 water of the North Sea. The lowest salinities and ^{238}U concentrations are observed in the surface of
195 southeast Zealand, which represent for Baltic seawater. Northern Zealand (Kattegat) is a mixing zone of
196 North Sea water and Baltic Sea water. The measured salinities in the bottom water at two locations in the
197 Kattegat are close to the salinity in the open seawater (35‰), two times higher than the surface water in
198 the Kattegat and four times higher than western Baltic seawater. This implies that bottom water in the
199 Kattegat is mainly from the North Sea (North Atlantic Ocean), while the surface water in this area is a
200 mixture of the water from the North Sea and Baltic Sea.

201 The distribution of ^{137}Cs (Figure S-1 and S-2) shows a reversed distribution pattern compared to ^{238}U ,
202 with highest ^{137}Cs activity for both surface and bottom water observed in Southeast Zealand (Møn) and
203 the lowest in the northern Zealand (Hesselø and Kattegat-413). This is attributed to the huge fallout of the
204 Chernobyl accident in the Baltic Sea region, which significantly increased the ^{137}Cs concentrations in the
205 Baltic Sea.³² Whereas the North Sea and North Atlantic seawater received much less fallout of Chernobyl
206 accident, meanwhile the discharges of ^{137}Cs from the two European reprocessing plants reduced
207 tremendously since the 1980's.³³ However, the naturally occurring ^{238}U has much higher concentrations in
208 open seawater (about 3-4 ng/ml) compared to the Baltic Sea (0.1-2.6 ng/ml)²⁶ which has significant fresh
209 water (< 0.5 ng/ml) input from the drainage area. All uranium concentrations obtained in this work
210 (N=51) are plotted versus salinity (Figure 5). A linear regression was performed on the data and the
211 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
212 slop of this linear regression agrees well with the best-fit line ($U = (0.100 \pm 0.006) \times S - (0.326 \pm$

213 0.206, $R^2= 0.78$) for worldwide studies in seawater reported previously.³⁴⁻³⁶ The positive linear ^{238}U -
214 salinity relationship might indicate that natural uranium (^{238}U) in the Baltic Sea mainly originates from
215 seawater introduced from the North Sea and the North Atlantic, its concentration decreases with the
216 increasing dilution by fresh water from riverine inflow to the Baltic Sea. The feed of natural uranium
217 from the catchment through rivers should be very limited compared to the seawater. The positive linear
218 correlation between uranium and salinity might also indicate the relative conservative mixing behavior of
219 uranium during the exchange of the North Sea and Baltic Sea water in the Danish Straits, which is in
220 consistent with precious observations.³⁷

221 ^{236}U source terms in Danish Seawater

222 In all samples, the $^{236}\text{U}/^{238}\text{U}$ atomic ratios of $(5.4-31.6) \times 10^{-9}$ are much higher than the theoretically
223 estimated pre-anthropogenic level of $10^{-14} - 10^{-10}$.^{3,38} This indicates seawater analyzed in this work are
224 dominated by anthropogenic ^{236}U . There are several possible sources of anthropogenic ^{236}U : 1) global
225 fallout of ^{236}U from nuclear weapons testing; 2) advective transport of ^{236}U from the North Sea originating
226 from discharges of the two major European nuclear reprocessing plants at Sellafield and La Hague; 3)
227 outflows of Baltic seawater carrying ^{236}U from the Chernobyl accident, river run-off and remobilization of
228 ^{236}U from sediment; 4) other local input (e.g., civil and military nuclear reactors).

229 **Global fallout**

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

236 Taking into account the inhomogeneous distribution of global fallout radionuclides, higher $^{236}\text{U}/^{238}\text{U}$
237 ratios than 1×10^{-9} should be expected in temperate regions, while lower values should be expected at
238 equator and the Antarctic. Actual $^{236}\text{U}/^{238}\text{U}$ atomic ratios for surface Atlantic Ocean seawater (presumably
239 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
240 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 $(0.9-$
241 $1.5) \times 10^{-9}$ for North Atlantic seawater (51.82N, 45.73W) collected from the similar latitude band as the
242 Danish seawater analyzed in this work (Figure 4).

