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Significance for oceanic tracer studies

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A 40-year marine record of ^{137}Cs and ^{99}Tc transported into the Danish Straits: Significance for oceanic tracer studies

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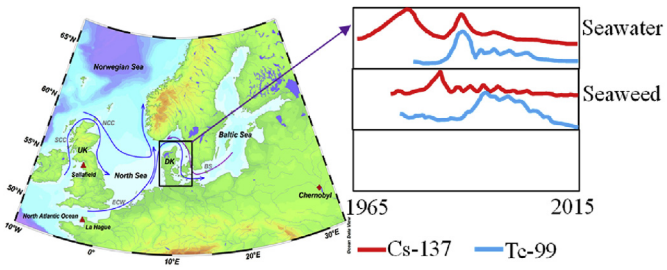
HIGHLIGHTS

- 40-year time-series for ^{137}Cs and ^{99}Tc in Danish marine samples are reported.
- Seasonal variation between ^{137}Cs and ^{99}Tc in *Fucus vesiculosus* are different.
- Three distinct events are observed in the time-series of ^{99}Tc/^{137}Cs activity ratio.
- Binary mixing model fits well with ^{99}Tc/^{137}Cs activity ratio-salinity correlation.
- Time-series data of ^{137}Cs and ^{99}Tc serve as useful oceanic tracers.

GRAPHICAL ABSTRACT



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ABSTRACT

This work reports comprehensive time-series datasets for ^{137}Cs and ^{99}Tc in marine samples from the Danish Straits over the past 40 years, where dynamic inputs from the two European nuclear reprocessing plants Sellafield (SF) and La Hague (LH) and Chernobyl accident are clearly archived. Distinct seasonal variations between ^{137}Cs and ^{99}Tc are observed in *Fucus vesiculosus* (*F. vesiculosus*), which needs to be taken into account when using F. vesiculosus as a bio-monitor to represent the concentration of radionuclides in seawater. Comparable transfer factor (TF) for ^{99}Tc from SF to Kattegat between our calculation and earlier studies indicates a relatively steady water mass transport over the past decades. Three distinct events are observed in the temporal evolution of ^{99}Tc/^{137}Cs activity ratio in F. vesiculosu with the first event corresponding with the increased ^{99}Tc discharge from SF, while the other two are very likely related to the major Baltic inflow (MBI) events. The correlation between the ^{99}Tc/^{137}Cs activity ratio and salinity fits well into the binary mixing line with the North Sea (NS) and the Baltic Sea (BS) as end members. A model simulation indicates that water mass from NS constitutes less than 50% in the surface water and 50–100% for most locations in the bottom water of the Danish Straits. Overall observations show that ^{137}Cs and ^{99}Tc in marine samples, especially ^{99}Tc/^{137}Cs isotope ratios, serve as useful oceanic tracers to study different natural processes, such as water mixing and transport dynamics.

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1. Introduction

^{137}Cs ($t_{½}$ = 30 y) and ^{99}Tc ($t_{½}$ = 211,000 y) are both anthropogenic fission products, with relatively high thermal fission yields (6–7% from both ^{235}U and ^{239}Pu) (Lehto and Hou, 2010). Major sources of ^{137}Cs in the marine environment are 1) global fallout

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from atmospheric nuclear weapons testing (ca. 1000 PBq) (UNSCEAR, 2000a); 2) release from the Chernobyl accident on the 26th of April, 1986 (ca. 85 PBq (UNSCEAR, 2000b)), with ca. 5 PBq distributed in the Baltic Sea (HELCOM-MORS, 2017; Nielsen et al., 1999) and Fukushima accident on 11th March, 2011 (ca. 15-20 PBq) (Aoyama et al., 2016); and 3) controlled discharges from nuclear installations, e.g., the two European nuclear reprocessing plants in Sellafield (SF) and La Hague (LH) with respective total release values of 41 PBq and 0.3 PBq during 1960–2000 (OSPAR commission, 2011).

The dominating sources (>90%) of ^{99}Tc in the world's oceans are from SF and LH with respective total discharges of ca. 1720 TBq and 154 TBq (Shi et al., 2012). Atmospheric nuclear weapons testing has released ca. 140 TBq of ^{99}Tc into the environment (Shi et al., 2012). Other sources, including nuclear power plants, medical applications of ^{99m}Tc and nuclear accidents (e.g. Chernobyl and Fukushima), constitute minor contributions (<1%) to the total ^{99}Tc inventory in the environment. It has been estimated that the Chernobyl accident has released in total of ca. 0.75 TBq ^{99}Tc (Shi et al., 2012).

Due to their high beta particle/photon yield and energy, long half-lives and high mobility, ^{137}Cs and ^{99}Tc are deemed important with respect to environmental radiological assessment. In the past decades, many studies have been carried out for ^{137}Cs and ^{99}Tc in contaminated marine environments to understand their distribution, transport and accumulation in biota. (Aarkrog et al., 2000; Brown et al., 1999; Herrmann et al., 1995; Keogh et al., 2007; Kershaw and Baxter, 1995; Kershaw et al., 1999; Patti et al., 1990; Povinec et al., 2003; Raaum and Christensen, 2005; Smith et al., 2001). Being conservative in the ocean, ^{137}Cs and ^{99}Tc are also considered as valuable oceanic tracers. In the 1990s, researchers used ^{137}Cs and ^{99}Tc discharged from SF and LH to estimate the transit times from the source points to different regions in the North Atlantic and Arctic Oceans (Dahlgaard, 1995; Dahlgaard et al., 1995). A few studies have also applied ^{99}Tc for validation of ocean circulation models (Karcher et al., 2004; Orre et al., 2007). In recent years, especially after the Fukushima accident, ^{137}Cs has been more popularly used as a tracer to study water mass movement and to validate oceanic models (Aoyama et al., 2006; Hirose and Aoyama, 2003; Miyao et al., 2000; Tsumune et al., 2013). However, ^{99}Tc is rarely applied as an oceanic tracer, possibly due to the tedious analytical processes and continuously decreasing levels in the marine environment. In any case, tracer studies using anthropogenic radionuclides based on long-term time-series data in the marine environment are still very scarce.

The Danish Straits is the transition area between the North Sea, which receives radioactive contaminants from SF and LH, and the Baltic Sea which is heavily contaminated by the Chernobyl accident (Qiao et al., 2017). The transport of radionuclides (e.g., ^{99}Tc, ^{129}I, ^{137}Cs, ^{236}U, etc.) between the North Sea and the Baltic Sea via the Danish Straits has been detected (Hou et al., 2002; Povinec et al., 2003; Qiao et al., 2017). In this work, we aim to study the long-term transport of ^{99}Tc and ^{137}Cs in the Danish marine environment and to explore their application in oceanic tracer studies. Time-series seawater and seaweed collected from the Danish Straits were analyzed for ^{99}Tc and ^{137}Cs. The seasonal variations for ^{99}Tc and ^{137}Cs activity concentrations in seaweed are investigated and possible explanations are discussed. The transfer factor (TF) from SF to Kattegat is calculated for comparison with earlier results. Water mixing dynamics in the Danish Straits are studied by plotting ^{99}Tc/^{137}Cs activity ratios and salinities in a binary mixing model.

2. Materials and methods

The Danish Straits comprise the Great Belt, the Little Belt, the Fehmarn Belt and the Sound (Højerslev et al., 1996; Jakobsen et al., 2010; Kristiansen and Aas, 2015; NOVA, 2003; Rosenberg et al., 2003; Sayin and Krauss, 1996), which connect the Baltic Sea to the North Sea through Kattegat and Skagerrak. The Danish Straits is of fundamental importance for the water exchange between the North Sea and the Baltic Sea. Detailed hydrological features of the Danish Straits are described in the supporting information. Fig. 1 shows the water circulation in the study area and sampling locations. *Fucus vesiculosus* (*F. vesiculosus*) was seasonally collected at Klint (55.97 °N, 11.58 °E), Kattegat, Denmark during 1983–2016. Surface (at a depth of 0–2 m) and bottom (at a depth of 21–28 m) seawater were collected from Klint during 1986–1995 and Hesselø (56.17 °N, 11.78 °E) during 1972–2016. Additional seawater samples were collected from 11 locations in the Danish Straits before (October 1985) and after (August 1986 and May 1987) the Chernobyl accident for ^{137}Cs analysis, as well as in June 1999, December 2002 and May 2003 for both ^{137}Cs and ^{99}Tc. The samples details, analytical methods used for processing the samples as well as the overall results for ^{137}Cs and ^{99}Tc are compiled in the supporting information.