243 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
244 ^{236}U concentration of 0.8×10^7 atom/L can be estimated as the global fallout level provided no mixing at
245 depth would be taken into account. If a similar concentration of ^{236}U originating from global fallout is
246 applicable to brackish seawater such as Baltic Sea, our ^{236}U concentrations of $(3.6-8.2) \times 10^7$ atom/L are
247 4-10 times higher than the estimated global-fallout value. This indicates that direct global fallout from the
248 atmospheric nuclear weapons testing is a minor contribution ($< 25\%$) to the total ^{236}U inventory in
249 Danish seawater.

250 **Reprocessing plants at Sellafield and La Hague through advective transport**

251 Significant amounts of anthropogenic radionuclides have being discharged from the two European
252 nuclear reprocessing plants since 1952 (Sellafield, UK) and 1966 (La Hague, France), which were
253 transported to the North Sea and further dispersed. So far, the highest $^{236}\text{U}/^{238}\text{U}$ atomic ratio of (2.8 ± 0.9)
254 $\times 10^{-6}$ in seawater was observed in the vicinity of Sellafield in the Irish Sea.⁷ $^{236}\text{U}/^{238}\text{U}$ atomic ratios of
255 $(6.4-15.8) \times 10^{-9}$ have been found in seawater along the eastern coast of Scotland and England reflecting
256 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
257 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
258 continental and Norwegian coasts.¹⁸

259 Our results for the $^{236}\text{U}/^{238}\text{U}$ atomic ratios of $(9.3-16.2) \times 10^{-9}$ in seawater collected from the western coast
260 of Jutland are slightly higher than the ratios of $(5.2-11.6) \times 10^{-9}$ reported for the central North Sea, and
261 comparable to the ratios of $(8.4-17.7) \times 10^{-9}$ for the European continental coastal areas of the North Sea in
262 2009.^{18,19} This might be due to the fact that contaminated water from La Hague (as well as that from
263 Sellafield) moves northward along the European continental coast,^{39,40} and therefore the ^{236}U
264 concentrations in the central North Sea are lower than those from coastal areas. Nevertheless, the general
265 concentrations of ^{236}U in Danish seawater are at the same magnitude as the North Sea water, and 10-100
266 times higher compared to other open oceans including the Atlantic, the Japan Sea (after the Fukushima
267 accident) and the Pacific that were mostly affected by ^{236}U input from global fallout.^{1,16,20,22,41,42} It should
268 be noted that, ^{236}U concentrations in saline Kattegat bottom seawater (stations 3 and 12) are nearly two
269 times higher than those in low salinity surface water. The notably elevated ^{236}U level in Danish seawater
270 and the ^{236}U difference between surface and bottom water in Kattegat suggests the ^{236}U input to Danish
271 seawater from the North Sea originating from the two European reprocessing plants.

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

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

286 **Advective transport of ²³⁶U via outflow from the Baltic Sea**

287 It has been reported that more than 95% of ¹²⁹I in the Baltic Sea originates from European reprocessing
288 facilities, especially from La Hague.⁴⁴ More than 30% of ¹²⁹I in the south Baltic and >93% in the
289 Kattegat originates from marine discharges and is transported by marine currents. Being similarly
290 conservative as ¹²⁹I, ²³⁶U should also be transported through the Kattegat into the South Baltic. However,
291 the ²³⁶U concentrations in seawater from south of Zealand are slightly lower but still at the same level as
292 those from Kattegat. For example, in the samples collected at Møn in the Baltic Sea, as high as $(4.7-5.7) \times$
293 10^7 atom/L of ²³⁶U were measured during 2013-2014, which is about two times higher than the ²³⁶U
294 concentrations in the Black Sea water and Danube river which feeds into Black Sea.^{21,45}

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

303 A simple binary mixing model was applied to shed some light on the source terms in the Baltic Sea. The
304 variations of ²³⁶U/²³⁸U atomic ratio and ²³⁶U concentration with the salinity were simulated in this model
305 assuming there were two major endpoint sources of ²³⁶U in the investigated region. One endpoint source
306 of ²³⁶U was the high salinity North Sea water carrying high reprocessing ²³⁶U (salinity=35‰, ²³⁸U=3.3
307 ug/L and ²³⁶U= 8×10^7 atom/L), while the other endpoint source was the fresh Baltic Sea water carrying

308 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}
309 and salinity = 2‰). Interestingly, the simulated variations of $^{236}\text{U}/^{238}\text{U}$ vs. salinity and ^{236}U concentration
310 vs. salinity (Figure 6) are in good agreement with the measurement data in this work. This confirms that
311 besides the reprocessing input, a source from the Baltic Sea also contributes to ^{236}U in the investigated
312 region. ^{236}U in the Baltic Sea might originate from a number of inputs as discussed below.

313 *Chernobyl accident*

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

320 $^{236}\text{U}/^{238}\text{U}$ atomic ratios of $10^{-6} - 10^{-3}$ have been measured in soils contaminated with fuel debris in the
321 close vicinity of the Chernobyl power plant. At a site up to a distance of 200 km from the Chernobyl,
322 $^{236}\text{U}/^{238}\text{U}$ atomic ratios were found to be $(2-4) \times 10^{-7}$.³ So far, little is known about the Chernobyl
323 deposition of ^{236}U into the Baltic Sea. However, only minor Chernobyl input of other actinides was
324 observed in the Baltic Sea and the surrounding areas.⁴⁶⁻⁴⁸ It is therefore reasonable to predict that the
325 atmospheric dispersion of ^{236}U into the Baltic Sea may not be of significance either, since uranium is no a
326 volatile element and the Chernobyl accident occurred 500–600 km away from the Baltic Sea.

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

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

332 The areal deposition of global fallout ^{236}U has been estimated to be 17.8×10^{12} atoms/m² based on the
333 analysis of soil samples in Japan.⁵² Several studies on ^{236}U inventories in different marine water columns
334 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
335 the global fallout deposition of ^{236}U into the Baltic Sea, the surface area of 451000 km² and the volume of
336 22000 km³, the ^{236}U concentration in the Baltic Sea should have reached 36.5×10^7 atom/L in the 1950-
337 1960s. Since the average residence time of Baltic Sea water is estimated to be 30-35 years (half exchange
338 time of about 20-25 years),^{54,55} after 60 years (the two times of residence time) the global-fallout derived
339 ^{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
340 value agrees well with those obtained in this work for seawaters collected close to Baltic Sea area, and
341 possibly support the notion of persisting influence of global fallout in the Baltic Sea. However, we do not
342 want to overemphasize this simple estimation.

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

344 There are many rivers around the Baltic Sea, which drain 1720000 km² and discharge about 480 km³/y.⁵¹
345 The fresh water inflow through river run-off has high impact on the Baltic Sea environment. It has been
346 reported that the fresh water carries a significant amount of pollutant including anthropogenic
347 radionuclides into the Baltic Sea.⁵¹ Unlike ^{238}U which mainly exists inside the mineral phase of soil,
348 global fallout ^{236}U is expected to be dissolved or loosely adsorbed on the surface of soil grains. Therefore,
349 ^{236}U can be easily leached out or flushed by precipitation and transported by river run-off.

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

355 $^{236}\text{U}/^{238}\text{U}$ atomic ratio has been reported in an Arctic ice core ⁵⁶) which is relevant for understanding ^{236}U
356 data from the North Atlantic and the Arctic Ocean.