3. Results and discussion

3.1. Temporal evolution of ^{137}Cs in seaweed and seawater

Time-series records for ^{137}Cs activity concentrations in *F. vesiculosus* from Klint (1983–2016) and in seawater from Klint (1986–1995) and Hesselø (1972–2016), together with the ^{137}Cs discharge history from SF and LH (Jackson, 2000; OSPAR, 2019; Povinec et al., 2003) are shown in Fig. 2. The levels of ^{137}Cs in Klint seaweed are 5–10 Bq/kg d. w. (dry weight) before Chernobyl (1983–1986), which is comparable to earlier observations (8–10 Bq/kg d. w.) for *F. vesiculosus* from the Baltic Sea during 1980–1983 (Aarkrog, 1985). Elevated ^{137}Cs concentration (13.5 Bq/kg d. w.) in seaweed started to appear in May 1986 (one month after the accident) and a sharp ^{137}Cs peak (up to 33 Bq/kg d.w.) occurred in June–August 1986 (Fig. 2 (a)), which is more than three times higher than the pre-accident level. Similar observations were reported for *F. vesiculous* along the Swedish east and south coasts, wherein ^{137}Cs levels increased by factors of 2–5 two months after the accident (Carlson and Holm, 1988).

The ^{137}Cs discharges from the European reprocessing plants were dominated by SF during 1970–1985. In comparison, the ^{137}Cs discharges before 1970 and after 1985 are nearly negligible (Fig. 2 (c)). Sampling of seaweed from Klint started from 1983, thus the peak discharges from SF in 1974–1978 could not be reflected by the ^{137}Cs time-series record in seaweed. Assuming that the average transit time from SF to Klint takes 4 years (Hou et al., 2000; Shi et al., 2013), the ^{137}Cs signal detected in Klint seaweed during 1983–1986 should refer to the SF discharges during 1979–1982, which was 2–3 PBq/y. Comparing to the total ^{137}Cs release of 85 PBq from the Chernobyl accident, the SF annual release during 1979–1982 is much lower.

Furthermore, radioactive discharges from SF are mostly transported northward along the Scottish coastline into the North Sea. From the North Sea, radionuclides are further transported via the Norwegian Coastal Current (NCC) and the Norwegian Atlantic Current (NAC) to the Arctic Ocean or via Kattegat and Danish Straits into the Baltic Sea. The water flow along North Sea-Kattegat is relatively small compared to the northward NCC and NAC (Orvik and Niiler, 2002). Therefore the reprocessing signal is diluted significantly when it reaches Kattegat. It has been estimated that only about 2% of the SF discharge was transferred to the Kattegat (Dahlgaard et al., 1995). The ^{137}Cs activity concentrations in *Fucus* were reported to decrease by a factor of 100 from SF to the Danish

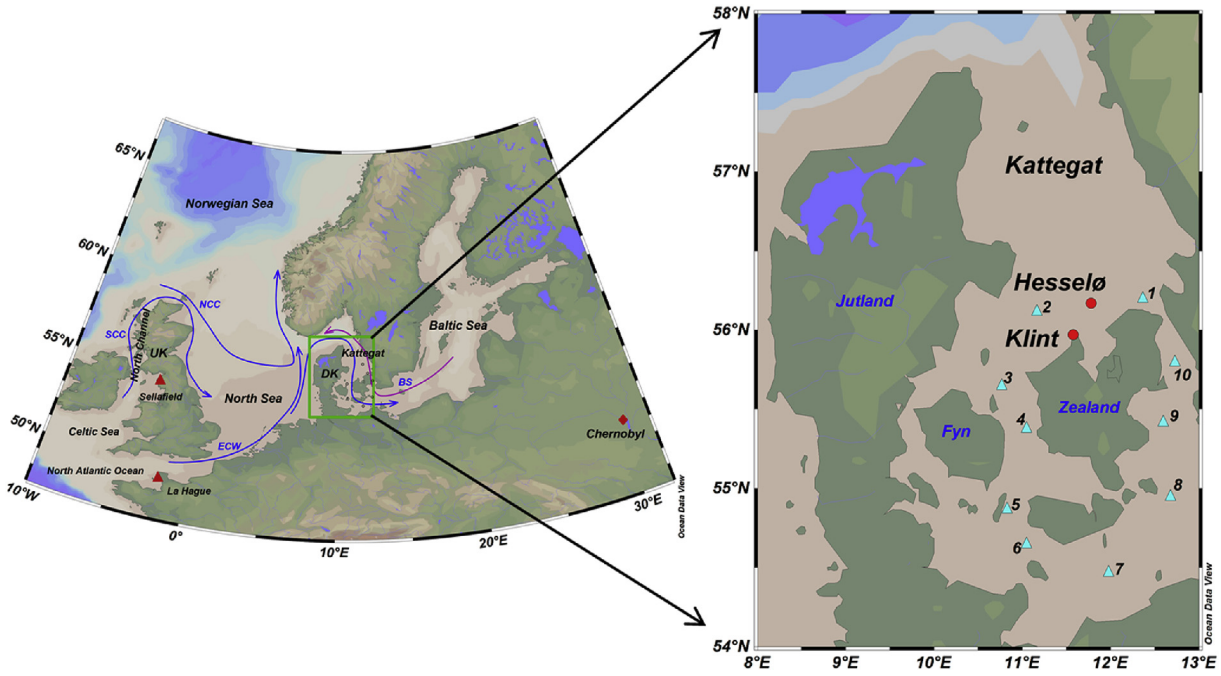

Fig. 1. Sampling stations for seaweed and seawater at Klint and Hesselø (red circle) and other 10 locations (blue triangle) in this work (1-Kullen, 2- Kattegat Southwest, 3-Asnæs Rev, 4-Halskov Rev, 5-Langeland Bælt, 6-Femern Bælt, 7-Gedser Odde, 8-Møn, 9-Sundet South, 10-Sundet North) and general water circulation in North Sea-Baltic Sea region (SCC, Scottish Coast Current; NCC, Norwegian Coast Current; ECW, English Channel waters, BS, Baltic Sea outflow). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