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

358 Another possible source of high ^{236}U levels in the Baltic Sea might be ^{236}U from the peak discharge era
359 from the reprocessing plants from 1970-1990, which has been transported into and then retained in Baltic
360 Sea water or sediment. It has been reported that the transport of the water mass from La Hague to Hesselø
361 takes about 1.5 year ⁴⁴, while the turnaround time for Baltic Sea water is estimated to be 30-35 years,^{54,55}
362 Therefore, the recent in-flow of saline water from the North Sea carries the signature of relatively low
363 $^{236}\text{U}/^{238}\text{U}$ atomic ratios would in line with the presently low reprocessing releases of ^{236}U . Whereas the
364 older and more saline water retained in the Baltic main basin may still preserve the higher $^{236}\text{U}/^{238}\text{U}$ ratios
365 of the North Sea water from 1970 - 1990. Coincidentally, the dilution of this saline water in Baltic Sea with
366 fresh water has led to a ^{236}U concentration independent of salinity. Such a dilution by fresh water (without
367 ^{236}U and ^{238}U) would not affect the isotopic ratio $^{236}\text{U}/^{238}\text{U}$ (compare Figure 6b).

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

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

389 If the early reprocessing derived ^{236}U stored in Baltic sediments is a major input of ^{236}U into the North
390 Sea, this might affect tracer applications of ^{236}U in the North Atlantic-Arctic Ocean. Regardless of the
391 extra ^{236}U source in the Baltic Sea, the seemingly enriched ratios may have to be considered when using
392 ^{236}U as a tracer. On the other hand, ^{236}U adds to the suit of available geochemical and oceanic tracers that
393 could find use in studies of water exchange, interaction between sediment and water in the Baltic Sea as
394 well as its relationship to the changes of the ecosystem, water condition and the climate in the Baltic Sea

395 **Local input of ^{236}U in Danish seawater**

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

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

407 **ASSOCIATED CONTENT**

408 **Supporting Information**

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

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415 **Notes**

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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

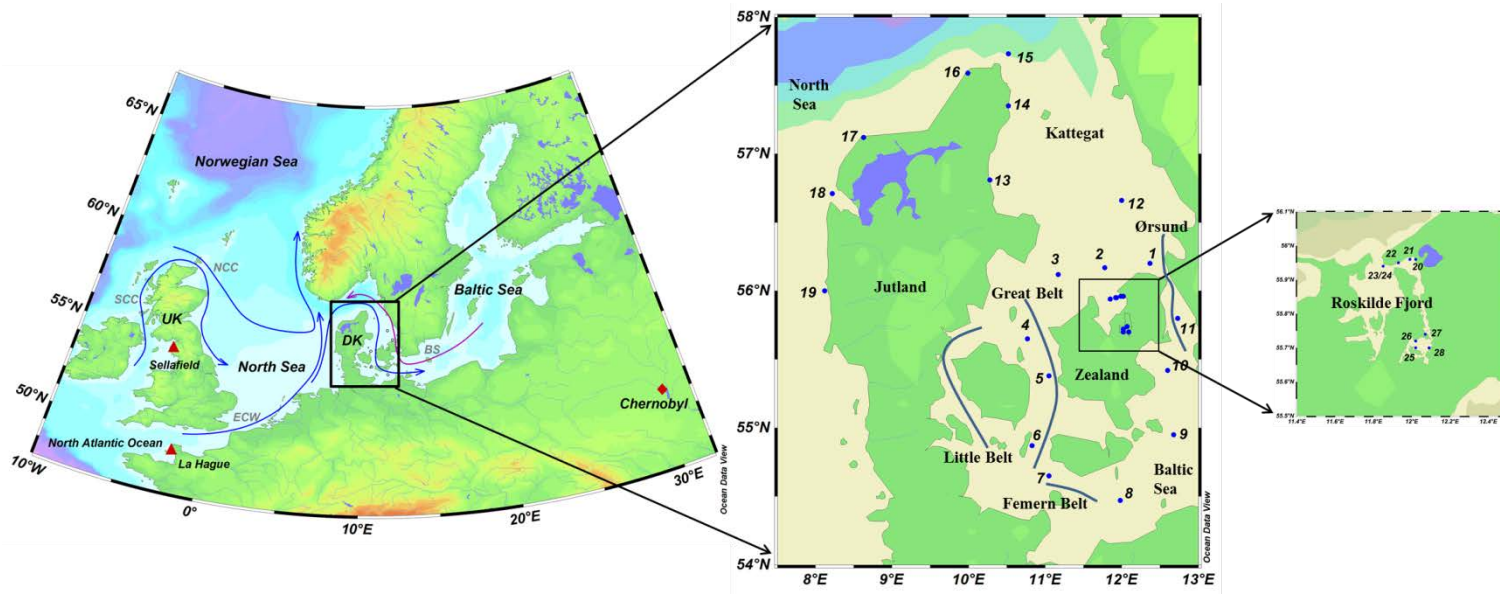
584 **Figure 4.** Comparison of $^{236}\text{U}/^{238}\text{U}$ atomic ratios in water samples from different locations

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).

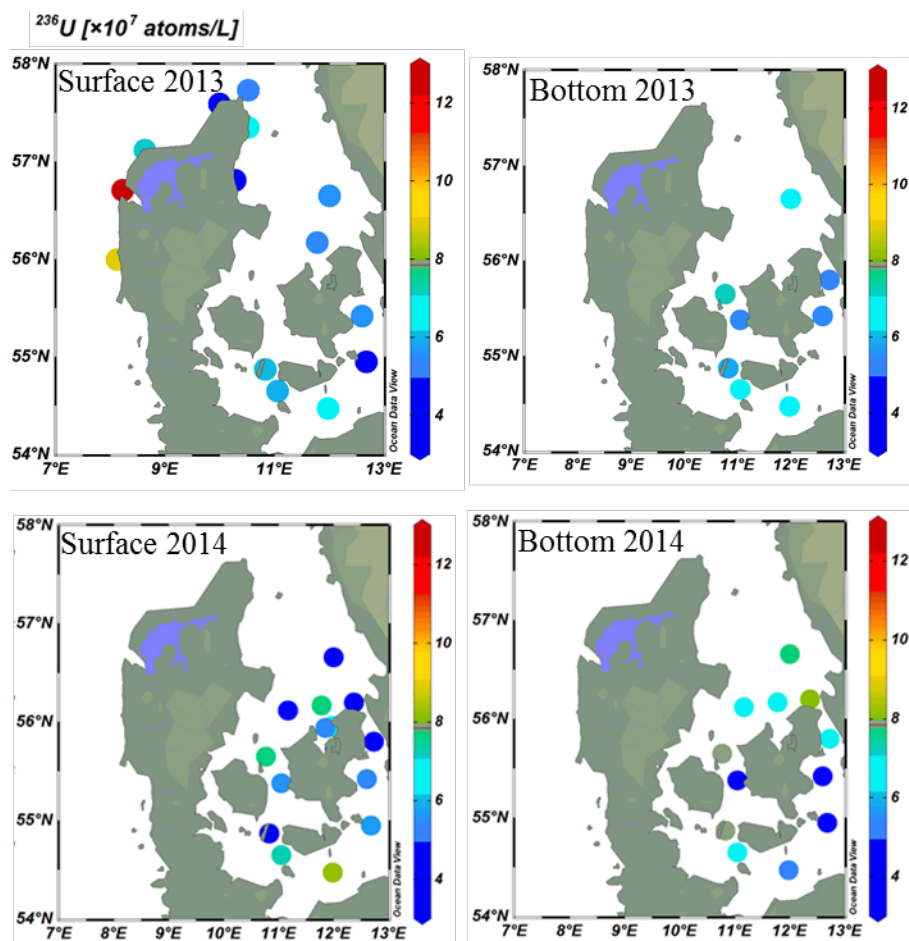


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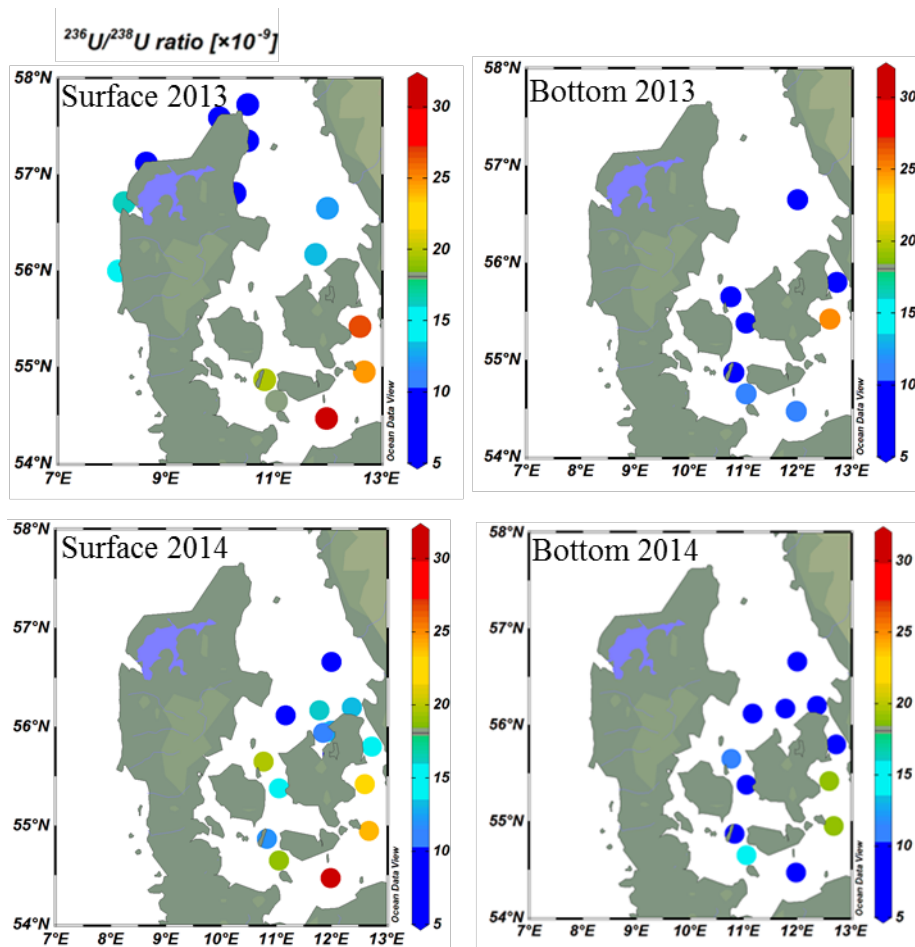
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593 **Figure 2.** Distribution of ^{236}U concentration (atom/L) in seawater along the Danish coasts in 2013 and
594 2014