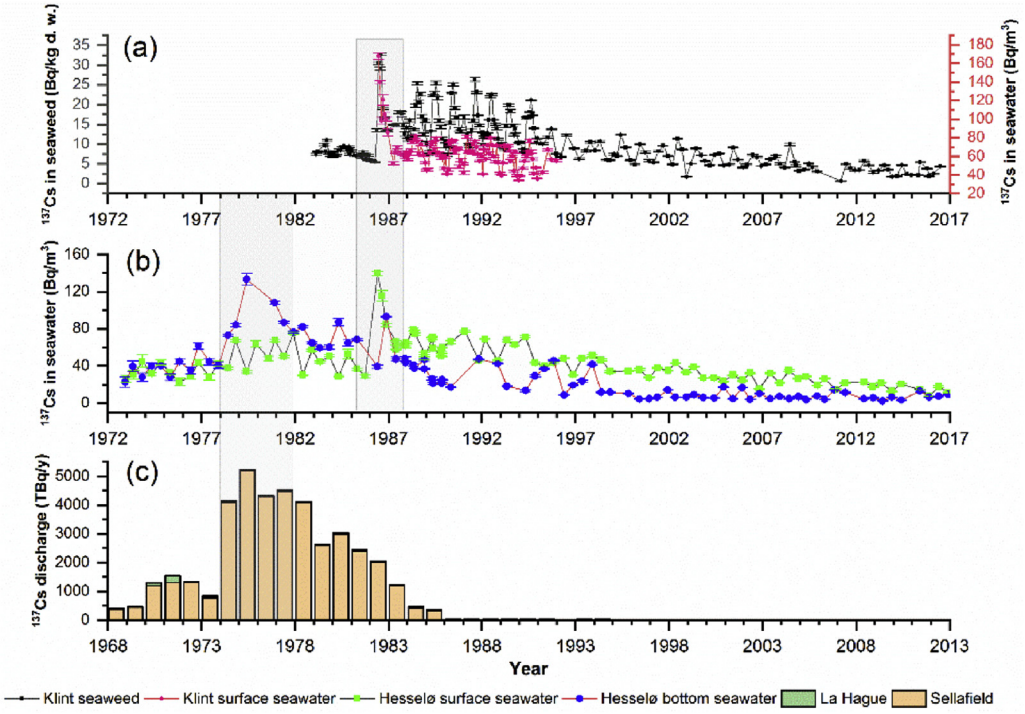

Fig. 2. Temporal evolution of ^{137}Cs activity concentrations in (a) F. vesiculosus and seawater collected from Klint, Denmark and (b) surface and bottom seawater from Hesselø, Denmark, and (c) ^{137}Cs discharge history from La Hague and Sellafield (The grey squares highlight the correspondences of the SF discharges with the detected ^{137}Cs in seaweed or seawater samples).

Straits in the early 1980s (Aarkrog, 1985). From 1986 the Chernobyl ^{137}Cs reached the Danish marine environment by the following pathways: 1) direct atmospheric deposition (dry and wet); 2) transport by Baltic Sea outflow and North Sea inflow; 3) river runoff from the catchment of the Danish-Swedish-German coast. The slow decrease of ^{137}Cs activity concentrations in Danish seaweed and seawater over 10 years after the Chernobyl accident could reflect this multiple transport of Chernobyl-related ^{137}Cs (Fig. 2 (a) and

(b)).

The ^{137}Cs time-series record (Fig. 2 (b)) for Hesselø's bottom seawater verifies the impact from both SF and the Chernobyl accident in the Danish environment. Peaked ^{137}Cs activity concentrations during 1978–1981 correspond well with the high ^{137}Cs discharges from SF for the period of 1974–1977, provided a 4-year transit time (Aarkrog, 1985; Aarkrog et al., 1985). The ^{137}Cs peak in August 1986 should be related to the Chernobyl accident, since the ^{137}Cs discharge from SF decreased since 1980, therefore making the introduction of such a peak in1986 unlikely.

In contrast to the Hesselø bottom water, ^{137}Cs temporal evolution in surface water shows a different feature. Here the reprocessing signal is not pronounced, and instead a sharp Chernobyl peak appears in May 1986. Similar features are also observed in both seaweed and surface seawater from Klint (Fig. 2 (a)). All findings indicate that 1) reprocessing discharges (predominantly from SF) influence surface water to a much less extent than bottom seawater; and 2) Chernobyl released ^{137}Cs is the dominating source since 1986 in the Danish marine environment.

3.2. Temporal evolution of ^{99}Tc in seaweed and seawater

The time-series records for ^{99}Tc activity concentration in *F. vesiculosus* from Klint (1988–2013) and in seawater from Hesselø (1998–2015), together with the ^{99}Tc discharge history from SF and LH (Jackson, 2000; OSPAR, 2019; Shi et al., 2012) are shown in Fig. 3. It is clear that the ^{99}Tc temporal evolutions have been strongly influenced by discharges from LH and SF. Throughout the 1980s and until 1993, ^{99}Tc discharges from LH constituted the main source in the North Sea, while from 1994 treatment of stockpiled historic wastes by the Actinide Removal Plant (EARP) at SF led to a notable spike of ^{99}Tc (Brown et al., 1999; Leonard et al., 1997). Nuclear weapons testing and the Chernobyl accident also contributed ^{99}Tc in the Danish marine environment, but both source terms are negligible compared to SF and LH (Carlson and Holm, n.d.; Dahlgaard et al., 1995).

From the time-series record in Klint seaweed, ^{99}Tc peaks (up to 150 Bq/kg d. w.) were observed between 1988 and 1991, which corresponds well with the increased release from LH during 1986–1988 (Fig. 3 (a) and (c)), considering a 2-year transit time from LH to Klint (Dahlgaard, 1995). Our observational data are in line with previous values (119 ± 10 Bq/kg d. w.) for *Fucus* from Kattegat in 1980–1983 (Aarkrog, 1985). The remarkable increase of ^{99}Tc in Klint seaweed from 1998 until 2001 corresponds well with the significant release from SF during 1994–1997, provided a 4-year transit time from SF to Klint (Aarkrog et al., 1985; Shi et al., 2013).

In the early 1990s, prior to EARP operations in 1994, ^{99}Tc activity concentrations in Danish seawater (data not shown here) were generally less than 1 Bq/m^3, and comparable to the values in the North Sea and Norwegian coastal areas (Orre et al., 2007). During the same period, ^{99}Tc levels in the northern French, Belgian, Dutch and German coastal waters were higher (in the range of 1–4 Bq/m^3), indicating the influence of LH discharges (Herrmann et al., 1995). The ^{99}Tc activity concentrations in Klint seaweed were at the level of 25 Bq/kg d.w. during 1992–1995 (Fig. 3(a)), implying no influence from the EARP operations on the Danish coast before the end of 1995.

The ^{99}Tc activity concentrations in *F. vesiculosus* increased from 1996 and reached a maximum value of 209 Bq/kg d.w. in March 2000. Comparable ^{99}Tc activity concentrations were reported for *F. vesiculosus* from coasts of Nordic seas, for example, 79–124 Bq/kg d.w. (v.s. 58–155 Bq/kg d.w. in our observations) at the Norwegian coast (Hillesøy, Troms) during 1997–1998 and 230 Bq/kg d.w. at the Swedish west coast in early 2000 (Lindahl et al., 2003). This may be

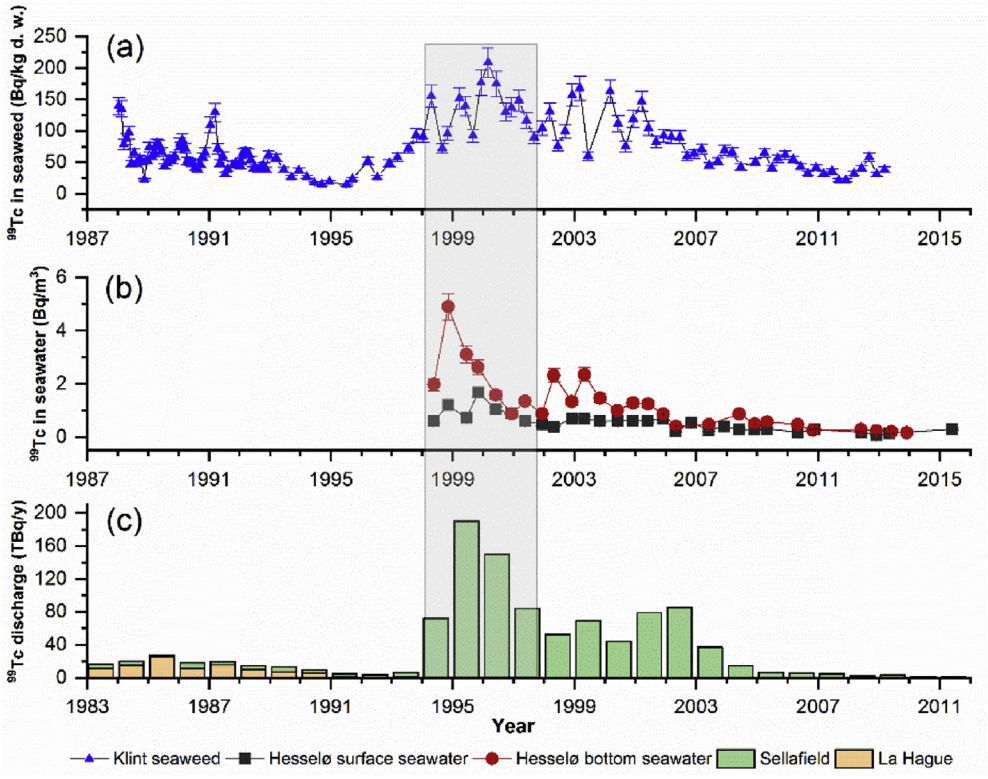

Fig. 3. Temporal distribution of ^{99}Tc activity concentrations in (a) F. vesiculosus collected from Klint, Denmark and (b) seawater collected from Hesselø, Denmark, and (c) discharge record of ^{99}Tc from La Hague and Sellafield (The grey squares highlight the correspondences of the SF discharges with the detected ^{99}Tc in seaweed or seawater samples).

due to a similar transit time (3–4 years) from SF to the Norwegian coast as to Danish Straits (Brown et al., 1999; Gerstmann, 2008). The annual ^{99}Tc discharges from SF have increased by a factor of about 50 since 1995 compared to the early 1990s (Fig. 3), while our observational data indicate that ^{99}Tc activity concentrations in Klint seaweed increased by a factor of 8. This could reflect the complex transport pathway from SF to the Danish Straits and mixing processes with other water flows.

3.3. Seasonal variation of ^{137}Cs and ^{99}Tc activity concentrations and concentration factors

As indicated in Fig. 4 (a), a clear seasonal variation is observed for ^{137}Cs in *F. vesiculosus* during 1987–1994, with the highest ^{137}Cs in summer (June–August) and the lowest in winter (December–February). The highest and lowest ^{137}Cs annual activity concentrations differ by a factor of approximately 2–3 during 1986–2016. Similar seasonal variation for ^{137}Cs has also been reported in *F. vesiculosus* collected from the south-eastern coast of Norway in 2002 (Raaum and Christensen, 2005) and the south coast of Sweden during 1986–1988 (Carlson and Holm, n.d.).

In general, the concentration of ^{137}Cs in seaweed should be related to the following parameters (Dahlgaard, 1992): 1) concentration of ^{137}Cs in seawater; 2) biological factors including uptake and elimination of ^{137}Cs affected by marine environmental conditions e.g., salinity, temperature and light intensity; 3) biological dilution due to growth; 4) physical decay of ^{137}Cs. Over short periods, the effect of physical decay of ^{137}Cs can be neglected due to its relatively long half-life.

The seasonal variation of ^{137}Cs activity concentration in Klint seawater corresponds well with the seaweed annual cycle during 1987–1994 (Fig. 4 (b)). The good correlation in seasonal variation between seawater and seaweed has also been observed for samples from the southern coast of Sweden (Carlson and Holm, n.d.) and southeastern coast of Norway (Raaum and Christensen, 2005). However, a closer look at the ^{137}Cs seasonal variation in Hesselø's seawater (Fig. 4 (c)) reveals that ^{137}Cs activity concentration in surface water is always lower in summer than winter before the Chernobyl accident, while after the accident this pattern is reversed. For the bottom water (Fig. 4 (d)), it seems the ^{137}Cs concentration is slightly higher during winter than summer in most cases, except for a few distinct years (e.g. 1980 and 1986).This is due to more efficient mixing between surface and bottom water in winter than in summer due to stronger winds in the winter season (NOVA, 2003). Therefore, surface water in Kattegat shows higher ^{137}Cs activity concentration in winter than in summer when ^{137}Cs dominates in bottom water (before the Chernobyl accident), while it turns into the opposite when ^{137}Cs dominates in surface water (after the Chernobyl accident).

Nevertheless, seasonal variation of ^{137}Cs in *F. vesiculosus* from

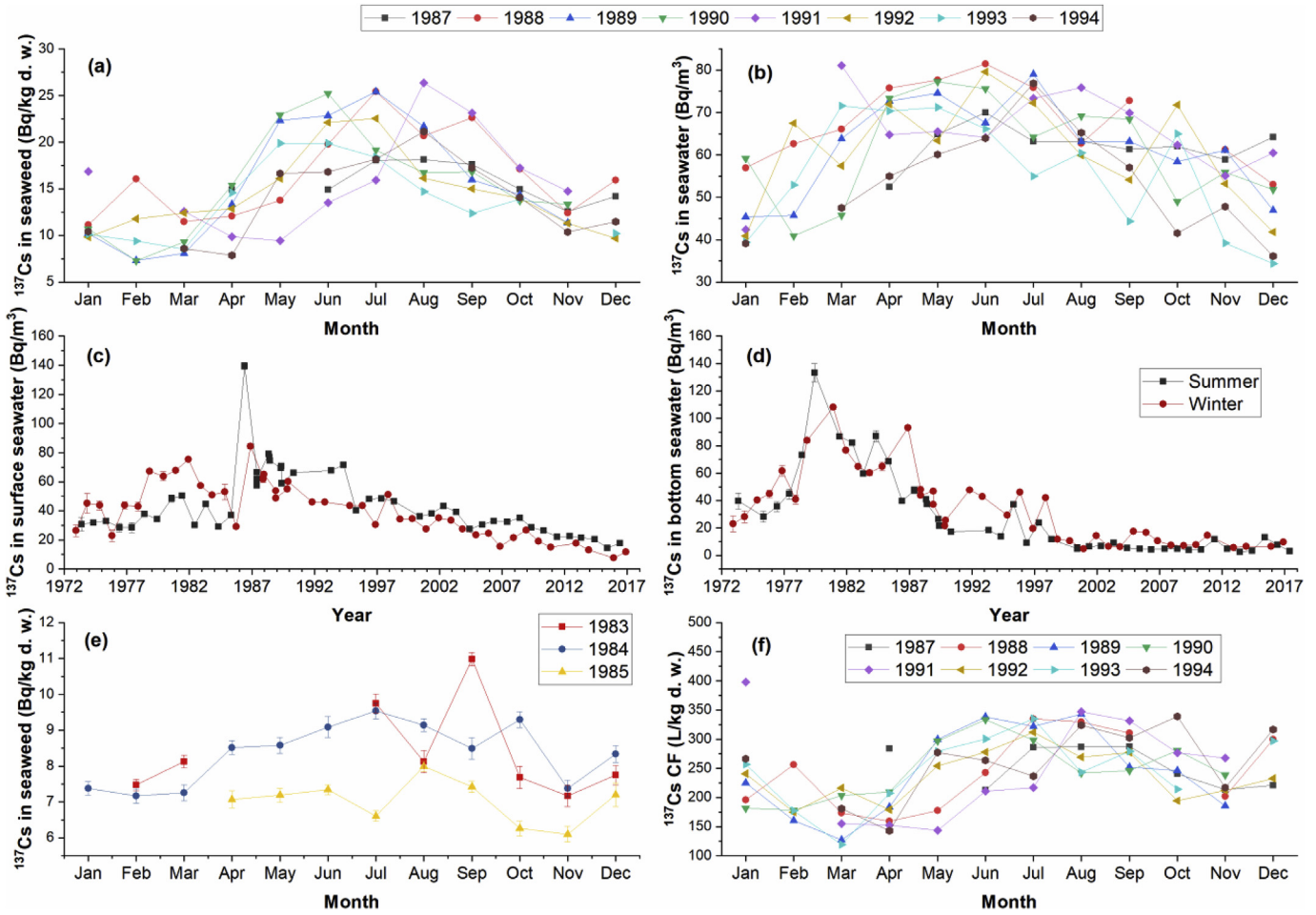

Fig. 4. Seasonal variation of ^{137}Cs activity concentrations in (a) seaweed and (b) surface seawater collected from Klint, Denmark during 1987-1994, (c) surface and (d) bottom seawater collected from Hesselø, Denmark during 1972-2017, (e) seaweed from Klint, Denmark during 1983-1985, as well as (f) seasonal variation of ^{137}Cs concentration factors in seaweed from Klint, Denmark during 1987-1994.