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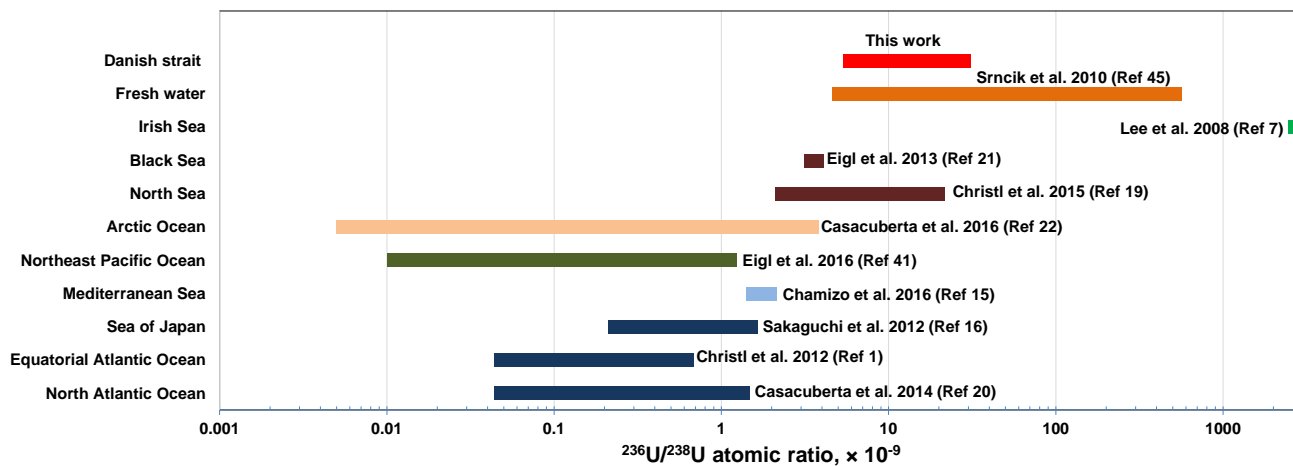
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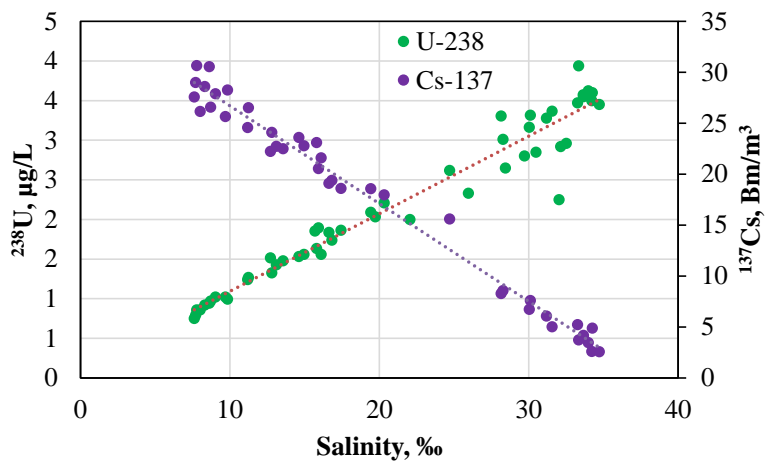
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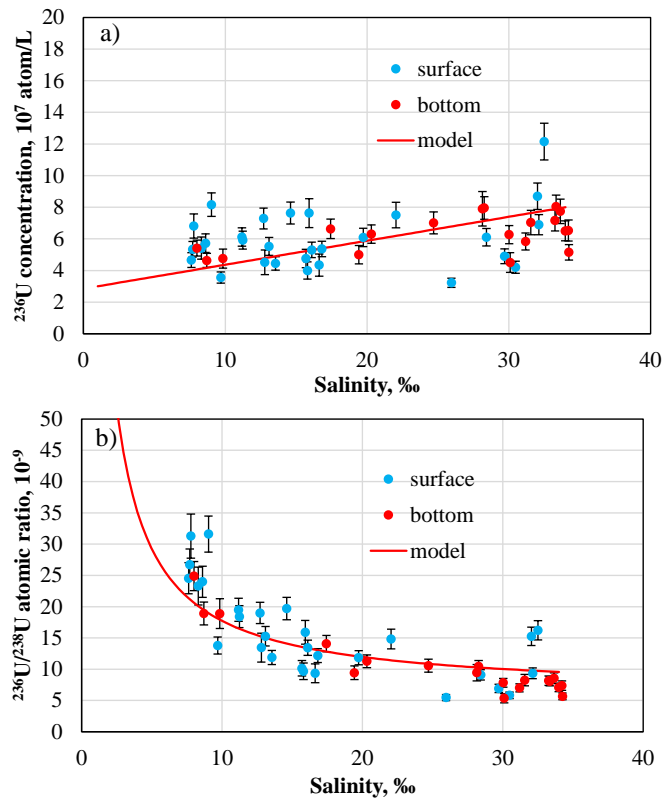


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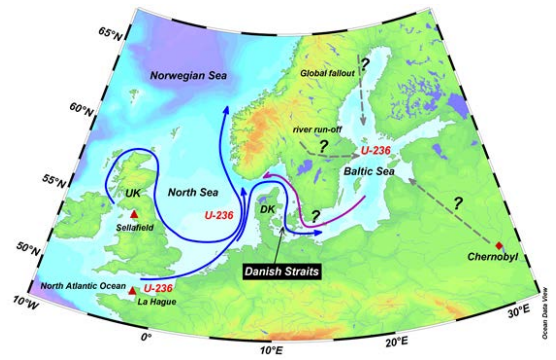
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Figure 6. Variation of ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios with salinity



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