Klint before the Chernobyl accident during 1983–1985 (Fig. 4 (e)), even though with a limited dataset, still indicates a relatively higher ^{137}Cs concentration in summer and a lower concentration in winter, which differs from the seasonal variation in surface seawater (Fig. 4 (c)). This indicates that ^{137}Cs concentrations in seawater might not be a major parameter affecting the ^{137}Cs annual cycle in *F. vesiculosus*, whereas the biological process may play a key role.

Computer model simulation on time-integration of ^{137}Cs has indicated that ^{137}Cs is readily released from *F. vesiculosus*, with an estimated biological half-life of 30–70 days (Dahlgaard, 1992). Laboratory experiments have shown the uptake of ^{137}Cs by *F. vesiculosus* is slow compared to other radionuclides (e.g., ^{54}Mn, ^{65}Zn, ^{60}Co, ^{99}Tc), and also more sensitive to salinity, temperature and light (Carlson and Erlandsson, 1991; Dahlgaard, 1992). Higher temperature and intensive light both significantly increase the uptake of ^{137}Cs, while a negative correlation between ^{137}Cs concentration in seaweed and seawater salinity has been observed (Carlson and Erlandsson, 1991; Dahlgaard, 1992; Raaum and Christensen, 2005). The ^{137}Cs activity concentrations accumulated in *F. vesiculosus* were 2.5 and 4 times lower when the seawater salinity increased from 8‰ to 15‰ and 24‰, respectively.

With a fast growth of seaweed in spring-summer, dilution of the ^{137}Cs concentration in the seaweed can potentially be introduced. For *F. vesiculosus* collected near to the island of Tromøya, Norway in 2002 (Raaum and Christensen, 2005), decreased ^{137}Cs concentration was observed in July and August following the peak value in spring-summer. In our study, ^{137}Cs concentration decreases for Klint seaweed in July and August are not notable.

The accumulation capacity of a specific species of biota to a radionuclide in the marine environment can be characterized by its concentration factor (CF), which is calculated as the radionuclide concentration (Bq/kg d.w.) in seaweed divided by the concentration (Bq/L) in seawater. Through 8 years' observation (1987–1994), CF for ^{137}Cs in Klint seaweed also demonstrates a seasonal variation (Fig. 4 (f)), with the highest values observed in summer (June–August). This could be due to the combined effects of biokinetics in *F. vesiculosus*, low salinity, high temperature and more light in summer, which prompts the ^{137}Cs uptake. Similar observations have been reported for seaweed from the south and east coasts of Sweden (Carlson and Holm, n.d.). This potentially indicates that the seasonal variation of ^{137}Cs in *F. vesiculosus* may rely on biological factors (e.g., salinity, temperature, light) to a larger extent than the ^{137}Cs concentration in seawater.

Compared to ^{137}Cs, ^{99}Tc activity concentrations in *F. vesiculosus* from Klint demonstrate a very different seasonal feature during 1988–1993, as the highest ^{99}Tc concentrations occur in winter and the lowest values in summer (Fig. 5 (a)). The ^{99}Tc data during 1999–2014 (Fig. 5 (c)) show the same significant seasonal variation ($P < 0.001$) as confirmed by an analysis of variance (VAR-3) (Vestergaard, 1964). Several researchers have observed similar seasonal variation for ^{99}Tc in *Fucus* from the Kattegat (Shi et al., 2013), Baltic Sea (Holm et al., 1986), English Channel (Patti et al., 1990) and the southeastern coast of Norway (Raaum and Christensen, 2005). However, there are contradictory explanations for the ^{99}Tc seasonal variation (Holm et al., 1986; Kershaw et al., 1999; Patti et al., 1990; Shi et al., 2013; Topcuoğlu and Fowler, 1984).

Our data (Fig. 5 (a) and (b)) show that activity concentrations of ^{99}Tc in seawater (1988–1989) do not correlate with the values in *F. vesiculosus*. Some other studies have observed that ^{99}Tc concentrations in seawater correspond well with the release from the point source, but ^{99}Tc concentrations in seaweed continued to increase even after the seawater concentrations had declined (Kershaw et al., 1999). It is reported that ^{99}Tc is readily taken up by *Fucus*, but not easily released in contrast to ^{137}Cs (Benco et al., 1986; Kershaw et al., 1999). Thus, *Fucus* tends to integrate short-term variations of ^{99}Tc concentration in seawater. The variability of ^{99}Tc in seaweed after the initial uptake has a periodicity of approximately 12 months. Unlike ^{137}Cs, no specific seasonal variation, but rather constant values are observed for CFs of ^{99}Tc (Fig. 5 (d)), which could be related to the integrated accumulation of ^{99}Tc in *F. vesiculosus*. It was also observed that the Tc is not irreversibly bound to the alga and depuration is mostly rapid in the terminal parts of the seaweed, resulting in a disproportionately large residual fraction of the radionuclide bound to the slow growing cylindrical axis after an elimination period of a month (Topcuoğlu and Fowler, 1984). Therefore, we consider that the low ^{99}Tc concentration in *F. vesiculosus* in summer to be most likely related to the biological dilution due to the growth of the plants, while the high concentration of ^{99}Tc in winter could be related to the integrated accumulation of ^{99}Tc especially in slowly growing parts of seaweed (e.g., cylindrical axis).

Compared to ^{137}Cs and ^{99}Tc seawater analysis (typically 50–200 L for each sample), smaller sample amounts (10–20 g) are required for seaweed, thus facilitating much more efficient and cost-effective sample handling. Besides, seaweed grow in fixed locations, where they are easy to collect and less affected by the weather and water dynamics conditions on a specific sampling day as in the case for seawater sampling. However, the two distinct seasonal variations for ^{137}Cs and ^{99}Tc in seaweed as observed here must be taken into account when planning the sampling intervals and interpreting observational results. As noted earlier, the maximum value in an annual cycle may be several times greater than the minimum value.

3.4. Transfer factors for ^{99}Tc

The transfer of a radionuclide from a source to a sample collected at a given location can be expressed by a transfer factor (TF) (Dahlgaard, 1995). In this work, the TF is calculated based on ^{99}Tc activity concentrations (Bq/m^3) in Kattegat surface (or bottom) water integrated over the ten-year period of 1998–2008, and divided by the corresponding total release (PBq/y) from SF during 1994–2004, provided a 4-year transit time from SF to Kattegat. The obtained TF is 7.9 ± 0.7 Bq·m^{-3}/PBq·y^{-1} for the surface water and 18.3 ± 2.0 Bq·m^{-3}/PBq·y^{-1} for bottom water, respectively. These values agree well with earlier estimation of 8 Bq·m^{-3}/PBq·yr^{-1} for Kattegat surface water using ^{99}Tc data from 1989 to 1991 (Dahlgaard et al., 1995) and the reported TF of 15 Bq·m^{-3}/PBq·y^{-1} for Kattegat bottom seawater based on ^{137}Cs, ^{134}Cs and ^{90}Sr data during 1980–1985 (Aarkrog, 1988). The consistent TFs indicate steady hydrodynamic conditions along the transport pathway from the Irish Sea via the North Sea to Kattegat during the past decades.

3.5. Oceanic tracer studies using ^{137}Cs and ^{99}Tc in the Danish Straits

3.5.1. Variation of ^{137}Cs and ^{99}Tc activity concentrations with salinity

The temporal evolutions of ^{137}Cs and ^{99}Tc in the Danish Straits reflect historical changes of contamination levels in the North Sea and Baltic Sea, as well as mixing processes between the two water bodies. As can be seen from Fig. 6 (a), ca. 1 year after the Chernobyl accident, the peak ^{137}Cs activity concentration exponentially decreased to the pre-Chernobyl level due to fast dispersion and water mixing, and then entered into a long-lasting (nearly 10 years) mode of fluctuation and slow decline from 1987 (Fig. 2 (a)). The sharp ^{137}Cs peaks in both surface seawater and seaweed in 1986 is presumed to be related to the direct atmospheric deposition of Chernobyl fallout, while the slow decrease is a combined effect of

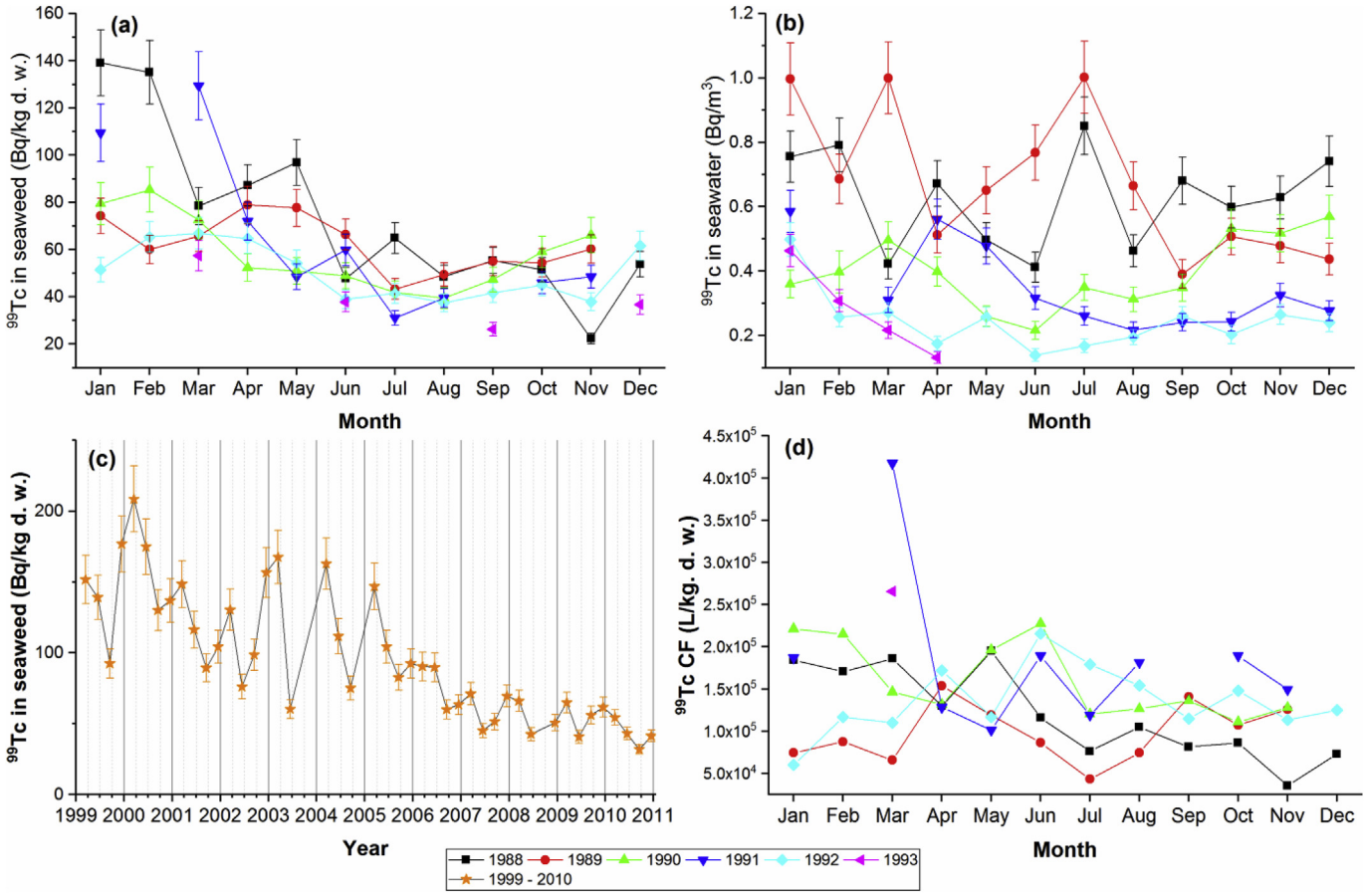

Fig. 5. Seasonal variation of ^{99}Tc activity concentrations in (a) F. vesiculosus, (b) surface seawater collected from Klint, Denmark in 1988-1993, in (c) F. vesiculous in 1999-2010, and (d) seasonal variation of concentration factors of ^{99}Tc during 1988-1993.

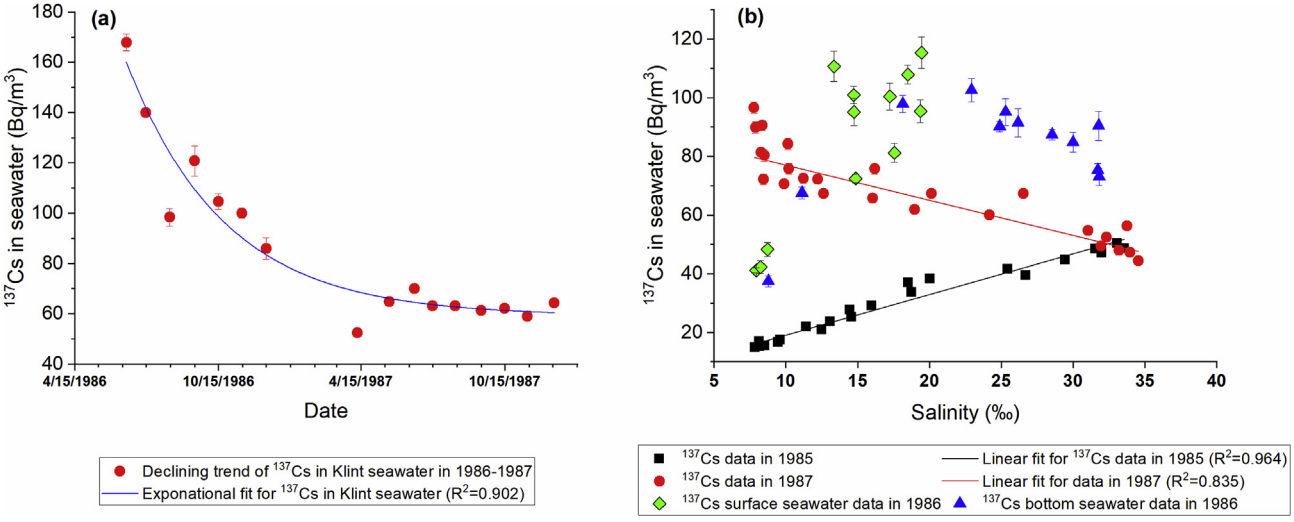

Fig. 6. ^{137}Cs activity concentration, which show a declining trend in (a) Klint surface seawater during 1986-1987, and (b) the different correlation patterns between ^{137}Cs seawater (both surface and bottom seawater from the 12 locations indicated in Fig. 1) concentration with salinity before and after the Chernobyl accident.

dilution by fresh water, North Sea water and the continuous ^{137}Cs input from the Baltic Sea (Aarkrog et al., 1991; Herrmann et al., 1995; Jiang et al., 1992; Povinec et al., 2003).

It is clear that the positive correlation between ^{137}Cs activity concentration and salinity in Danish seawater is changed to a negative correlation about 1 year after Chernobyl accident (Fig. 6 (b)), which reflects the major ^{137}Cs injection in the Danish Straits shifted from reprocessing signal carried by North Sea water to the Chernobyl signal carried by the Baltic Sea outflow water. During the transit year (1986), surface seawater with elevated ^{137}Cs levels still

kept the positive correlation with salinity (green diamonds in Fig. S3 (b)), while ^{137}Cs in bottom seawater from most locations already formed a negative correlation with salinity (blue triangles in Fig. 6 (b)). Fig. 7 shows a positive correlation between ^{99}Tc activity concentration and salinity in Danish seawater collected in 1999. This positive correlation is not affected by the variation of annual discharge from SF and LH (data are not shown here), implying that reprocessing input is consistently the major source of ^{99}Tc in the Danish Straits.

3.5.2. Indication of major Baltic inflow (MBI) by ^{99}Tc/^{137}Cs activity ratios

The temporal evolutions of ^{99}Tc/^{137}Cs activity ratios in *F. vesiculosus* from Klint, and surface and bottom seawater from Hesselø, are plotted in Fig. 8. Clear seasonal variation of ^{99}Tc/^{137}Cs is observed, as was expected based on seasonal variations of ^{99}Tc and ^{137}Cs activity concentrations discussed earlier. During 1988–1996, ^{99}Tc/^{137}Cs activity ratios in *F. vesiculosus* varied within the range of 1–13, with the annual average ^{99}Tc/^{137}Cs activity ratio slightly decreasing with time (grey columns in Fig. 8 (a)). Since 1997, the ^{99}Tc/^{137}Cs activity ratio started to increase and three peaks are notable in samples collected during March 2000, December 2002 and March 2011. Annual average ^{99}Tc/^{137}Cs activity ratios also indicate similar features with the highest value in 2002, followed by 2000 and 2011.

The peak ^{99}Tc/^{137}Cs activity ratio in March 2000 reflects the arrival of increased ^{99}Tc discharge signal from SF due to the EARP operation started in 1994, which corresponds well with the highest ^{99}Tc/^{137}Cs activity ratio detected in the Hesselø surface water in November 1999 (Fig. 8 (c)). However, the highest ^{99}Tc/^{137}Cs activity ratio in the Hesselø bottom water is observed during November 1998, which is one year earlier than the surface water. This indicates an approximately one-year difference between the transfer times from SF to Kattegat in the bottom water compared to the surface water.

An exceptionally high ^{99}Tc/^{137}Cs activity ratio appeared during November 2002 (Fig. 8 (b)). This could not be explained merely by the variation of the ^{99}Tc and ^{137}Cs input functions in the Danish Straits, since the corresponding SF discharges in 1998–1999 are not higher than earlier years and no other additional ^{137}Cs and ^{99}Tc sources could exist. Interestingly, high ^{99}Tc/^{137}Cs activity ratios are also observed in the Hesselø bottom water during the 2002–2003 period (Fig. 8 (d)). It is reported that, during 2002 and 2003, exceptional Baltic Sea inflow events carrying highly saline and oxygen-rich water from the North Sea were recorded between Germany and Denmark at the Darss Sill (Feistel et al., 2003a, 2003b; Lehmann et al., 2004; Mohrholz et al., 2015). These include baroclinic warm water inflow during August/September 2002 and the major Baltic inflow (MBI) (insensitivity index (FM96) = 20) in January 2003 (Lehmann et al., 2004; Mohrholz et al., 2015). The exceptionally high ^{99}Tc/^{137}Cs could be related to the occurrence of a persistent warm water anomaly over a period of eight weeks in 2002 (Feistel et al., 2003b), which increased the transport of North Sea water carrying ^{99}Tc from SF.

The third ^{99}Tc/^{137}Cs peak in March 2011 may have some connection to the smaller MBI (insensitivity index (FM96) = 10) event registered in 2010–2011 (Mohrholz, 2018; Mohrholz et al., 2015). There was also a noticeable increase in the ^{99}Tc/^{137}Cs activity ratio in the Hesselø surface seawater during June 2015, which may be an indication of the very strong MBI event (insensitivity index (FM96) = 40) which occurred during December 2014 (Mohrholz, 2018; Rak, 2016). In any case, more research needs to be performed to help confirm their correlation with the two MBI events.

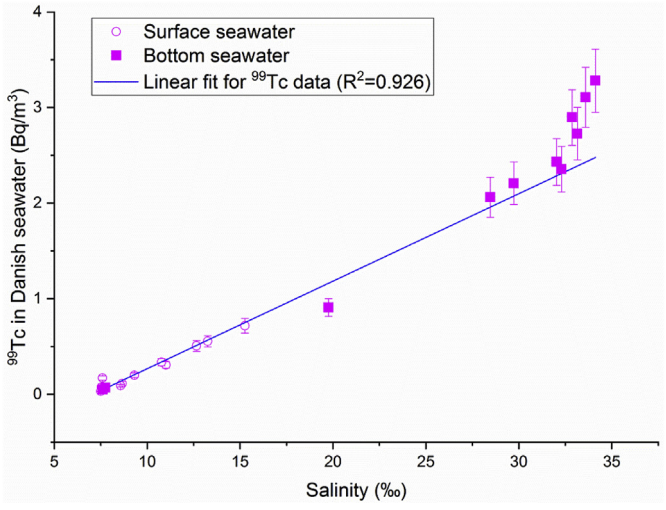

Fig. 7. Correlation between ^{99}Tc concentration in Danish seawater collected in 1999 and salinity.

3.5.3. Binary mixing model

Observational data for the ^{99}Tc/^{137}Cs activity ratio and salinity in seawater from 12 locations in the Danish Straits (see Fig. 1) during June 1999 and December 2002–May 2003 are plotted in the diagram with the binary mixing curves in Fig. 9. The three end members in the diagram represent the North Sea (salinity 35.5‰, ^{99}Tc/^{137}Cs activity ratio 0.6), the German Bight (salinity 29.7‰, ^{99}Tc/^{137}Cs activity ratio 0.06) and the Baltic Sea (salinity 7.0‰, ^{99}Tc/^{137}Cs activity ratio 0.004). Detailed parameters for each end member are listed in Table S1. Freshwater input is not considered in the binary mixing model because precipitation and river runoff carrying Global fallout of ^{99}Tc and ^{137}Cs have rather low salinity levels (<0.1) and ^{99}Tc/^{137}Cs activity ratios (10^{-4} - 10^{-5}) (Lindahl et al., 2003). Most observational data in 1999 and 2002–2003 fit well with the binary mixing line between the North Sea (NS) and the Baltic Sea (BS), with bottom samples close to the end of NS and surface samples close to BS, confirming that the Danish Straits are dominated by water masses from the NS and BS. Few surface water data points in Fig. 9 fit into the binary mixing line between BS and the German Bight (GB), indicating a small contribution from the GB compared to the BS and NS. This agrees well with earlier findings using other tracers, e.g. dissolved organic carbon (DOM) (Stedmon et al., 2010). Quantitative estimation is made by plotting the percentage contributions of NS and GB in the binary mixing line (red and black quartered circles in Fig. 9). It indicates that water mass from the NS constitutes less than 50% in the surface water and 50–100% for most locations in the bottom water in the Danish Straits.

From the data and results discussed here, we believe that isotopic ratios of ^{99}Tc/^{137}Cs in seawater and seaweed reflect not only the variation of source input in the marine environment, but also the water dynamics and mixing processes. ^{99}Tc/^{137}Cs ratio in brown seaweed is sensitive to the changes in water dynamics, which has a high potential for studying time-resolved hydrological events. ^{99}Tc/^{137}Cs ratios in seawater can be used for quantitative estimation of the water mass composition in a mixing zone. Time-series observational data for ^{137}Cs and ^{99}Tc and their ratios obtained in this study may also be used to validate oceanic models, such as the Hiromb-Boos Model (HBM) (Nerger et al., 2014; Poulsen et al., 2014) and to reveal future water circulation patterns.

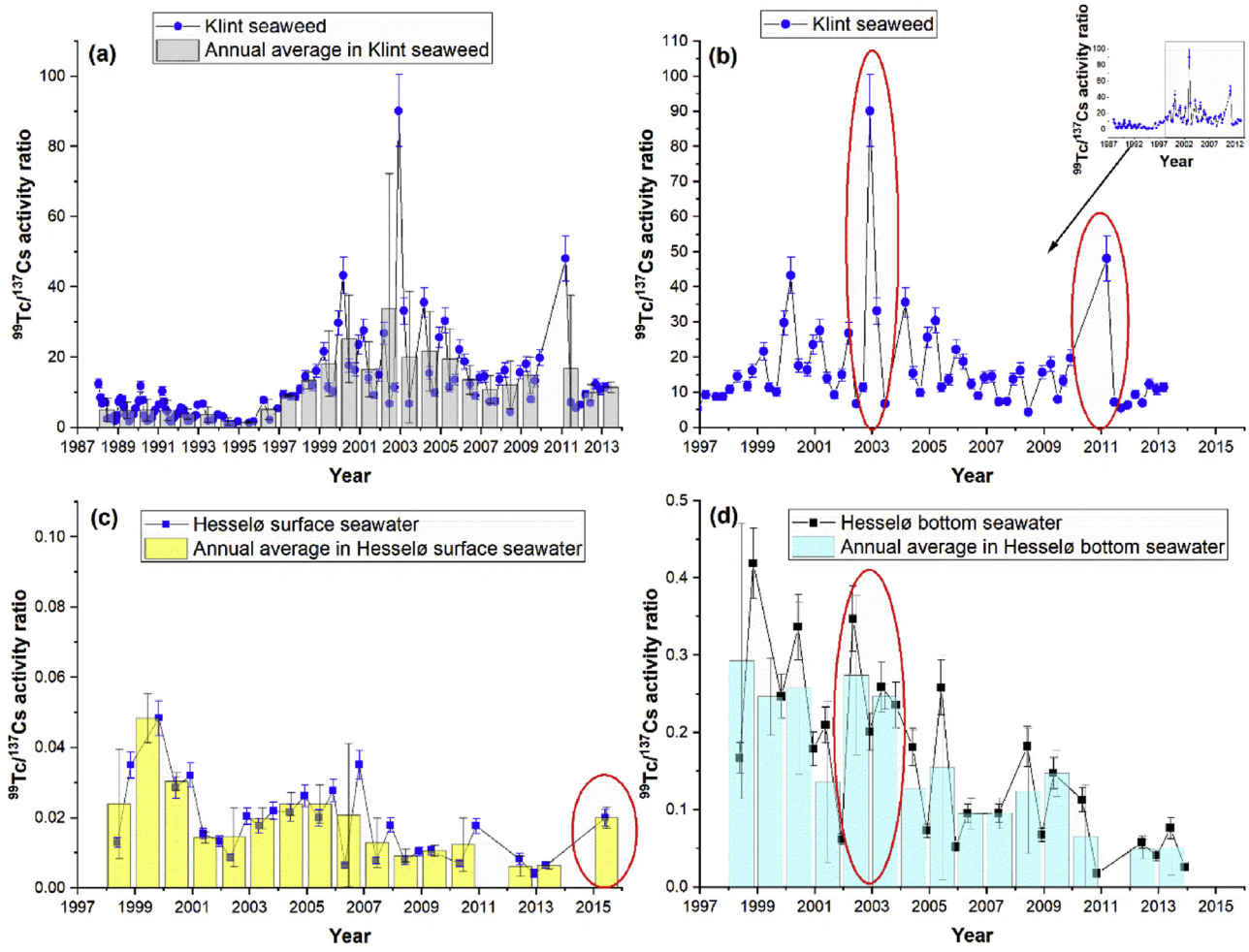

Fig. 8. Temporal evolution of $^{99}Tc/^{137}Cs$ activity ratios in Klint seaweed and Hesselø seawater (The red the ellipses highlight the elevated $^{99}Tc/^{137}Cs$ activity ratios observed in (b) Klint seaweed in 2002–2003 and 2011, (c) Hesselø surface seawater in 2015 and (d) Hesselø bottom water durign 2002–2003). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

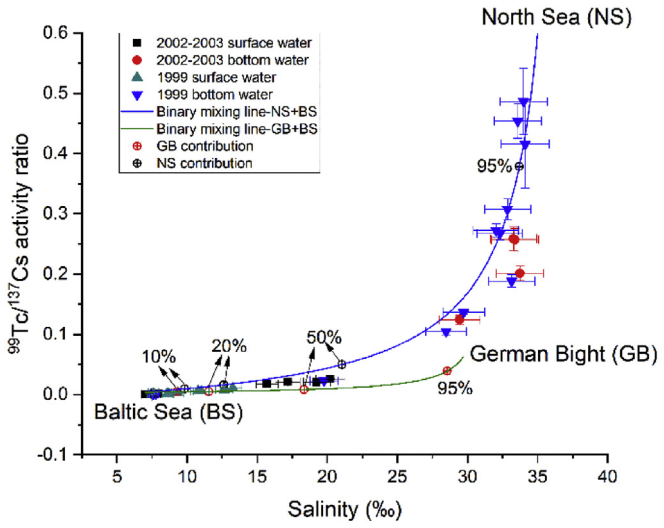

Fig. 9. Variation of $^{99}Tc/^{137}Cs$ activity ratios with salinity for Danish seawater in 1999 and 2002–2003 and simulation with binary mixing model.

4. Conclusion and perspectives

The 40-year time-series records of ^{137}Cs and ^{99}Tc obtained in this work confirm that ^{137}Cs in the Danish Straits is mainly from reprocessing discharges before 1986, and dominated by the Chernobyl accident fallout since May 1986, while the major source of ^{99}Tc is from LH during 1988–1994 and from SF since 1995. The ^{137}Cs and ^{99}Tc activity concentrations obtained range respectively within 2.6–167.9 Bq/m^3 and 0.1–4.9 Bq/m^3 in seawater, and 0.7–32.7 Bq/kg d. w. and 13.9–208.6 Bq/kg d. w. in *F. vesiculosus*. The $^{99}Tc/^{137}Cs$ activity ratios are 0.004–0.05, 0.02–0.4 and 1–90 in surface seawater, bottom seawater and *F. vesiculosus*, respectively. Distinct seasonal variations are observed between ^{137}Cs and ^{99}Tc in *F. vesiculosus*, with the highest ^{137}Cs and the lowest ^{99}Tc level in summer, whereas the lowest ^{137}Cs and the highest ^{99}Tc occur during winter. Referring to their annual cycles in seawater and CFs, we believe that the ^{137}Cs seasonal variation in *F. vesiculosus* is mostly connected to biological uptake, while the low ^{99}Tc level in *F. vesiculosus* during summer should be related to biological dilution. Based on integrated ^{99}Tc discharges (1994–2004) and ^{99}Tc activity concentrations in seawater (1998–2008), the TF from SF to Kattegat is calculated to be 7.9 ± 0.9 Bq·m^{-3}/PBq·y^{-1} for surface water and 18.3 ± 2.0 Bq·m^{-3}/PBq·y^{-1} for bottom water, respectively. These TFs are comparable to the estimation from earlier

years (1980s), which indicates a relatively steady water mass transport from the Irish Sea through the North Sea to Kattegat over the past decades. An exponential decrease of ^{137}Cs in surface seawater, to reach pre-Chernobyl level within 1 year, and a clear shift in ^{137}Cs-salinity correlation before and after Chernobyl indicates a fast dispersion and water mixing in the Danish Straits. Meanwhile, the long-lasting (nearly 10 years) fluctuation and slow decline in ^{137}Cs activity concentration since 1987 indicates multiple inputs of ^{137}Cs from the Baltic Sea and North Sea. Overall time-series records of ^{137}Cs and ^{99}Tc in the Danish Straits could serve well as oceanic tracers for investigating the flow mixing dynamics between the North Sea and the Baltic Sea. Application of ^{137}Cs and ^{99}Tc as oceanic tracers to study water mixing processes and the use of time-series record of their activity ratio to retrieve historical events in other marine regions could also be foreseen.

Author contribution statement

Jixin Qiao: Conceptualization, Methodology, Investigation, Data curation, Writing- Original draft preparation. Kasper Andersson: Investigation, Data Curation, Writing- Reviewing and Editing, Sven Nielsen: Formal analysis, Resources, Data Curation, Writing - Review & Editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.125595.

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